Yield Stress Fluids, Meeting #1

1. Introduction to yield stress fluids
   understand definition/caveats of apparent yield stress fluids
   develop a feel for yield stress and viscosity values

2. Rheometry with yield stress fluids
   identify and avoid slip artifacts
   correct for parallel plate artifacts
   recognize LAOS response of yield stress fluids

Randy H. Ewoldt
June 26, 2009

Part of the summer 2009 Reading Group:
Yielding, Yield Stresses, Viscoelastoplasticity
Non-Newtonian Fluids (NNF) Laboratory, led by Prof. Gareth McKinley
References


• Bonn, D. and M. M. Denn, "Yield Stress Fluids Slowly Yield to Analysis," Science 324(5933), 1401-1402 (2009)


Yield Stress Fluids:
Apparently solid at low stress, \( \sigma < \sigma_Y \)
Apparently fluid at high stress, \( \sigma > \sigma_Y \)
e.g. paint, toothpaste, hand lotion,
concrete, snail slime, nuclear waste sludge

Idealized example:
linear scale

Idealized example:
log-log scale
Toothpaste

Carbopol 980, polymer microgel (0.2wt%)

Tomato puree

Viscosity, $\eta = \frac{\sigma}{\dot{\gamma}}$

Mayonnaise

Apparent yield stress fluids:
1. Initially “high” viscosity
2. Dramatic viscosity drop over narrow range of stress
3. Flows

Detailed experiments
Viscosity, $\eta \approx 10^8$ Pa.s

Ig Nobel Award, Physics (2005) - Presented jointly to John Mainstone and Thomas Parnell of the University of Queensland, Australia, for patiently conducting the so-called pitch drop experiment that began in the year 1927 — in which a glob of congealed black tar pitch has been slowly dripping through a funnel, at a rate of approximately one drop every nine years.

Started: 1927
Drop #1: 1938
Drop #8: 2000 (12 years between drops #7 and #8)
Drop #9: ????
MIT engineers find way to slow concrete creep to a crawl
An estimated 5 to 8 percent of all human-generated atmospheric CO2 worldwide comes from the concrete industry.

Concrete creep is caused by the rearrangement of particles at the nano-scale.

The basic building block of cement paste at the nano-scale -- calcium-silicate-hydrates, or C-S-H -- is granular in nature.

A more dense phase of C-S-H can be induced by additional smaller particles that fit into the spaces between the nano-granules of C-S-H, which greatly hinders the movement of the C-S-H granules over time.

The rate of creep is logarithmic, which means slowing creep increases durability exponentially.

A nano-indentation device allows them to measure in minutes creep properties that are usually measured in year-long creep experiments at the macroscopic scale.
Apparent yield stress fluids?

Blood

Hematocrit content

Olivine (a rock), various grain sizes

Plasticine (modelling material, like putty)

Barnes, JNNFM, 1999
Slime & simulant rheology: Flow

Carbopol (polymer microgel)
Carbopol 940 in DIW, pH $\rightarrow 7$ with NaOH

Magnetorheological Fluid

LORD Corp. MRF-132DG carbonyl iron particles (1-20µm) in silicone oil

AR-G2 rotational rheometer, parallel plates with 600 grit sandpaper, \( h=500\mu m \)

\[ D=40\text{mm for ambient test} \]
\[ D=20\text{mm for magnetic field tests} \]

Using MRF Rheometer Cell from Murat Ocalan, Ph.D. Thesis (in progress), MIT

Magnetorheological fluid

(b)

Corrected Viscosity, $\eta$ [Pa.s]

Corrected Shear Stress, $\sigma_R$ [Pa]

Magnetic Field
- $B=0.462$ T
- $B=0.221$ T
- $B=0.100$ T
- $B=0.046$ T
- $B=0.030$ T
- $B=0.012$ T
- Ambient
Apparent Yield Stress Fluids

Some quotes from Barnes, JNNFM, 1999

Yield stresses were usually only a ‘figment of peoples’ extrapolation

The existence of an essentially horizontal region in a double-logarithmic plot of stress versus strain rate is the most satisfactory criterion for the existence of a ‘yield stress’
(quote from Evans [36])

[Barnes] is in substantial agreement with Evans in this view, especially if then term ‘yield stress’ is prefixed with the adjective ‘apparent’!

