Rheological Fingerprinting: Using LAOS to Physically Interpret the Nonlinear Behavior of Complex Fluids and Soft Solids

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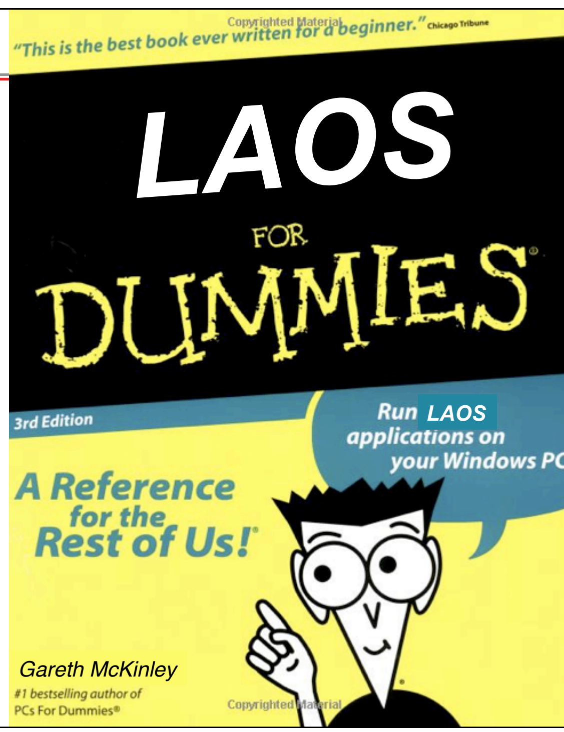

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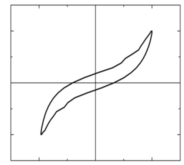
Outline

- **Rheological fingerprinting** of a complex fluid
- Large Amplitude Oscillatory Shear (LAOS)
  - Useful ways to characterize nonlinear properties of complex fluids
  - How to quantify the measured response?



- Wormlike Micellar Solutions
  - Commonly used in shampoos/conditioners
  - Single mode linear viscoelastic response?
  - How do we characterize the nonlinear response?
- The nonlinear rheology of snail slime
  - What is a mucin gel? How does it work?
  - How do we characterize the nonlinear response?
- Gluten Gels as prototypical dough
  - LAOS for soft viscoelastic solids & gels
  - How to characterize the thixotropy & nonlinear response?
- Yielding Materials; viscoelastoplasticity

- Sponsors:
  - Schlumberger Foundation, Kraft Foods, Procter & Gamble
  - NSF Graduate Research Fellowship

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Bibliography

- Some useful references for further reading:

  - Dealy, J.M. and Wissbrun, K.F., Melt Rheology and its Role in Plastics Processing: Theory and Applications, Van Nostrand Reinhold, New York, 1990.
  - Giacomin, A.J. and Dealy, J.M., "Large Amplitude Oscillatory Shear", Techniques in Rheological Measurements, Vol.1, A. A. Collyer (ed.), Chapman & Hall, London, 1993.
  - Ganeriwala, S.A. and Rotz, C.A., Fourier Transform Mechanical Analysis for Determining the Nonlinear Viscoelastic Properties of Polymers, *Polym. Sci & Eng.*, **27**(2), (1987), 165-178.
  - Wilhelm, M., Fourier-Transform Rheology, *Macromol. Mat. & Eng.*, **287**(2), (2002), 83-105.
  - Cho, K.S., Hyun, K., Ahn, K. and Lee, S.-J., A geometrical Interpretation of Large Amplitude Oscillatory Shear Flow, *J. Rheol.*, **49**(3), (2005), 747-758.
  - Ewoldt, R., Clasen, C., Hosoi, A.E. and McKinley, G.H., Rheological Fingerprinting of Gastropod Pedal Mucus and Bioinspired Complex Fluids for Adhesive Locomotion, *Soft. Matter*, **3**(5), (2006), 634-643.
  - Ewoldt, R.H., McKinley, G.H. and Hosoi, A.E., New Measures for Characterizing Nonlinear Viscoelasticity in Large Amplitude Oscillatory Shear Flow, *J. Rheol.* , **52**(6), (2008), 1427-1458.
  - Ewoldt, R.H., Winter, P., Maxey, J. and McKinley, G.H., Large Amplitude Oscillatory Shear of Pseudoplastic and Elastoviscoplastic Materials, *Rheol. Acta*, **49**(2), (2009), 191.

- Hyun, K., Wilhelm, M., Klein, C.O., Cho, K.S., Nam, J.G., Ahn, K.H., Lee, S.J., Ewoldt, R.H. and McKinley, G.H., A Review of Nonlinear Oscillatory Shear Tests: Analysis and Application of Large Amplitude Oscillatory Shear (LAOS); *Prog. Polym. Sci*, (2011), **36** 1697-1753 (56pp).

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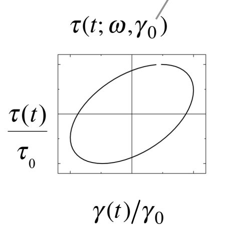
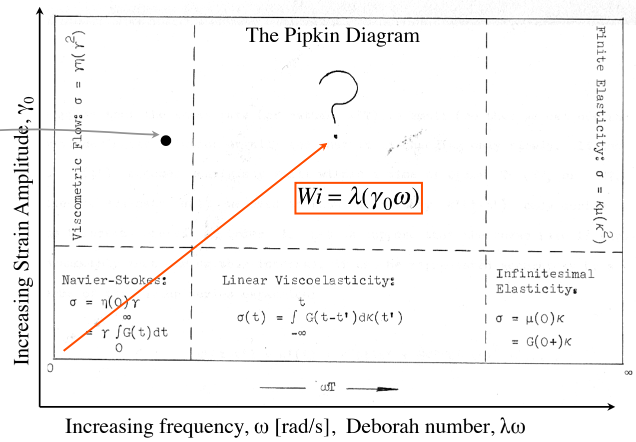
Motivation for LAOS

- Develop rheological methods that leverage the capabilities of modern instrumentation to probe the **nonlinear** properties of complex fluids and soft solids?
  - Foods and consumer products (gels, foams, surfactant systems) gluten gel, micellar solutions, gastropod pedal mucus (snail slime)

- *"… the whole infinite-dimensional space of shearing strain is projected onto two dimensions"*
- *"Nothing very systematic is known about the interior region…"*



Bowditch-Lissajous Curve



A.C. Pipkin, Lectures on Viscoelastic Theory, Springer, NewYork (1972)

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Linear Viscoelasticity & Ellipses

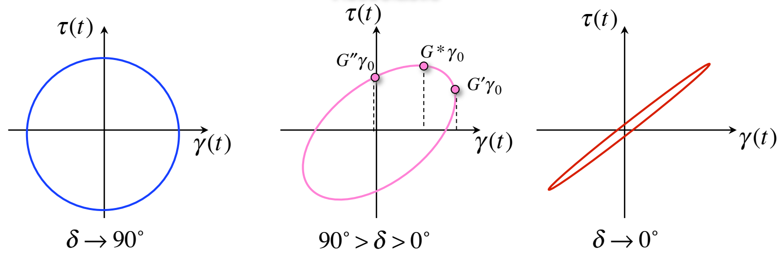
- The equation for a linear viscoelastic response can be re-written (by eliminating time *t*) to show that the Lissajous figure for stress is **elliptical** when represented vs. shear strain or shear-rate.

