How Complex are Complex Fluids?

PSS Talk

Christian Jones

September 9, 2024

About Me

Doran, J., 2023

- 3rd year SAMBa student.
- Working towards a PhD involving viscoelastic fluids!
- Former PSS organiser (with Corin)
- Tuba player with City of Bath.

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- From North Wales!

Amdanaf Fi

Doran, J., 2023

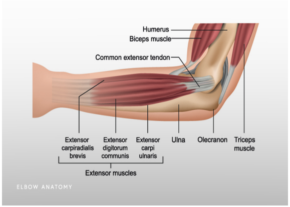
- Myfyriwr 3ydd blwyddyn SAMBa.
- Gweithio tuag at PhD gan gynnwys hylifau fiscoelastig!
- Cyn-drefnydd PSS (gyda Corin)
- Chwaraewr Tiwba gyd band City of Bath
- Yn dod o Ogledd Cymru!

Complex Fluids?

- Many materials we encounter have viscoelastic properties.
  - Viscosity: measure of resistance to flow.
  - Elasticity: ability of a material to return to its original state after removal of deforming forces.
- Characterised by a *relaxation time* — quantifies ‘memory’ of deformation history.

eggs.ca, 2023

iStock, 2021



Verma, N., 2023

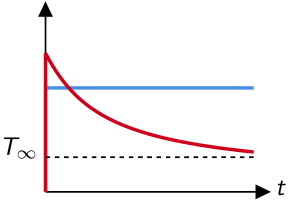
Polymeric Fluids

- Polymer — long chain molecule formed of repeating units/monomers.
- Polymer melt — a thermoplastic heated to a temperature above its melting point.
- (Dilute) polymer solution — polymer molecules suspended in a solvent.

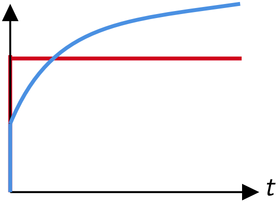
Cabrera, X., 2020.

Properties of Polymeric Fluids

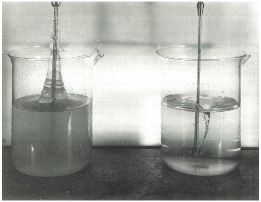
Stress Relaxation:



Creep:

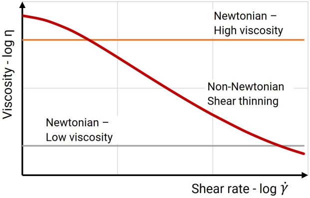


Normal Stress Effects:



Tanner, R. I., 2000

'Variable' Viscosity:

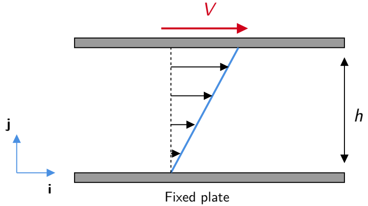


Østergård, A. L., 2020.

Variable Viscosity

- Shear thinning — shear viscosity η_s should drop with shear rate $\dot{\gamma}$.

$$\mathbf{u} = (\dot{\gamma} y, 0, 0)^T, \ \dot{\gamma} = \frac{V}{h}$$



- Strain hardening — elongational viscosity η_e should increase with elongation rate $\dot{\epsilon}$.

$$\mathbf{u} = (\dot{\epsilon} x, -\tfrac{1}{2}\dot{\epsilon} y, -\tfrac{1}{2}\dot{\epsilon} z)^T$$

Viscoelastic Modelling

Overview

Q. How can we model these materials?

A. Use conservation laws.

1. Mass:

$$\nabla \cdot \mathbf{u} = 0.$$

2. Momentum:

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\mathbf{u} \right) = -\nabla p + \nabla \cdot \boldsymbol{T}, \quad \boldsymbol{T}^T = \boldsymbol{T}.$$

With this notation, we also have

$$\eta_s = \frac{T_{12}}{\dot{\gamma}}, \quad \eta_e = \frac{T_{11} - T_{22}}{\dot{\epsilon}}.$$