Nguyen and Boger [38] reviewed experimental methods of measuring the flow properties of yield stress fluids in 1992: … the especial value of which is the emphasis on possible sources of error in measurement.

Despite the practical importance, there is no reliable way at present to predict the onset of flow.

Perhaps the main difficulty with much of the literature on yield stress fluids is the prevailing presumption that the solid-liquid transition occurs at a single invariant stress. This assumption ignores the fact that the microstructure may adjust dynamically when flow begins.

Foams, emulsions, and Carbopol gels (such as hair gel) are probably closest to “ideal” yield stress materials, because they do not usually show measurable rejuvenation or aging; in these cases, a yield stress may be a material property.

In the few direct comparisons between computed and experimental velocity fields for the falling sphere, the agreement is poor (14), probably because the yielding process in the experimental fluids is not adequately described by the models. Much fundamental work thus remains to be done.
Examples of “ideal” yield stress fluids
(negligible thixotropy)

• Nivea Lotion ~ 4 Pa
• Gilette foamy shaving cream ~10 Pa
• Aloe gel ~60 Pa
• Nivea Cream, Toothpaste and Mayo ~200-300 Pa
• Magnetorheological fluid 10 ~ 10,000 Pa
Experimental Issue: Slip

(log) viscosity

proper flow curve

pseudo yield stress

pseudo Newtonian region

(log) shear stress
Sandpaper required to avoid slip

Nivea Lotion

shear stress (Pa)

100.0

10.00

1.00

1.00E-6 0.01 100.0

shear rate (1/s)

FILLED)
P/P w/ sandpaper,
3 different gaps

OPEN)
P/P, NO sandpaper,
3 different gaps

Sandpaper from
McMaster-Carr
Part #) 47185A51
Adhesive-back
sandpaper, 8” dia. disc, 600 grit
Flow curves: different perspectives

NiveaLotion-001f
NiveaLotion-S02-h1050-0001f, Steady state flow step
NiveaLotion-S02-h450-0001f, Steady state flow step
NiveaLotion-S02-h700-0001f, Steady state flow step
NiveaLotion-S03-h1050-0001f, Steady state flow step
NiveaLotion-S03-h450-0001f, Steady state flow step
NiveaLotion-S03-h700-0001f, Steady state flow step
NiveaLotion-S04-h1050-0001f, Steady state flow step

NiveaLotion-001f
NiveaLotion-S02-h1050-0001f, Steady state flow step
NiveaLotion-S02-h450-0001f, Steady state flow step
NiveaLotion-S02-h700-0001f, Steady state flow step
NiveaLotion-S03-h1050-0001f, Steady state flow step
NiveaLotion-S03-h450-0001f, Steady state flow step
NiveaLotion-S03-h700-0001f, Steady state flow step
NiveaLotion-S04-h1050-0001f, Steady state flow step
Parallel plate correction, steady flow

Shear Stress, $\sigma$ [Pa]

Shear Rate [s$^{-1}$]

- Nivea Lotion
- Parallel plates with sandpaper
- $D=40\text{mm}$
- OPEN: Apparent stress
- FILLED True stress
- $h=1050\ \mu\text{m}$
- $h=700\ \mu\text{m}$
- $h=450\ \mu\text{m}$
Parallel plate stress correction

Torque balance

\[ M = 2\pi \int_0^R \sigma(r)r^2 dr \]

Linear assumption

\[ \sigma(r) = Hr \]

Apparent rim stress

\[ \sigma_A(R) = \frac{2M}{\pi R^3} \]

Error for perfect plastic

for \( \sigma(r) = \sigma_Y \)

\[ \frac{\sigma_A}{\sigma_Y} \rightarrow \frac{4}{3} \]

Correction formula

\[ \sigma_R = \frac{M}{2\pi R^3} \left[ 3 + \frac{d \ln M}{d \ln \dot{\gamma}_R} \right] \]

\[ \sigma_R = \frac{\sigma_A}{4} \left[ 3 + \frac{d \ln \sigma_A}{d \ln \dot{\gamma}_R} \right] \]

4/3 ratio mentioned by Brunn and Asoud, Rheol. Acta, 2002
Parallel plate stress correction,
Nivea lotion steady flow

Shear Stress, $\sigma$ [Pa]

Shear Rate [s$^{-1}$]

- OPEN: Apparent stress
- FILLED True stress

- $h=1050$ $\mu$m
- $h=700$ $\mu$m
- $h=450$ $\mu$m

Nivea Lotion
Parallel plates with sandpaper
D=40mm
Roughened Cone – Works!