$$\gamma(t) = \gamma_0 \sin\omega t \qquad \tau = \gamma_0\left[G'\sin\omega t + G''\cos\omega t\right]$$

$$\boxed{\tau^2 - 2G'\tau\gamma + \gamma^2\left(G'^2 + G''^2\right) = \left(G''\gamma_0\right)^2}$$

- For further reading, see wikipedia or http://ibiblio.org/e-notes/Lis/Lissa.htm

Viscous dominated Viscoelastic elastic dominated



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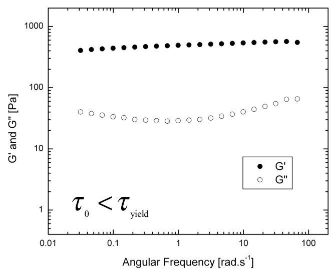
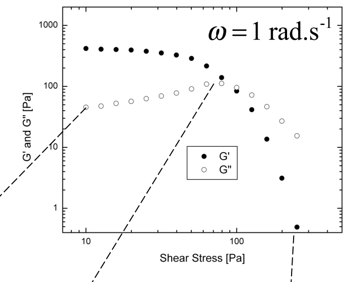
Lissajous Figures for Yielding Materials (Gels, Pastes…)

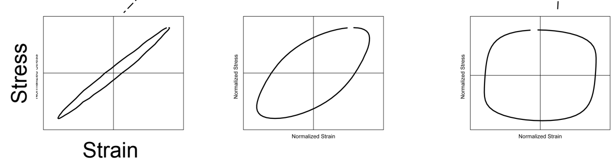
- Impose oscillatory stress $\tau(t) = \tau_0 \sin(\omega t)$
- Measure $\gamma(t)$ and represent yielding transition as *Lissajous figures*





4cm 2° steel cone, T=22°C

The Lissajous figure for a linear viscoelastic response is **always** elliptical



…construct a **rheological fingerprint** of material nonlinearity

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Nathaniel Bowditch (1773-1838)

- "I have now traced the mathematical analysis and experimental illustration of the Lissajous curves from France to Gt. Britain…to their home in Salem, MA. **The so-called Lissajous curves are the Bowditch curves**…They will continue, probably to be called the Lissajous curves. But their history should be known and will be known; though it is not necessary for the reputation of the self-taught mathematician, Dr. Nathaniel Bowditch"…

  J. Lovering, Hollis Prof. of Physics, Harvard College "Anticipation of the Lissajous Curves",
  Proc. Am. Acad. Arts & Sci. **16** (1881).

- Originally published in N. Bowditch, *Mem. Am. Acad. Arts. Sci* **3**, 413-436 (1815)

http://en.wikipedia.org/wiki/Nathaniel_Bowditch

In 1787, aged fourteen, Bowditch began to study algebra and two years later he taught himself calculus. He also taught himself Latin in 1790 and French in 1792 so he was able to read mathematic works such as Isaac Newton's *Philosophiae Naturа Principia Mathematica*. At seventeen, he wrote a letter to a Harvard University professor pointing out an error in the *Principia*.…

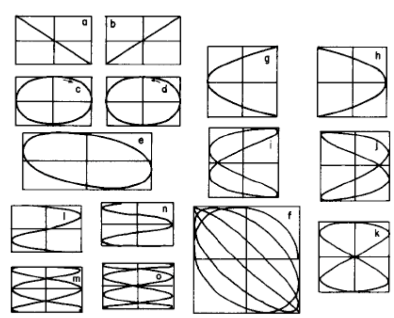


Fig. 3. Tracings of drawings of the orbits of two mutually orthogonal oscillations, published by N. Bowditch (Ref. 3). Drawings a, b, c, and d

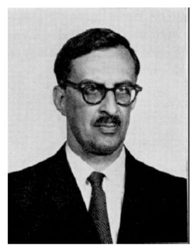
A.D. Crowell, *Am. J. Phys* 1981

Tools for Analyzing Nonlinear Oscillatory Flows

- **Pipkin Space** Pipkin, 1972
- **Bowditch-Lissajous curves** W. Philippoff, *Trans Soc. Rheol*. **10,** 1964
  Dealy & Wissbrun *Melt Processing* 1990; Giacomin & coworkers
- **Fourier Transform Rheology** Willhelm et al., *Macromol. Mater Eng*. 2002
- **Geometrical Interpretation of Lissajous Curves** Cho, Ahn et al., *JoR* 2005
  Kim, Hyun, Cho, *KARJ* 2006

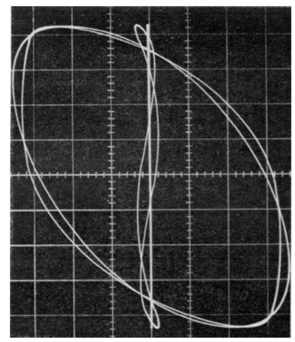
Presentation of the Bingham Medal to
Wladimir Philippoff

E. B. BAGLEY, *Canadian Industries Limited, McMasterville, Canada*



The Bingham Medal of the Society of Rheology for 1962 was presented to Dr. Wladimir Philippoff of the Esso Research and Engineering Company, Linden, New Jersey, in recognition of his outstanding contributions to the phenomenological rheology of viscoelastic materials. His dedication to experimental rheology over a period of almost thirty years has been manifested by his broad interests in new phenomena, in a wide range of materials, and in methods of measurement. He recognizes the basic scientific principle that theory and experiment are mutually dependent—that theory without experiment and experiment without theory are equally sterile. Undismayed by

VIBRATIONAL MEASUREMENTS 325



g. 4. Resolving the non-Newtonian recording into first and third harmonics with the electronic computer.

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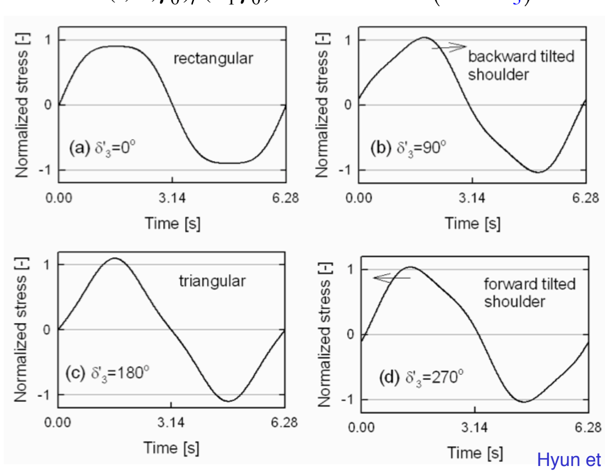
Time-Domain Representation

- Even if we only think about the third harmonic, representation becomes complicated, because relative **phase** of the waves is important:

$$\tau(t;\omega,\gamma_0)/(G_1^*\gamma_0) = \sin\omega t + 0.1\sin(3\omega t + \delta_3)$$



How do we relate phase angle to higher harmonic information?