Viscoelastic Modelling

Specifying $\boldsymbol{T}$

We still need to specify $\boldsymbol{T}$!

$$\rho\left(\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u}\cdot\nabla)\mathbf{u}\right) = -\nabla p + \nabla\cdot\boldsymbol{T}.$$

- $\boldsymbol{T} = \mathbf{0} \longrightarrow$ *inviscid fluids*.
- $\boldsymbol{T} = \eta\left[\nabla\mathbf{u} + \nabla\mathbf{u}^{T}\right] := 2\eta\boldsymbol{D} \longrightarrow$ *Newtonian fluids*.
- $\boldsymbol{T} = 2\eta(\dot{\gamma})\boldsymbol{D} \longrightarrow$ *generalised Newtonian fluids*.

None of these really help us...

Viscoelastic Modelling

Constitutive Equations

Can we do better?

Viscoelastic Modelling

Constitutive Equations

Can we do better?

- Acierno et. al.
- Chang et. al.
- Chilcott-Rallison
- Corotational Jeffreys
- Corotational Maxwell
- Curtiss-Bird
- Doi-Edwards
- Elastic Dumbbell
- Extended Pom-Pom
- Extended WM
- FENE
- FENE-P
- Giesekus
- Green-Tobolsky
- Jeffreys
- Johnson-Segelman
- Kaye-BKZ
- Kelvin-Voigt
- Leonov
- Lodge
- Maxwell
- Maxwell-Wiechert
- Modified UCM
- Oldroyd 8 Constant
- Oldroyd-B
- Phan-Thien-Tanner
- Pom-Pom
- Rolie-Poly
- Rouse
- Tanner-Simmons
- Upper Convected Maxwell
- White-Metzner
- Yamamoto

Viscoelastic Modelling

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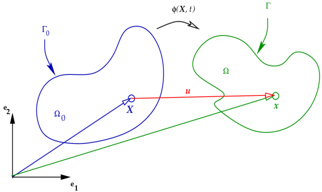
Viscoelastic Modelling

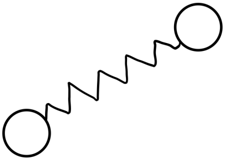
Constitutive Equations

Models fall into four categories:

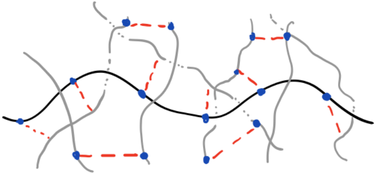
Continuum:



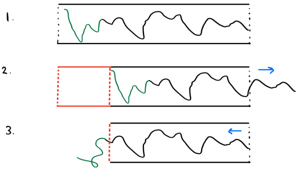
Dumbbell:



Network:



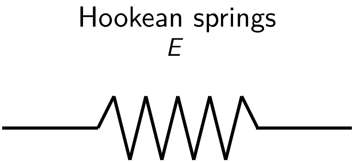
Reptation:

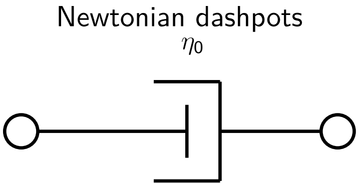


Maxwell Model

Spring-Dashpot Schematics

- Need to capture effects of elasticity and viscosity.
- Initially work in 1D.
- Represent materials schematically.



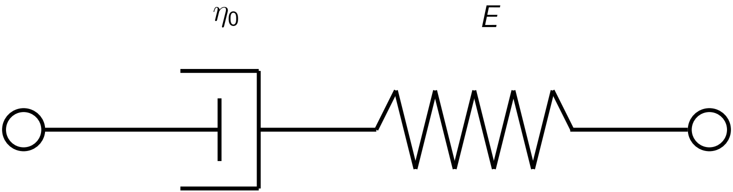


- Build models by combining these elements!