Nivea Lotion on AR-G2
3 different samples to show repeatability (S02, S04, S05)
all geometries with sandpaper
P/P) D=40mm, with plate-plate correction
Cone) D=60mm, $\alpha=2^\circ$, no correction necessary
Nivea lotion flow curve

Nivea Lotion
3 different samples to show repeatability (S02, S04, S05)

all geometries with sandpaper
P/P) D=40mm,
    with plate-plate correction
Cone) D=60mm, $\alpha=2^\circ$,
    no correction necessary
Creep tests, low stress

Cannot determine a steady flow viscosity below the yield stress

NEGATIVE strain-rates? Is this remnant elastic recovery from the previous flow test? I saw this also with the stress-ramp flow tests, from high-to-low stresses, that at sufficiently low stresses the strain-rate was negative (see Sample #1). Or maybe it’s instrument artifact?
Repeatability with Rough Cone

Nivea Lotion

shear stress (Pa)

shear rate (1/s)

S05-Run1, initial flow test
S06-Run1, initial flow test
S06-Run5, flow after LAOS
Yield Stress Models

\begin{align*}
\sigma_B &= \sigma_Y + \mu_p \dot{\gamma} \\
\sigma_{H-B} &= \sigma_Y + K \dot{\gamma}^m \\
\sqrt{\sigma_{\text{Casson}}} &= \sqrt{\sigma_Y} + \sqrt{\mu_p \dot{\gamma}} \\
\sigma_{\text{Carreau}} &= \dot{\gamma} \eta_0 \left(1 + (\lambda \dot{\gamma})^2\right)^{\frac{n-1}{2}}
\end{align*}

Bingham

H-B

Casson

Sisko

(Sisko is subset of Carreau)

Barnes, JNNFM, 1999 (hypothetical data)
Linear viscoelasticity

![Graph showing the relationship between angular frequency and G' and G''](image)

- Frequency sweep step
- 0.5% strain amplitude

NiveaLotion-S06-ConeSP-0004o
Large amplitude oscillatory shear

Run 2) 10 rad/s
Run 3) 1 rad/s

"strain-controlled"
LAOS on AR-G2

G' (Pa)

G'' (Pa)
Nivea lotion LAOS

\( \gamma_0 = 0.13\% \)

\( \gamma_0 = 1\% \)

\( \gamma_0 = 10.6\% \)

\( \gamma_0 = 108\% \)

\( \gamma_0 = 1052\% \)

\( \omega = 10 \text{ rad/s} \)

Needs inertia correction to determine sample stress
Model responses to LAOS
Pseudoplastic and yield stress fluid response to LAOS

Purely viscous Carreau model
\[ \sigma(\dot{\gamma}) = \dot{\gamma}\eta_0 \left(1 + (\dot{\gamma})^2\right)^{\frac{n-1}{2}} \]
n = 0 : yield stress
n = 1 : Newtonian

LAOS deformation
\[ \dot{\gamma}(t) = \gamma_0 \omega \cos \omega t \]

Response:

\[ y = \frac{\dot{\gamma}(t)}{\dot{\gamma}_0} = \cos \omega t \]
Pseudoplastic and yield stress fluid response to LAOS

Purely viscous Carreau model

\[ \sigma(\dot{\gamma}) = \dot{\gamma}\eta_0 \left(1 + \left(\lambda\dot{\gamma}\right)^2\right)^{\frac{n-1}{2}} \]

\( n = 0 \): yield stress  
\( n = 1 \): Newtonian

LAOS deformation

\[ \dot{\gamma}(t) = \gamma_0 \omega \cos \omega t \]

Response:

\[ \frac{\sigma(t)}{\sigma_{\text{max}}} \text{ at } \lambda\gamma_0 \omega = 10 \]

Ewoldt et al., submitted
Response of an elastic Bingham fluid to oscillatory shear

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Department of Chemical Engineering, Princeton University