Hyun et al. *Prog. Polym Sci, 2010*

Fig. 8. The normalized stress data at different values of the phase angle for the third harmonic from Eq. (19) at a fixed frequency ω = 1rad/s (a) $\delta'_3 = 0°$ (b) $\delta'_3 = 90°$ (c) $\delta'_3 = 180°$ (d) $\delta'_3 = 270°$. There are various shapes of the

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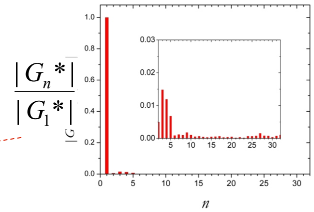
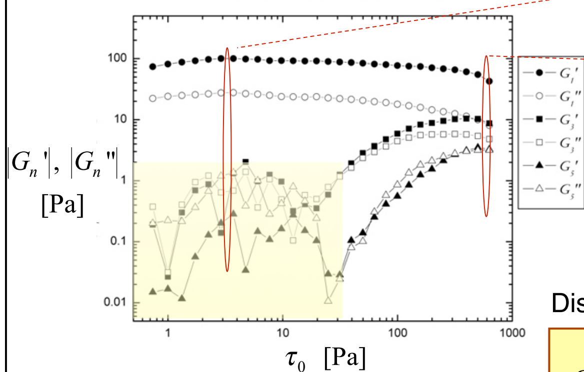
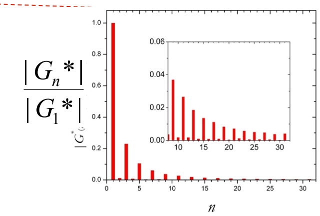
Fourier Transform Rheometry

- Single harmonic input $\gamma(t) = \gamma_0 \sin \omega t$
- Measure $\tau(t) = \gamma_0 \sum_{n=odd} \left[G_n' \sin n\omega t + G_n'' \cos n\omega t \right]$
- Quantitatively robust, but lacking in *physical interpretation*







Snail Pedal Mucus
2cm steel plate, T=22°C, 180μm gap

Dissipation:

$$G_1'' = \frac{E_d}{\pi \gamma_0^2} = \frac{\oint \tau d\gamma}{\pi \gamma_0^2}$$

Ganeriwala and Rotz, *Polym. Eng. Sci.*, 1987; Willhelm et al. *Macromol. Mater Eng.* 2002

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Physical Interpretation of LAOS Deformations

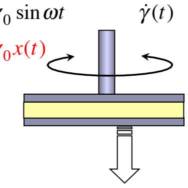
- General Fourier decomposition $\tau = \gamma_0 \sum_{n \text{ odd}} G_n'' \cos(n\omega t) + G_n' \sin(n\omega t)$

A New Approach

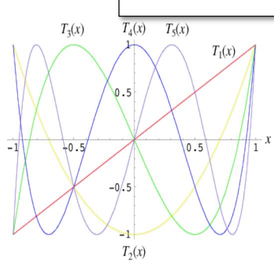
- Consider strain and strain rate as independent *orthogonal* inputs
- Decompose output stress using symmetry arguments into 'elastic' (*x*) and 'viscous' (*y*) contributions
- Represent the material response or *Transfer Function* in terms of **Chebyshev polynomials** in x and y:

$\gamma(t) = \gamma_0 \sin \omega t = \gamma_0 x(t)$

$\dot{\gamma}(t) = (\gamma_0 \omega) \cos \omega t = \dot{\gamma}_0 y(t)$



$$\tau(t;\omega,\gamma_0) \equiv \tau_{elastic}\left(\gamma(t)\right) + \tau_{viscous}\left(\dot{\gamma}(t)\right) = \gamma_0 \sum_{i=1}^{N} e_i T_i(x) + \gamma_0 \omega \sum_{i=1}^{N} v_i T_i(y)$$



BENEFITS

- Chebyshev polynomials are orthogonal and offer near-optimal polynomial interpolation
- The **Chebyshev coefficients** (v_i & e_i) have physical interpretations with respect to familiar rheological concepts such as *shear-thinning* and *strain-stiffening*
- Temporal response can always be reconstructed using identities for Chebyshev polynomials

$T_i(x) \equiv T_i(\sin \omega t) = (-1)^{i+1} \sin(i\omega t)$ $T_i(y) \equiv T_i(\cos \omega t) = \cos(i\omega t)$

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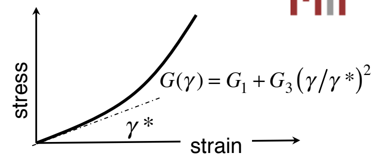
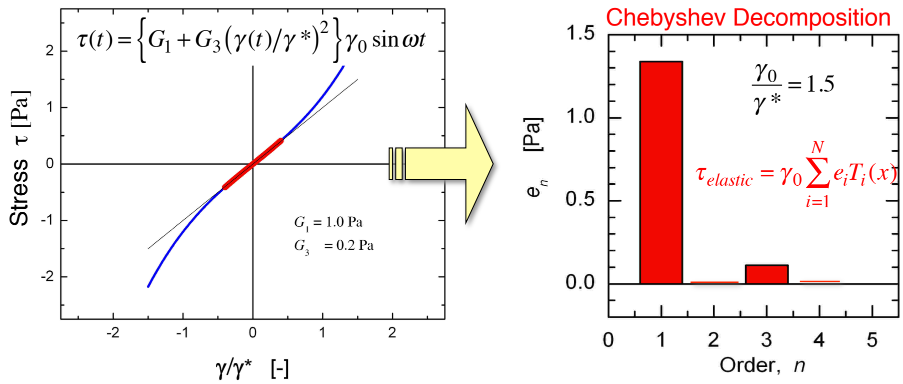
Example: Nonlinear Elastic Solid

- LAOS for nonlinear elastic solid
  - Strain-stiffening modulus: $\tau = G(\gamma)\gamma$
- Higher order terms are mutually orthogonal…



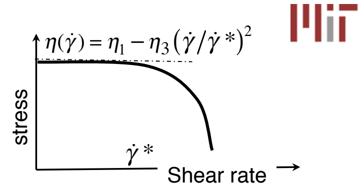


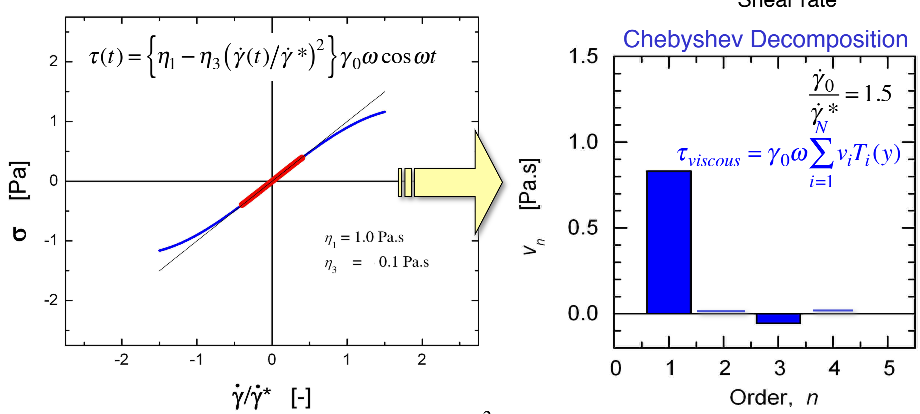
- Material Moduli: $\boxed{e_1 = G_1' = G_1 + \frac{3}{4}\left(\frac{\gamma_0}{\gamma^*}\right)^2 G_3}$ $e_3 = -G_3' = +\frac{1}{4}\left(\frac{\gamma_0}{\gamma^*}\right)^2 G_3$

Linear elastic limit *Direct measure of the nonlinearity* 13

Example: Generalized Newtonian Fluid

- LAOS for shear-thinning viscous fluid
  - Rate-dependent viscosity: $\tau = \eta(\dot\gamma)\dot\gamma$