Maxwell Model

Maxwell Material

The simplest construction we can make is

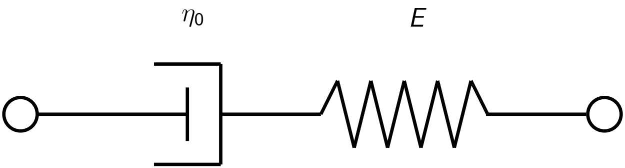


We need to relate the stress T to the strain ϵ.

$$\epsilon = \frac{\text{change in length}}{\text{original length}}.$$

Maxwell Model

Maxwell Equation



Components

Spring: $T_S = E\epsilon_S$ (Hooke's Law)

Dashpot: $T_D = \eta_0 \frac{\partial \epsilon_D}{\partial t}$ (Newton's Law of Viscosity)

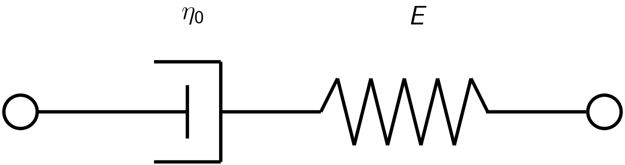
Total

Stress: $T = T_S = T_D.$

Strain: $\epsilon = \epsilon_S + \epsilon_D.$

Maxwell Model

Maxwell Equation



Differentiating total strain yields:

$$T + \lambda \frac{\partial T}{\partial t} = \eta_0 \frac{\partial \epsilon}{\partial t},$$

with relaxation time $\lambda = \frac{\eta_0}{E}$.

This is the Maxwell equation!

Maxwell, J. C. 1867.

Maxwell Model

Is this any good?

In three dimensions:

$$\boldsymbol{T} + \lambda \frac{\partial \boldsymbol{T}}{\partial t} = 2\eta_0 \boldsymbol{D}.$$

Predictions:

- Viscous and elastic limits!
- Stress relaxation — for a step strain ($2\boldsymbol{D} = \boldsymbol{\epsilon_0}\delta(t)$),

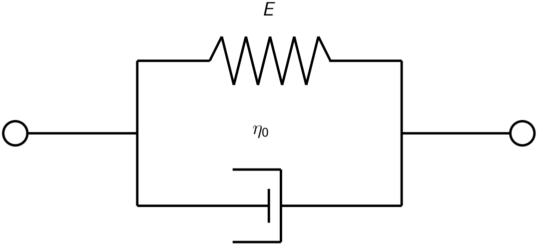
$$\boldsymbol{T} = \boldsymbol{\epsilon}_0 \frac{\eta_0}{\lambda} \mathrm{e}^{-t/\lambda} H(t).$$

- Creep — response to step stress is linear.
- Shear — no shear thinning ($\eta_s = \eta_0$).
- Elongation — no strain hardening ($\eta_e = 3\eta_0$).

Further Spring and Dashpot Models

How else can we relate strain (ϵ) and stress (T)?

1. Kelvin-Voigt



$$T = E\epsilon + \eta_0 \frac{\partial \epsilon}{\partial t}.$$

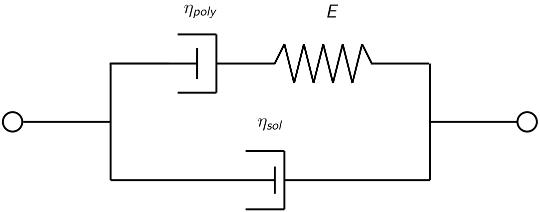
Captures creep behaviour better at expense of stress relaxation.

Thompson, W. 1878.

Further Spring and Dashpot Models

How else can we relate strain (ϵ) and stress (T)?