Abstract: The response of an elastic Bingham fluid to oscillatory strain has been modeled and compared with experiments on an oil-in-water emulsion. The newly developed model includes elastic solid deformation below the yield stress (or strain), and Newtonian flow above the yield stress. In sinusoidal oscillatory deformations at low strain amplitudes the stress response is sinusoidal and in phase with the strain. At large strain amplitudes, above the yield stress, the stress response is non-linear and is out of phase with strain because of the storage and release of elastic recoverable strain. In oscillatory deformation between parallel disks the non-uniform strain in the radial direction causes the location of the yield surface to move in-and-out during each oscillation. The radial location of the yield surface is calculated and the resulting torque on the stationary disk is determined. Torque waveforms are calculated for various strains and frequencies and compared to experiments on a model oil-in-water emulsion. Model parameters are evaluated independently: the elastic modulus of the emulsion is determined from data at low strains, the yield strain is determined from the phase shift between torque and strain, and the Bingham viscosity is determined from the frequency dependence of the torque at high strains. Using these parameters the torque waveforms are predicted quantitatively for all strains and frequencies. In accord with the model predictions the phase shift is found to depend on strain but to be independent of frequency.

Key words: Elastic Bingham fluid, yield stress, oscillatory shear, oil-in-water emulsion, nonlinear rheological behavior
Elastic Bingham model

\[ \sigma = G \gamma^E \quad |\gamma^E| < \gamma_Y \]

Elastic before yield

\[ \sigma = \sigma_Y + \mu \dot{\gamma} \quad |\gamma^E| = \gamma_Y \]

Bingham model after yield

Important things to keep in mind:

1) Not a full continuum model as represented here
2) Elastic strain can be recovered when flow reverses
3) Strain-induced yielding, therefore a well defined yield surface in plate-plate tests

Elastic Bingham model - LAOS

\[ \sigma = G \gamma^E \] \quad \gamma^E < \gamma_Y \\
\[ \sigma = \sigma_Y + \mu \dot{\gamma} \] \quad \gamma^E = \gamma_Y \\

Elastic before yield

Bingham model after yield

\[ \Gamma_0 = \frac{\gamma_0}{\gamma_Y} \sim \frac{\text{maximum imposed strain}}{\text{yield strain}} \]

\[ N = \frac{\mu \dot{\gamma}_0 \omega}{\sigma_Y} \sim \frac{\text{maximum viscous stress}}{\text{yield stress}} \]

Fig. 4. Parallel disk geometry. The upper disk oscillates with frequency \( \omega \) and strain amplitude at disk edge \( A_R \)

Fig. 5. Elastic strain as a function of radial position. When \( |\Gamma_E| < 1 \), the fluid behaves as an elastic solid. When \( |\Gamma_E| = 1 \), the fluid flows. At any given time, the smallest radial position at which \( |\Gamma_E| = 1 \) defines the yield surface.

Elastic Bingham model - LAOS

\[ \sigma = G\gamma^E \quad \left| \gamma^E \right| < \gamma_Y \]

\[ \sigma = \sigma_Y + \mu_p \dot{\gamma} \quad \left| \gamma^E \right| = \gamma_Y \]

Elastic before yield

Bingham model after yield

\[ \Gamma_0 = \frac{\gamma_0}{\gamma_Y} \quad N = \frac{\mu_p \gamma_0 \omega}{\sigma_Y} \]

Fig. 4. Parallel disk geometry. The upper disk oscillates with frequency \( \omega \) and strain amplitude at disk edge \( A_R \)

Fig. 6. Torque waveforms for an elastic Bingham fluid between oscillating parallel disks. Parameters \( \Gamma_0 \) and \( N \) can be interpreted as the normalized strain amplitude (at disk edge) and normalized frequency, respectively. Imposed strain is represented by broken lines

Elastic Bingham model - LAOS

\[ \sigma = G\gamma^E \quad \left| \gamma^E \right| < \gamma_Y \]
\[ \sigma = \sigma_Y + \mu_p \dot{\gamma} \quad \left| \gamma^E \right| = \gamma_Y \]

Elastic before yield
Bingham model after yield

\[ \Gamma_0 = \frac{\gamma_0}{\gamma_Y} \quad N = \frac{\mu_p \gamma_0 \omega}{\sigma_Y} \]

Fig. 4. Parallel disk geometry. The upper disk oscillates with frequency \( \omega \) and strain amplitude at disk edge \( A_R \)