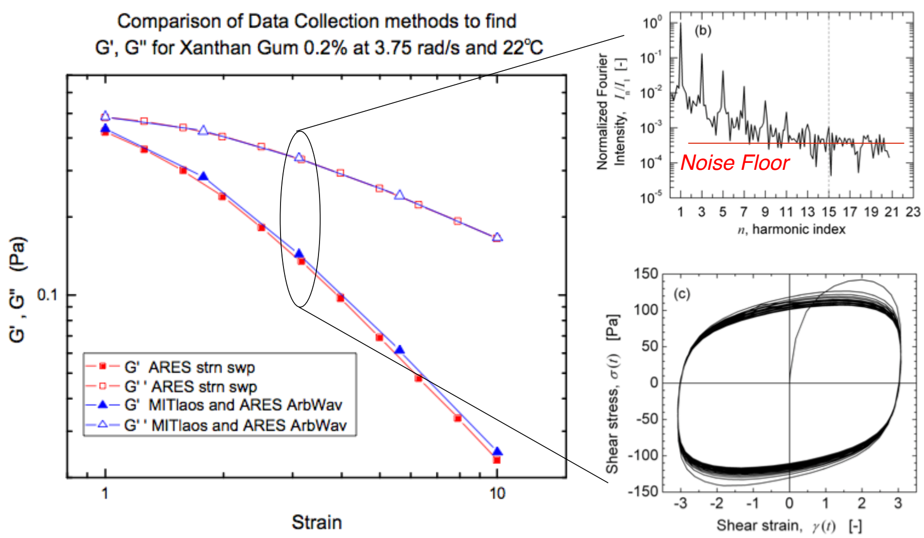




- Viscosity: $\boxed{v_1 \equiv \eta_1' = \eta_1 - \frac{3}{4}\left(\frac{\gamma_0}{\gamma^*}\right)^2 \eta_3}$ $v_3 \equiv \eta_3' = -\frac{1}{4}\left(\frac{\gamma_0}{\gamma^*}\right)^2 \eta_3$

Newtonian limit *Direct measure of the nonlinearity* 14

Consistency Check!



Ewoldt, Hosoi, McKinley, *J. Rheol.* **52**(6), 2008
Ewoldt, Winter, Maxey, McKinley, *Rheol. Acta* 2010

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Additional Physical Quantifiers of Nonlinearity

Strain-stiffening index, S

- G_M': small-strain (tangent) modulus
- G_L': large-strain (secant) modulus

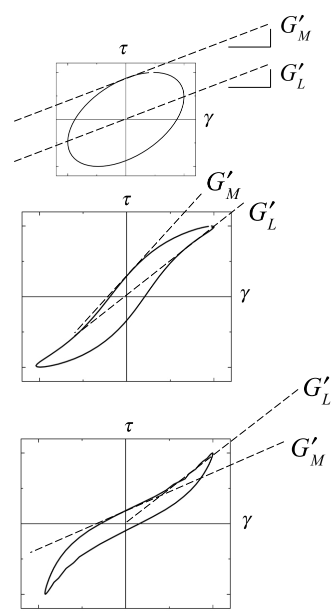
$$G'_M = \left.\frac{d\tau}{d\gamma}\right|_{\gamma=0} = e_1 - 3e_3 + 5e_5 + ... = \sum_{n=odd} nG'_n$$

$$G'_L = \left.\frac{\tau}{\gamma}\right|_{\gamma=\gamma_0} = e_1 + e_3 + e_5 + ... = \sum_{n=odd} G'_n (-1)^{(n-1)/2}$$

$$S = \frac{G'_L}{G'_M} = \frac{\sum_{n=odd} G'_n (-1)^{(n-1)/2}}{\sum_{n=odd} nG'_n} = \frac{e_1 + e_3 + e_5 ...}{e_1 - 3e_3 + 5e_5 ...}$$

- $S = G_L'/G_M' = 1$ for linear viscoelastic material
- $S < 1$ for strain softening
- $S > 1$ for strain stiffening

Similar framework for nonlinear *viscous* response; plot stress against strain-**rate:**
Thickening ratio $T = \frac{\eta'_L}{\eta'_M} = \frac{(\nu_1 + \nu_3 + \nu_5 ...)}{(\nu_1 - 3\nu_3 + 5\nu_5 ...)}$



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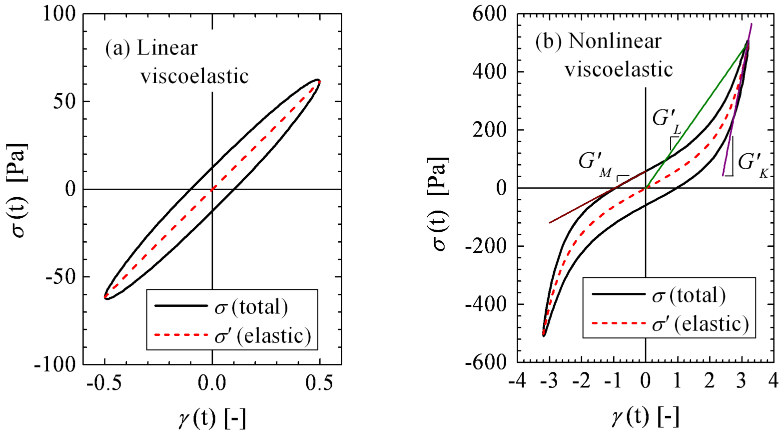
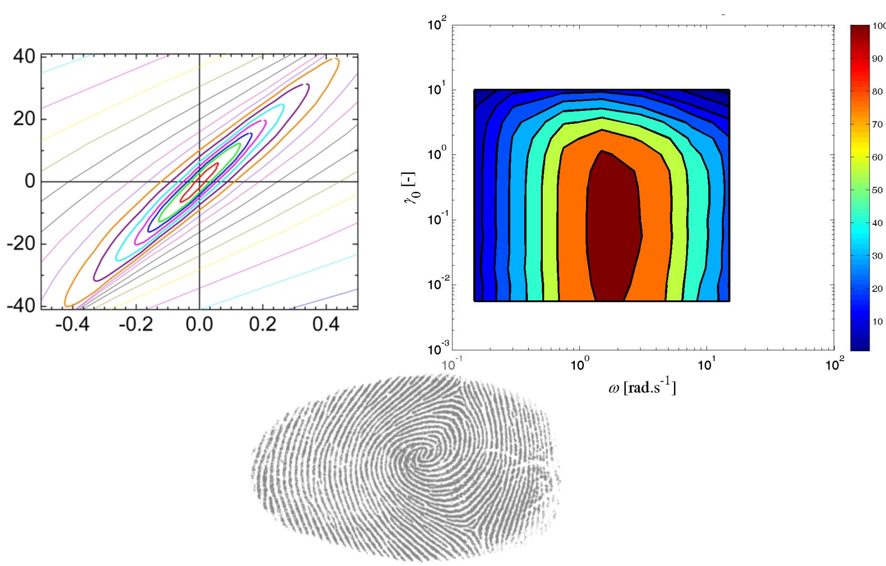
Example: Evaluating Measures of Nonlinear Moduli