2. Jeffreys'



$$T + \lambda \frac{\partial T}{\partial t} = \eta_0 \left(\frac{\partial \epsilon}{\partial t} + \lambda_r \frac{\partial^2 \epsilon}{\partial t^2} \right).$$

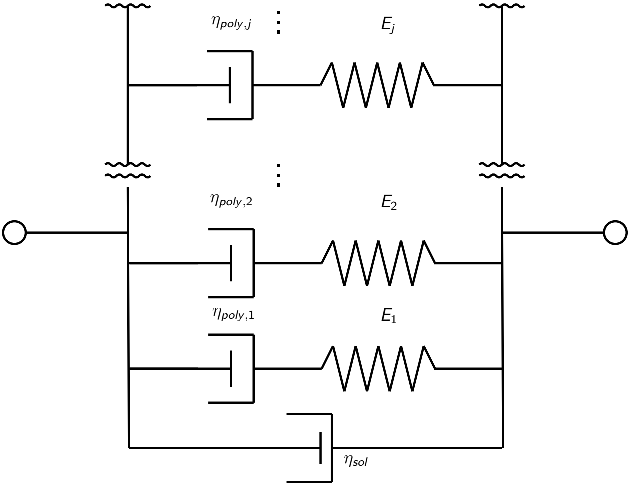
- Relaxation time: $\lambda = \frac{\eta_{poly}}{E}$
- Zero-shear viscosity: $\eta_0 = \eta_{poly} + \eta_{sol}$
- Retardation time: $\lambda_r = \frac{\eta_{sol}\eta_{poly}}{E\eta_0}$

Jeffreys, H., 1929.

Further Spring and Dashpot Models

How else can we relate strain (ϵ) and stress (T)?

3. Maxwell-Wiechert (equation omitted!)



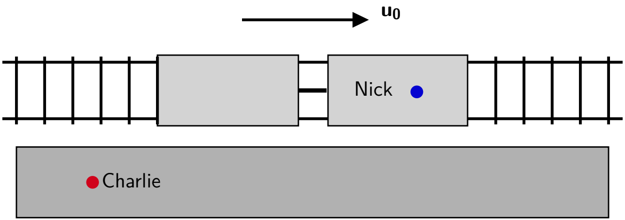
A Major Problem!

- None of these models hold for large deformations!
- Why? They are not *frame invariant*.
    - Relation between stress and strain needs to be independent of the frame of reference.
- Return to the Maxwell equation:

$$\boldsymbol{T} + \lambda \frac{\partial \boldsymbol{T}}{\partial t} = 2\eta_0 \boldsymbol{D}.$$

- Note this depends only on stresses ($\boldsymbol{T}$) and velocity gradients ($\boldsymbol{D}$).

A Major Problem!

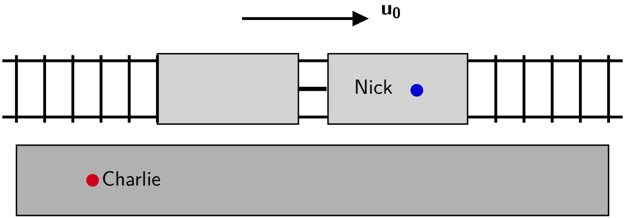


Example:

- Two identical fluids: one in a stationary frame (Charlie); one on a train with constant velocity $\mathbf{u}_0$ (Nick).
- Both fluids should be described by the same Maxwell equation.
- However, Charlie sees Nick's change in stress as

$$\frac{\partial}{\partial t} T_{ij}(\mathbf{x} + \mathbf{u}_0 t, t) = \frac{\partial}{\partial t} T_{ij} + \mathbf{u}_0 \cdot \nabla T_{ij}.$$

A Major Solution!



- Fix: replace $\frac{\partial}{\partial t}$ with a new time derivative!
- Choose an *upper convected derivative*:

$$\overset{\nabla}{\boldsymbol{S}} := \frac{\partial \boldsymbol{S}}{\partial t} + (\mathbf{u} \cdot \nabla)\boldsymbol{S} - (\nabla \mathbf{u})\boldsymbol{S} - \boldsymbol{S}(\nabla \mathbf{u})^T.$$

- This is now frame invariant!

A Major Solution!

New equations!