Fig. 9. Frequency dependence of torque waveforms. Experimental curves are for an oil-in-water emulsion. Model curves are based on the following parameters: \( \gamma_0 = 33\% \), \( G = 3000 \) dyn/cm\(^2\), \( \mu = 15 \) poise. Frequency is in rad/s

Elastic Bingham model – Pipkin space

\[ \sigma = G\dot{\gamma}^E \quad \left| \gamma^E \right| < \gamma_Y \]

Elastic before yield

\[ \sigma = \sigma_Y + \mu_p \dot{\gamma} \quad \left| \gamma^E \right| = \gamma_Y \]

Bingham model after yield

\[ \Gamma_0 = \frac{\gamma_0}{\gamma_Y} \]

\[ \Gamma_{0,\text{max}} = 6.0 \]

\[ \Gamma_0 = 6.0 \quad N = .003 \quad \Gamma_0 = 6.0 \quad N = .3 \]

\[ \Gamma_0 = 3.0 \quad N = .0015 \quad \Gamma_0 = 3.0 \quad N = .15 \]

\[ \Gamma_0 = .3 \quad N = .00015 \quad \Gamma_0 = .3 \quad N = .015 \]

\[ N_{\text{max}} = 0.3 \]

\[ N = \frac{\mu_p \gamma_0 \omega}{\sigma_Y} \]

LAOS plate-plate artifacts

1. Smoothes out sharp transitions, since a portion of the material is always in the linear strain regime

2. Over-estimates stress for shear-thinning fluids, by factor of 4/3 for a perfect plastic response

Lissajous curves of (apparent) stress $\sigma(t)$ vs. strain $\gamma(t)$.

Maximum (apparent) stress shown above curve, $\sigma_A/\sigma_Y$
Elastic Bingham model - LAOS

\[ \sigma = G \gamma^E \quad |\gamma^E| < \gamma_Y \]

Elastic before yield

\[ \sigma = \sigma_Y + \mu_p \dot{\gamma} \quad |\gamma^E| = \gamma_Y \]

Bingham model after yield

(a) Homogeneous strain

\[ \Gamma_0 = \frac{\gamma_0}{\gamma_Y} \]

(b) Torsional parallel plate

\[ \Gamma_0 = \frac{\gamma_0}{\gamma_Y} \]

Elastic Bingham model - LAOS

\[
\sigma = G \gamma^E \quad |\gamma^E| < \gamma_Y
\]

Elastic before yield

\[
\sigma = \sigma_Y + \mu_p \dot{\gamma} \quad |\gamma^E| = \gamma_Y
\]

Bingham model after yield

\[
\Gamma_0 = \frac{\gamma_0}{\gamma_Y}
\]

\[
N = \frac{\mu_p \gamma_0 \omega}{\sigma_Y}
\]

Perfect plastic dissipation ratio

\[ \phi = \frac{E_d}{(E_d)_{pp}} = \frac{\pi \gamma_0^2 G''}{(2 \gamma_0)(2 \sigma_{\max})} \]

\[ \begin{align*}
\rightarrow 1 & \quad \text{Perfect Plastic} \\
\pi/4 = 0.785 & \quad \text{Newtonian} \\
\rightarrow 0 & \quad \text{Purely Elastic}
\end{align*} \]
Experiments

![Graph showing viscosity vs. shear rate for Xanthan gum 0.2 wt% with different viscosity models and correction methods.]

- **Xanthan gum 0.2 wt%**
- **true viscosity**
- **apparent viscosity**
- **parallel disk correction**
- **Carreau model fits**
Shear-thinning xanthan gum (0.2wt%)
Drilling fluid

\[
\phi \equiv \frac{E_d}{(E_d)_{pp}} = \frac{\pi \gamma_0 G''_1}{4\sigma_{\text{max}}} \begin{cases} \rightarrow 1 & \text{Perfect Plastic} \\ \rightarrow \pi/4 = 0.785 & \text{Newtonian} \\ \rightarrow 0 & \text{Purely Elastic} \end{cases}
\]
Nivea lotion LAOS

\( \gamma_0 = 0.13\% \)

\( \gamma_0 = 1\% \)

\( \gamma_0 = 10.6\% \)

\( \gamma_0 = 108\% \)

\( \gamma_0 = 1052\% \)

Needs inertia correction
Outline revisited

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