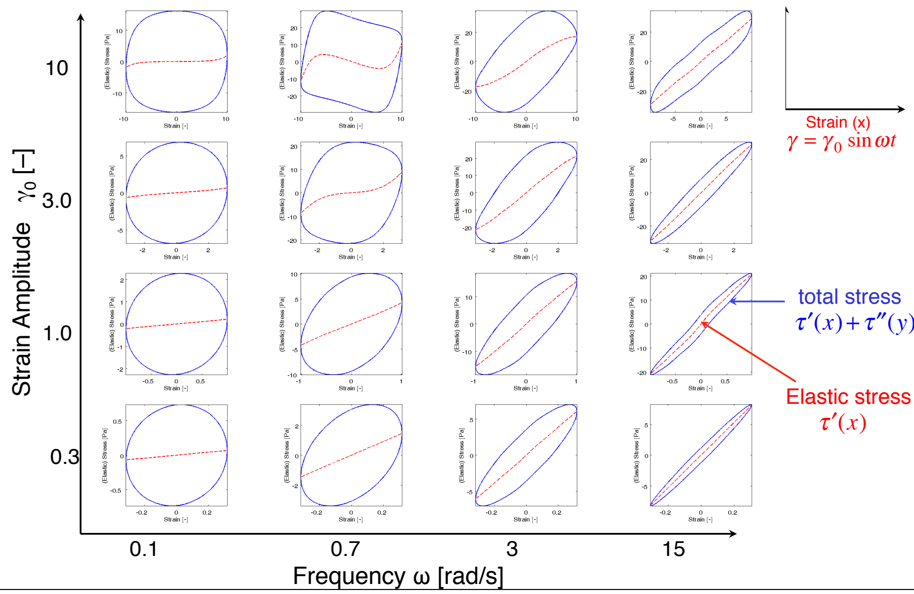
$\gamma_0 = 0.5$		$\gamma_0 = 3.2$	
123	G_1' [Pa]	121	(prior standard)
121	G_M' [Pa]	59.1	tangent, minimum strain
123	G_L' [Pa]	157	secant, large strain
122	G_K' [Pa]	580	tangent, large strain
+0.4%	$e_3 / e_1 * 100$ [%]	+23.8%	intra-cycle elastic nonlinearity

Rheological Fingerprinting of complex fluids



Example: Wormlike Micellar Fluid

- 100 mM CPyCl/50 mM NaSal: A useful example because the linear viscoelastic envelope is almost perfectly described by a Maxwell model



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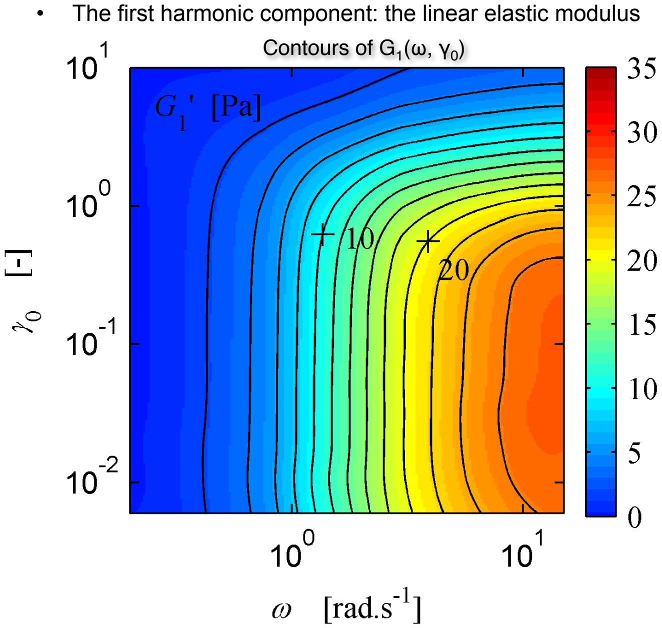
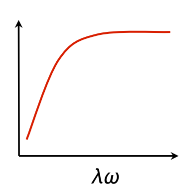
Example: Wormlike Micellar Fluid

- The first harmonic component: the linear elastic modulus



$$G_1'(\omega) = \frac{G(\lambda\omega)^2}{1+(\lambda\omega)^2}$$



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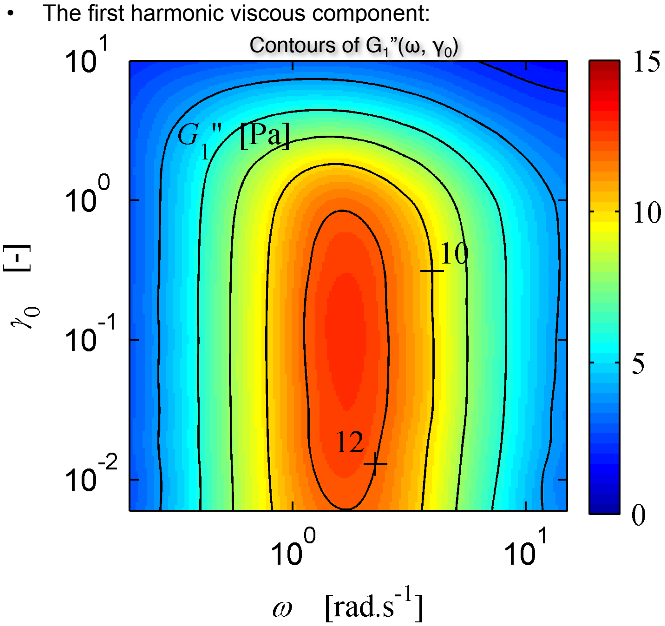
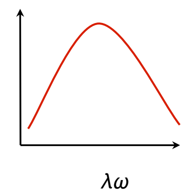
Example: Wormlike Micellar Fluid

- The first harmonic viscous component:

$$G_1''(\omega, \gamma_0) = \omega\, \nu_1$$



$$G_1''(\omega) = \frac{G(\lambda\omega)}{1+(\lambda\omega)^2}$$



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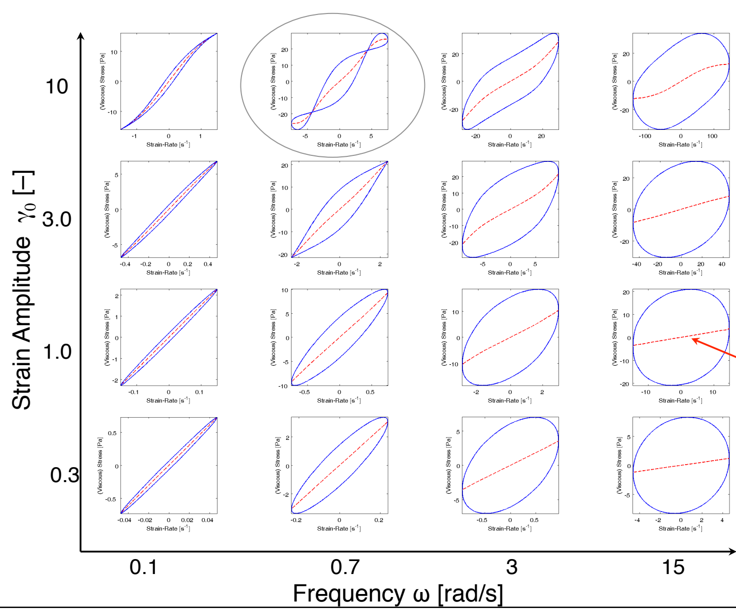
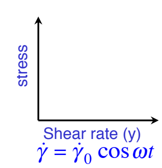
Example: Wormlike Micellar Fluid