- Maxwell $\longrightarrow$ Upper Convected Maxwell (UCM)

$$\boldsymbol{T} + \lambda \overset{\nabla}{\boldsymbol{T}} = 2\eta_0 \boldsymbol{D}.$$

- Jeffreys' $\longrightarrow$ Oldroyd-B

$$\boldsymbol{T} + \lambda \overset{\nabla}{\boldsymbol{T}} = 2\eta_0(\boldsymbol{D} + \lambda_r \overset{\nabla}{\boldsymbol{D}}).$$

Note that setting $\lambda_r = 0$ gives UCM; setting $\lambda_r = \lambda$ gives the Newtonian stress tensor.

Oldroyd, J. G., 1950.

UCM/Oldroyd-B

$$\boldsymbol{T} + \lambda \overset{\nabla}{\boldsymbol{T}} = 2\eta_0(\boldsymbol{D} + \lambda_r \overset{\nabla}{\boldsymbol{D}})$$

Predictions:

- Stress relaxation/creep inherited from Maxwell model.
- Shear:

$$\eta_s = \eta_0, \quad T_{11} - T_{22} = 2\eta_0(\lambda - \lambda_r)\dot{\gamma}^2, \quad T_{22} - T_{33} = 0.$$

- Extension:

$$\eta_e = \eta_0 \left[\frac{2(1 - \lambda_r \dot{\epsilon})}{1 - 2\lambda\dot{\epsilon}} + \frac{1 + \lambda_r \dot{\epsilon}}{1 + \lambda\dot{\epsilon}} \right]$$

We obtain strain hardening (with a vengeance!)

Going Further

We can improve on this... but the equations become unwieldly!

- White-Metzner:
  Viscosity and relaxation time shear rate dependent.

- Extended White-Metzner:
  Viscosity and relaxation time dependent on trace of stress tensor.

- Corotational UCM:
  Swap $\overset{\nabla}{\boldsymbol{T}}$ with a *Jaumann* time derivative.

Does moving beyond continuum mechanics help?

White, J. L. and Metzner, A. B., 1960/Souvaliotis, A. and Beris, A. N. 1992/Jaumann, G., 1911

A Dumbbell Model

- Polymers aren't points!
- Suppose they are subject to *direction dependent drag*.
- In absence of solvent ($\eta_{sol} = 0$, $\eta_p = \eta_0$), modify UCM equation as

$$\lambda \overset{\nabla}{\boldsymbol{T}} + \boldsymbol{M}\boldsymbol{T} = 2\eta_0 \boldsymbol{D}.$$

- Choosing $\boldsymbol{M} = \boldsymbol{I} + \frac{\alpha\lambda}{\eta_0}\boldsymbol{T}$ gives the *Giesekus* model:

$$\lambda \overset{\nabla}{\boldsymbol{T}} + \boldsymbol{T} + \frac{\alpha\lambda}{\eta_0}\boldsymbol{T}^2 = 2\eta_0 \boldsymbol{D}, \quad \alpha \in (0, 1).$$

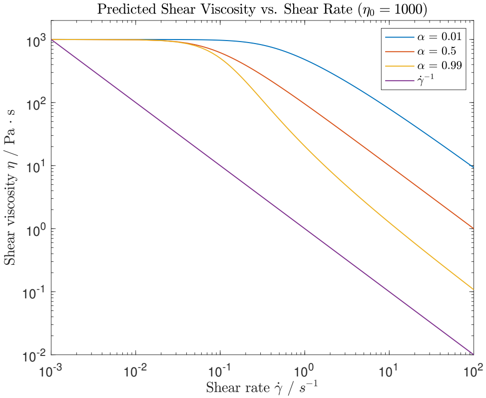
- This is no longer linear in stress!

Giesekus, H., 1966.