- Rotate by 90˚ (x → y) to view 'viscous stress' contribution





Viscous stress
$\tau'(x)$

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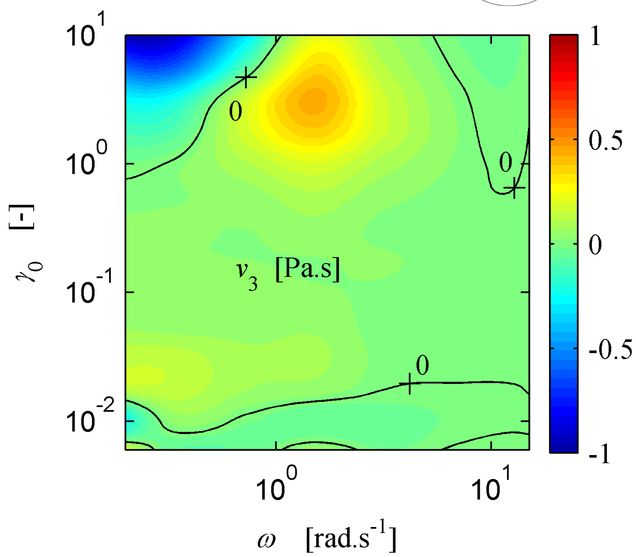
Example: Wormlike Micellar Fluid

- Measure of viscoelastic nonlinearity: v_3

$$\tau_v = \gamma_0 \{e_1 T_1(x) + e_3 T_3(x)...\} + (\gamma_0 \omega)\{v_1 T_1(y) + v_3 T_3(y)...\}$$



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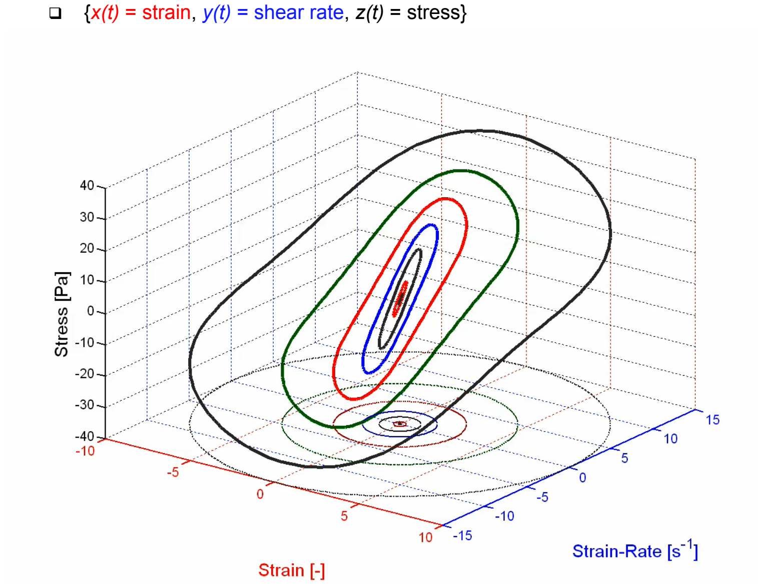
Phase Plane Portrait

- The material response studied in this example can also be compactly represented as three-dimensional trajectories in space:
  - {*x(t)* = strain, *y(t)* = shear rate, *z(t)* = stress}



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Fluids with Yield Stresses/Critical Stresses

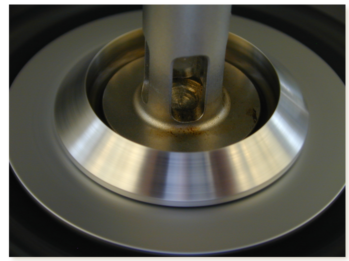
How "yield-stressy" is a given fluid?

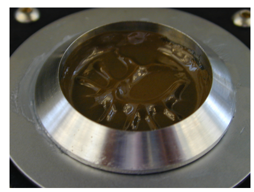
General Characteristics of Drilling Muds:
- Yield stress is important (removal of cuttings, suspension of densifying solids)
- Time dependent rheological properties
- Exposed to various timescales and magnitudes of deformation downhole

Most common rheometric tests
- Steady flow: $\eta(\dot{\gamma})$ steady state nonlinear viscous properties
- Thixotropic loops: $\eta(\dot{\gamma}_{\mathrm{up}}), \eta(\dot{\gamma}_{\mathrm{down}})$ time-dependent viscous properties
- Linear viscoelasticity: $G'(\omega)$, $G''(\omega)$

A more-complete characterization?
- Large amplitude oscillatory shear (LAOS) systematically spans the timescale and magnitude of deformation
- Probes time-dependent nonlinear viscous *and* elastic properties
- Connects steady flow viscosity, linear viscoelastic moduli, and nonlinear viscoelastic properties

Oil-based Drilling Mud (Invert Emulsion)
J. Maxey, Halliburton





Ewoldt, Winter, Maxey, McKinley, *Rheol. Acta.* ***49****(2), 2010.*

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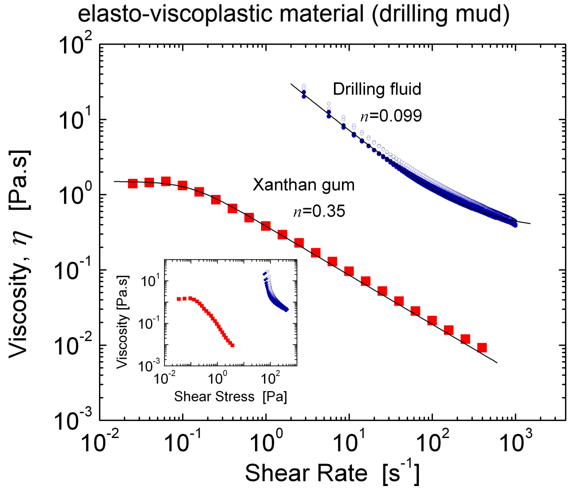
Characterization in Steady Shear

- Compare response of a shear-thinning ('pseudoplastic material') and a real elasto-viscoplastic material (drilling mud)



Carreau model fits shown by lines

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

Dynamic yield stress of drilling mud $\sigma_y \sim 70$ Pa

What about the elastic properties?

ARES-LS displacement controlled rheometer (TA Instruments)

Aqueous Xanthan gum solution (0.2wt%), steady flow data (cone, D=50mm, T=22° C)

Invert emulsion drilling fluid, thixotropic loops test (parallel disks with sandpaper, D=25mm, T=49°C) closed circles for disk correction

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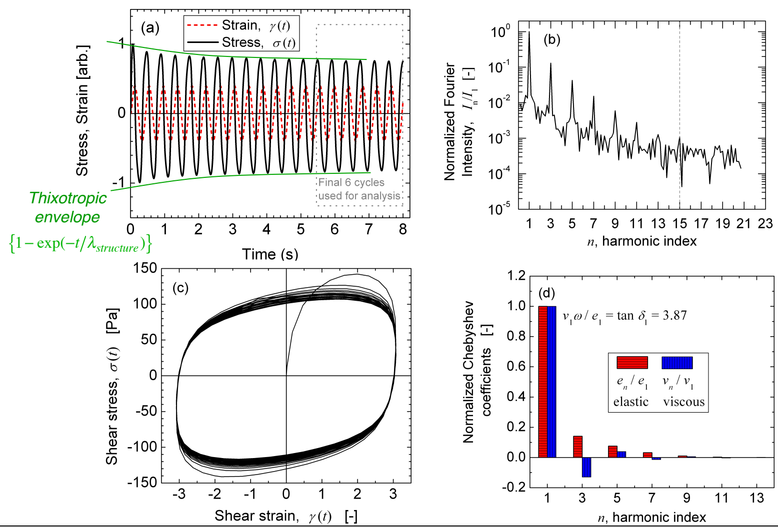
LAOS Data Analysis

MITlaos (Ewoldt & Winter, 2008) used for processing

- From *full* raw data, select final 6 steady cycles (after initial thixotropic response)
- Fourier transform (FT) spectrum is calculated, along with other measures including Chebyshev coefficients and nonlinear moduli



Example:
Drilling fluid
ω=15 rad/s,
γ_0=3.16

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Perfect plastic dissipation ratio

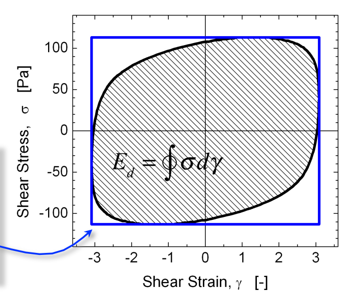
- So how do I quantify 'how square' the Bowditch-Lissajous curve is?

Perfectly plastic response appears as a rectangular elastic response curve

Compare dissipated energy (enclosed area) to that of a corresponding *perfectly plastic response:*

$$\sigma(t) = \sigma_Y \operatorname{sgn}(\dot{\gamma}(t))$$

$$G'_n = 0 \qquad G''_n = \frac{4}{\pi}\frac{\sigma_Y}{\gamma_o}\frac{1}{n}(-1)^{\frac{n-1}{2}} \qquad n: \text{odd}$$



Example:
Drilling fluid
ω=15 rad/s
γ_0=3.16

Perfect plastic dissipation ratio

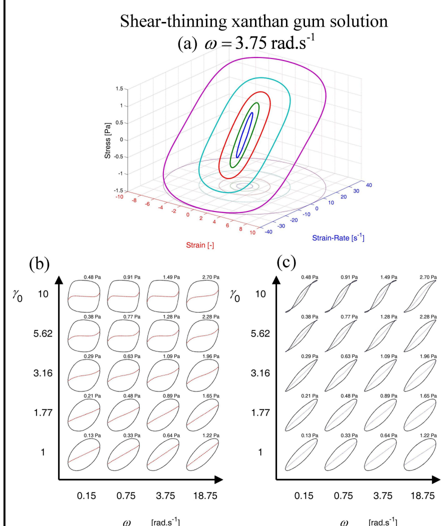
$$\phi = \frac{E_d}{(E_d)_{pp}} = \frac{\pi\gamma_0^2 G''_1}{(2\gamma_0)(2\sigma_{max})} \begin{cases} \to 1 & \text{Perfect Plastic} \\ \to \pi/4 = 0.785 & \text{Newtonian} \\ \to 0 & \text{Purely Elastic} \end{cases}$$

$$\phi = \frac{\pi G''}{4|G^*|} = \frac{\pi}{4}\sin\delta$$ Linear viscoelastic response

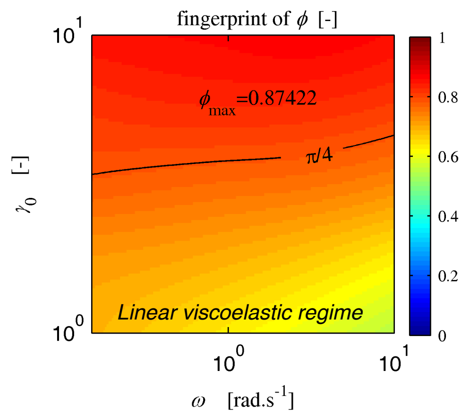
$$\sigma_{max} = f(\gamma_0, G'_n, G''_n)$$ General nonlinear viscoelastic response

Ewoldt et al., *Rheol. Acta, 2010*

Shear-thinning Xanthan Gum



$$\phi = \frac{E_d}{(E_d)_{pp}} \begin{cases} \to 1 & \text{Perfect Plastic} \\ \to \pi/4 = 0.785 & \text{Newtonian} \\ \to 0 & \text{Purely Elastic} \end{cases}$$



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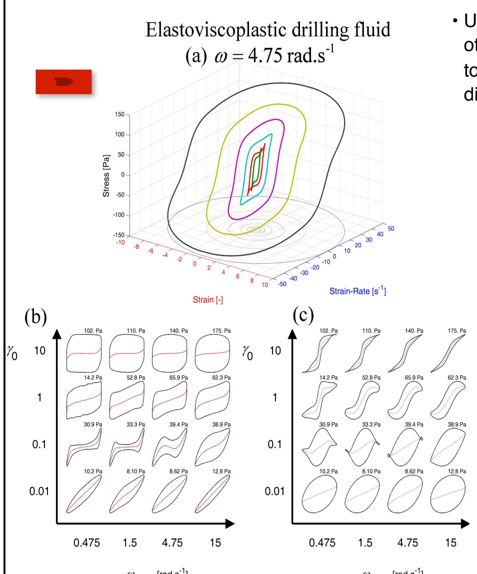
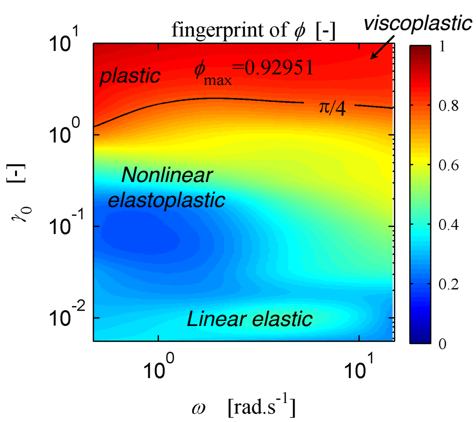
Ewoldt et al., *Rheol.Acta, 2010*

Elastoviscoplastic drilling fluid



- Use perfect plastic dissipation ratio in conjunction with other tools (Lissajous figures, chebyshev coefficients..) to provide a complete finger print and identification of different material responses

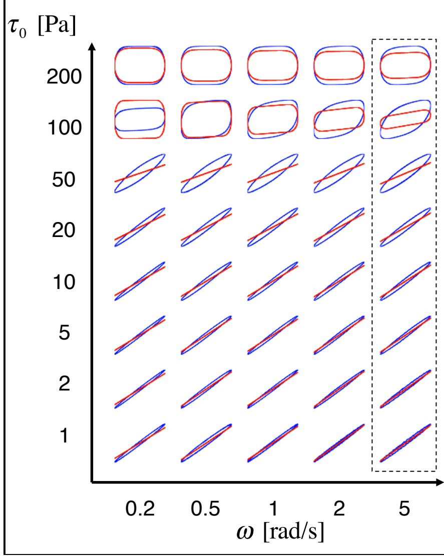
$$\phi = \frac{E_d}{(E_d)_{pp}} \begin{cases} \to 1 & \text{Perfect Plastic} \\ \to \pi/4 = 0.785 & \text{Newtonian} \\ \to 0 & \text{Purely Elastic} \end{cases}$$



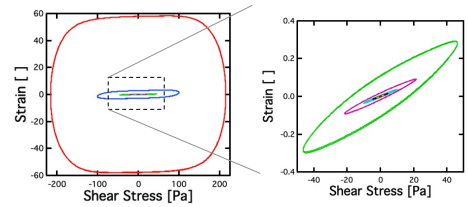
Ewoldt et al., *Rheol.Acta, accepted*

LAOS in a Controlled Stress Rheometer (LAOStress)

- LAOS is a great experimental methodology to probe differences between yielded/unyielded regime as well as limitations of constitutive models.