Giesekus Predictions

Shear Viscosity

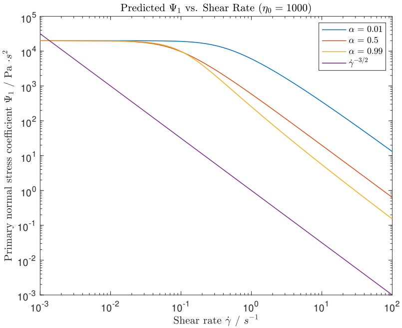
We actually predict shear thinning!

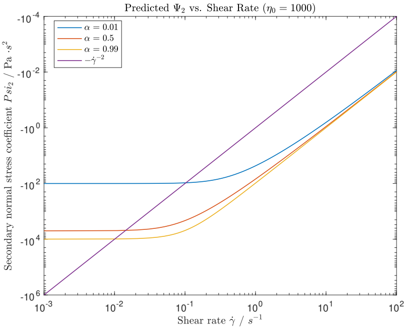


Giesekus Predictions

Shear Normal Stress Coefficients

Positive primary normal stresses; *negative* secondary normal stresses.

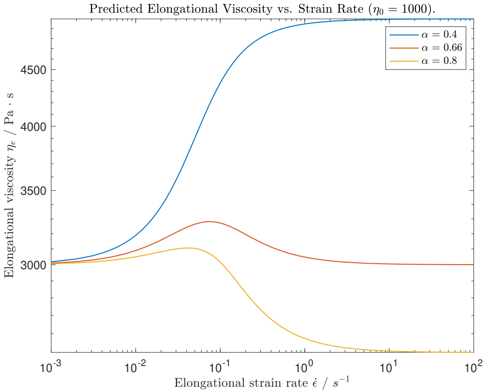




Giesekus Predictions

Elongational Viscosity

Strain *hardening* for $\alpha < 2/3$; strain *softening* for $\alpha \geq 2/3$.



Bird et. al.:($\alpha < 1/2$) (1987)

Giesekus Predictions

In fact...

Constitutive model	Small-strain	Steady viscometric η	N_1	N_2	Steady elongation	Start/stop in shearing flow	Elongational start/recoil	Single shear step	Double-step shear	Remark
Newtonian, eqn (1.7)	P	M	U	U	M	P	U	U	U	Infinite stresses in step strains.
Generalized Newtonian, e.g. eqns (4.4, 4.11)	P	E	U	U	M	P	U	U	U	Infinite stresses in step strains.
Lodge–Maxwell, (UCM) eqns (4.25, 5.150)	E	M	M	U	P	M	M	M	M	Useful for illustrative purposes.
Giesekus eqn (5.111)	E	E	E	G-E	G	G	G	M	M	

...Giesekus can have fairly good predictions in many situations!

Tanner, R. I., 2000.

Summary

So far, we have

- Discussed the basics of viscoelastic modelling.
- Looked at some mechanical-based continuum models and motivated the UCM model.
- Discussed a more complicated model which can make more useful predictions.

One final question...

Summary

So far, we have

- Discussed the basics of viscoelastic modelling.
- Looked at some mechanical-based continuum models and motivated the UCM model.
- Discussed a more complicated model which can make more useful predictions.

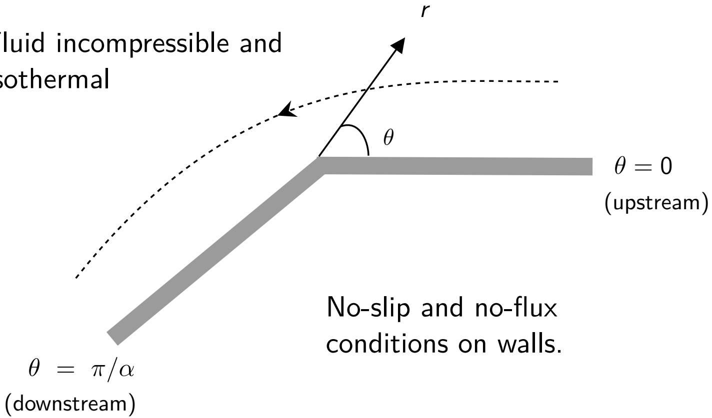
One final question...

Why am I here!?

What About a More Complex Flow?

Planar, steady flow around corner of angle $\theta = \pi/\alpha$. $(1/2 \leq \alpha < 1)$

Fluid incompressible and isothermal



No-slip and no-flux conditions on walls.

PhD aim: *Apply asymptotic techniques to study White-Metzner fluids.*

White-Metzner?

Dimensionless equations:

$$\nabla \cdot \mathbf{u} = 0,$$
$$\mathrm{Re}(\mathbf{u} \cdot \nabla)\mathbf{u} = -\nabla p + \nabla \cdot \boldsymbol{T},$$
$$\boldsymbol{T} + \mathrm{Wi}\dot{\gamma}^{n-1} \overset{\nabla}{\boldsymbol{T}} = 2\dot{\gamma}^{n-1}\boldsymbol{D}.$$

Obtain Reynolds (Re) and Weissenberg (Wi) numbers:

$$\mathrm{Re} = \frac{[\text{inertial forces}]}{[\text{viscous forces}]}; \quad \mathrm{Wi} = \frac{[\text{elastic forces}]}{[\text{viscous forces}]}.$$

These equations are complicated...

White-Metzner?

...and I've gone through a lot of A3 paper this year!

What Does 500+ Sheets of A3 Give You?

White-Metzner Equations:

$$2\mathrm{Wi}nf''|f''|^{n-1}t_{uw} = \left[n - 2\mathrm{Wi}f'|f''|^{n-1}((3-2\alpha)n+\alpha-1)\right](f')^2\, t_{uu} - (2(2-\alpha)n+\alpha-1)\mathrm{Wi}f\,(f')^2\,|f''|^{n-1}t'_{uu}.$$

Momentum equation:

What Does 500+ Sheets of A3 Give You?

White-Metzner Equations:

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$$n\mathrm{Wi}f''|f''|^{n-1}t_{ww} = \left[n + \mathrm{Wi}(\alpha-1)nf'|f''|^{n-1}\right](f')^2\, t_{uw} \\ - (2(2-\alpha)n+\alpha-1)\mathrm{Wi}f\,(f')^2\,|f''|^{n-1}t'_{uw}.$$

Momentum equation:

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$$n\mathrm{Wi}f''|f''|^{n-1}t_{ww} = [n + \mathrm{Wi}(\alpha-1)nf'|f''|^{n-1}]\,(f')^2\,t_{uw} \\ - (2(2-\alpha)n+\alpha-1)\mathrm{Wi}f\,(f')^2\,|f''|^{n-1}t'_{uw}.$$

$$n\,(f')^2 = nt_{ww} + 2((2-\alpha)n+(\alpha-1))\mathrm{Wi}f'|f''|^{n-1}t_{ww} \\ - (2(2-\alpha)n+\alpha-1)f|f''|^{n-1}t'_{ww}$$

Momentum equation:

What Does 500+ Sheets of A3 Give You?

White-Metzner Equations:

$$\begin{aligned} 2\mathrm{Wi}nf''|f''|^{n-1}t_{uw} &= [n - 2\mathrm{Wi}f'|f''|^{n-1}((3-2\alpha)n+\alpha-1)]\left(f'\right)^2 t_{uu} \\ &\quad - (2(2-\alpha)n+\alpha-1)\mathrm{Wi}f\left(f'\right)^2|f''|^{n-1}t'_{uu}. \end{aligned}$$