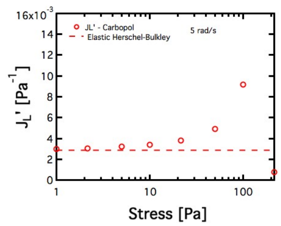


ω = 5 rad/s:



Corresponding nonlinear *compliance* measures:

$$J'_M = \frac{d\gamma}{d\tau}\Big|_{\tau=0} \qquad J'_L = \frac{\gamma}{\tau}\Big|_{\tau=\tau_0}$$



The EHB model is fairly simple:

$$\gamma = \gamma^e + \gamma^p \; ; \; \gamma^e = \frac{\tau}{G}$$

$$\dot{\gamma}^p = \begin{cases} 0 & \text{if } |\tau| \le \tau_y \\ \left(\frac{|\tau| - \tau_y}{k}\right)^{1/n} & \text{if } |\tau| \ge \tau_y \end{cases}$$

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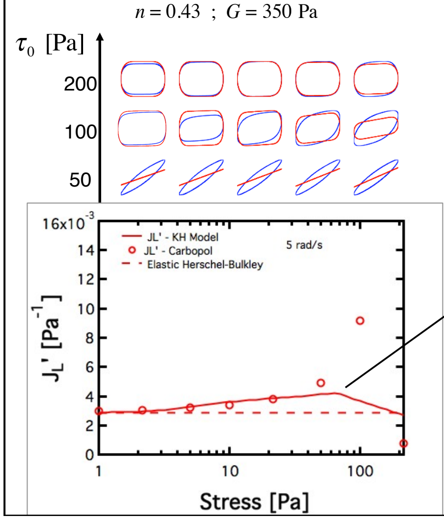
Using LAOS to Improve Predicted Rheological Behavior

- Use LAOS to improve constitutive models and then determine the relevant model parameters; e.g. a *kinematic hardening (KH)* model for elastoviscoplasticity

EHB Model - Carbopol

$\tau_y = 45$ Pa ; $k = 26$ Pa.s^n

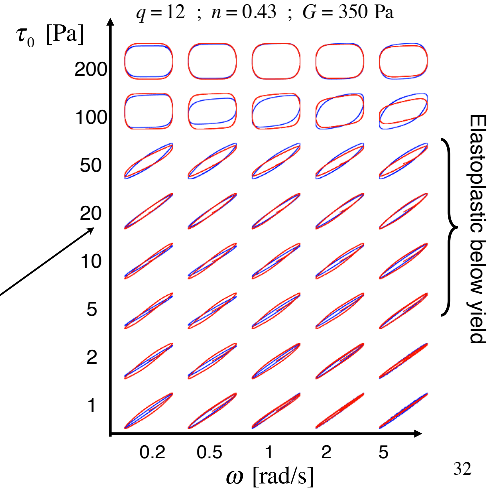
$n = 0.43$; $G = 350$ Pa



KH Model - Carbopol

$C = 540$ Pa ; $k = 26$ Pa.s^n

$q = 12$; $n = 0.43$; $G = 350$ Pa



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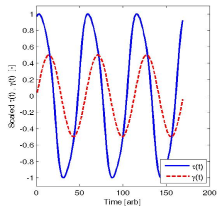
Summary of *Rheological Fingerprinting*

- A physical interpretation and language for LAOS experiments in complex fluids
- Framework of elastic/viscous stress decomposition plus **Chebyshev coefficents**

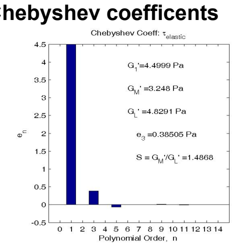
Time Series



$$T_n(y) = \cos(n\omega t)$$

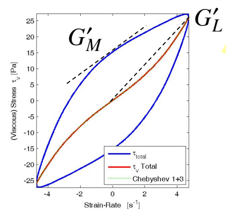
$$y = \frac{\dot{\gamma}(t)}{\gamma_0 \omega}$$

Harmonic Coefficients



$$\tau(t;\omega,\gamma_0) \equiv \tau_{elastic}\left(\gamma(t)\right) + \tau_{viscous}\left(\dot{\gamma}(t)\right) = \gamma_0 \sum_{i=1}^{N} e_i T_i(x) + \gamma_0 \omega \sum_{i=1}^{N} v_i T_i(y)$$

Bowditch-Lissajous Figures



Measures of Nonlinearity

$$G'_M = \left.\frac{d\tau}{d\gamma}\right|_{\gamma=0} = e_1 - 3e_3 + 5e_5 + \ldots \qquad S = \frac{G'_L}{G'_M}$$

$$G'_L = \left.\frac{\tau}{\gamma}\right|_{\gamma=\gamma_0} = e_1 + e_3 + e_5 + \ldots \qquad T = \frac{\eta'_L}{\eta'_M}$$

- Also applicable to thixotropic and 'yield stress' responses: *elasto-visco-plastic* materials

(Ewoldt, Winter, Maxey & McKinley; *Rheol. Acta*, **49**(2), 2010)

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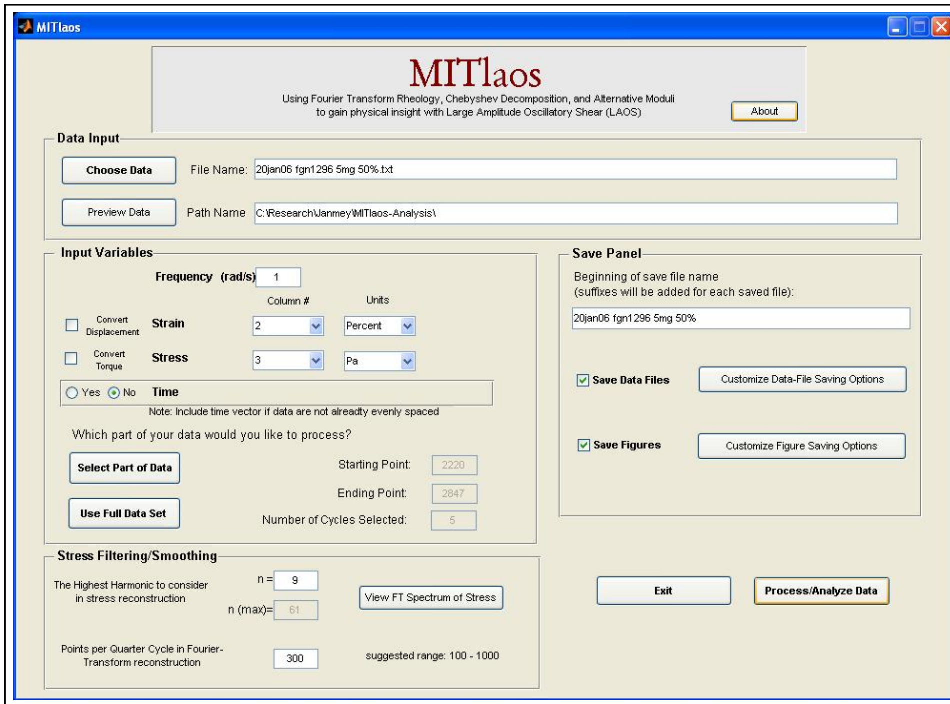

MITlaos Matlab program available for use by anyone….contact mitlaos@mit.edu