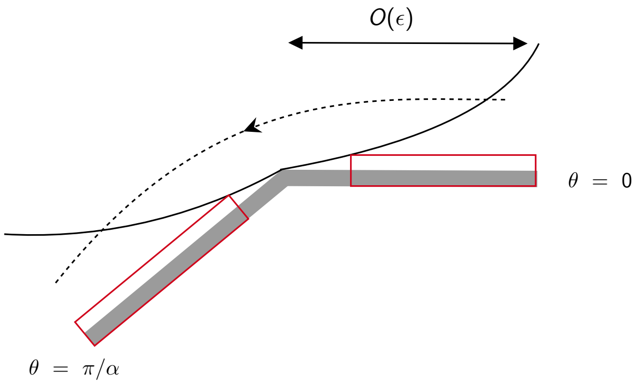
$$\begin{aligned} n\mathrm{Wi}f''|f''|^{n-1}t_{ww} &= [n + \mathrm{Wi}(\alpha-1)nf'|f''|^{n-1}]\left(f'\right)^2 t_{uw} \\ &\quad - (2(2-\alpha)n+\alpha-1)\mathrm{Wi}f\left(f'\right)^2|f''|^{n-1}t'_{uw}. \end{aligned}$$

$$\begin{aligned} n\left(f'\right)^2 &= nt_{ww} + 2((2-\alpha)n+(\alpha-1))\mathrm{Wi}f'|f''|^{n-1}t_{ww} \\ &\quad - (2(2-\alpha)n+\alpha-1)f|f''|^{n-1}t'_{ww} \end{aligned}$$

Momentum equation:

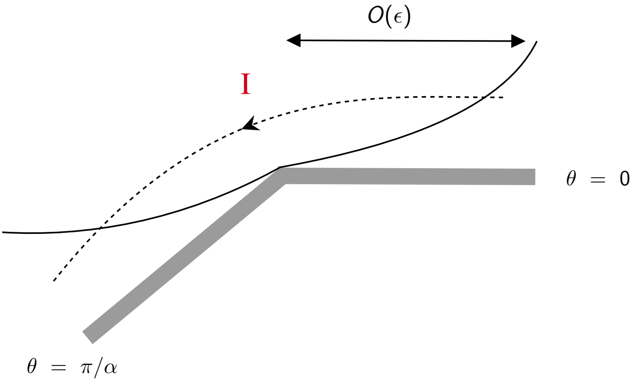
$$\begin{aligned} nt'_{uw} &= 2n(\alpha-1)\mathrm{Wi}p_0 + [(4-2\alpha)n+\alpha-1]ff't'_{uu} \\ &\quad + [(4-3\alpha)n+(\alpha-1)]\left(f'\right)^2 t_{uu} \\ &\quad + [2(2-\alpha)n+\alpha-1]ff''t_{uu}. \end{aligned}$$

So What Can I Tell You?



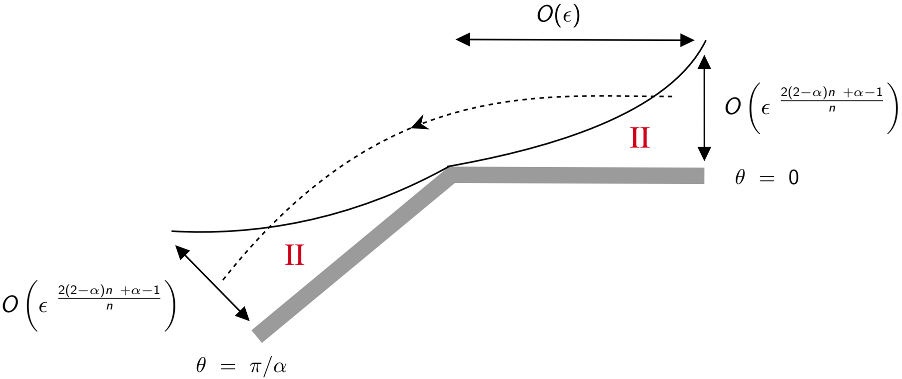
1. Flow near walls is (to leading order) simple shear.

So What Can I Tell You?



2. Fluid behaves elastically as it flows round the corner (Region I).

So What Can I Tell You?



3. Viscous effects remain important in Regions II. Similarity equations tell us the velocity/stresses in the fluid!

A Final Thought

Complex fluids are complex...

A Final Thought

Complex fluids are complex...but they aren't scary!

Thank you for listening!

Diolch yn fawr i wrando!

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