Rheological Fingerprinting of Complex Fluids and Soft Solids

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HATSOPOULOS MICROFLUIDS LABORATORY

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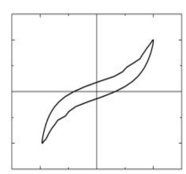
Outline

- ***Rheological fingerprinting*** of a complex fluid or soft solid
- 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
  - How do we characterize the nonlinear response?

- Connecting to Constitutive Models
  - Extracting Constitutive parameters
- What's Going on Inside
  - Kinematics and Structural Probes
- Yielding Materials; viscoelastoplasticity
  - Carbopol Gels
  - LAOS for soft viscoelastic solids & gels
- A mystery food (CSI; Lisbon)…

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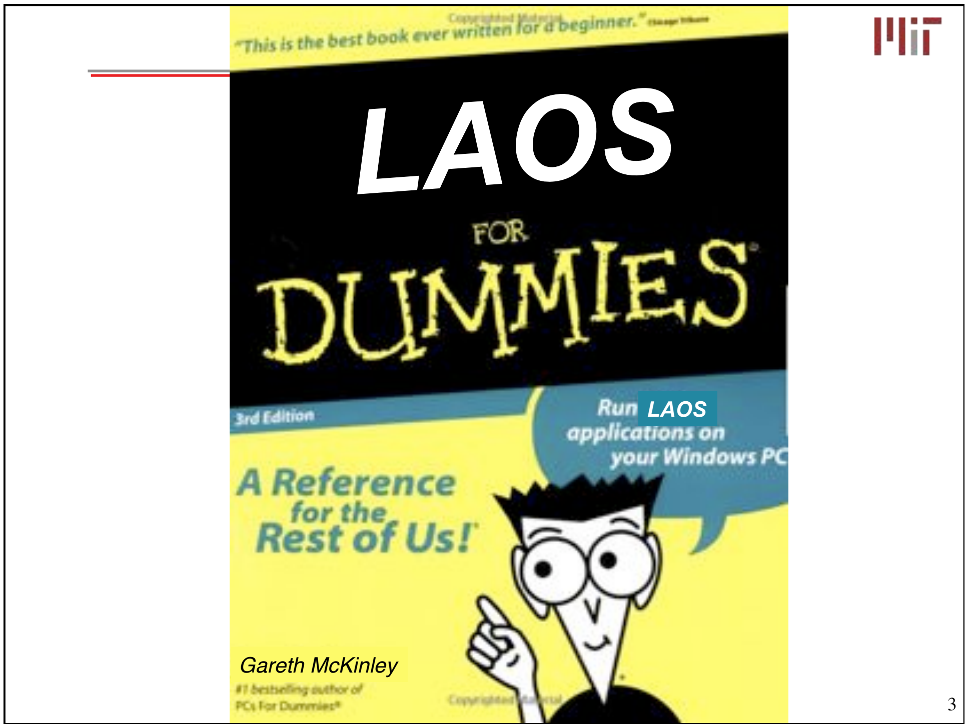

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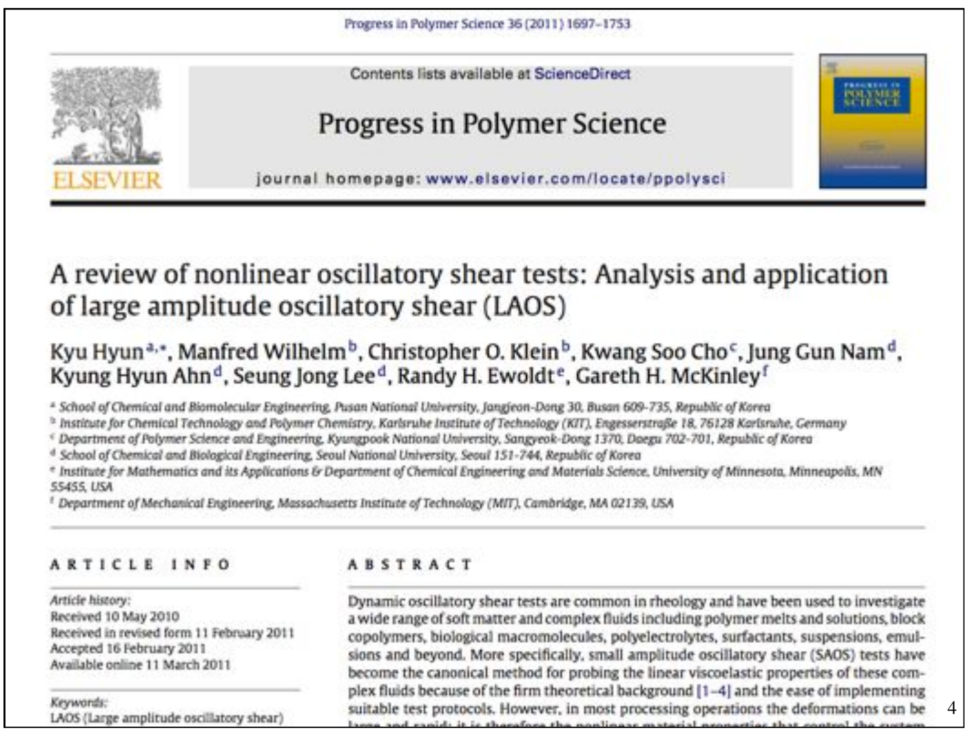

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A review of nonlinear oscillatory shear tests: Analysis and application of large amplitude oscillatory shear (LAOS)

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ABSTRACT

Dynamic oscillatory shear tests are common in rheology and have been used to investigate a wide range of soft matter and complex fluids including polymer melts and solutions, block copolymers, biological macromolecules, polyelectrolytes, surfactants, suspensions, emulsions and beyond. More specifically, small amplitude oscillatory shear (SAOS) tests have become the canonical method for probing the linear viscoelastic properties of these complex fluids because of the firm theoretical background [1–4] and the ease of implementing suitable test protocols. However, in most processing operations the deformations can be

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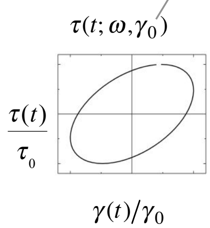
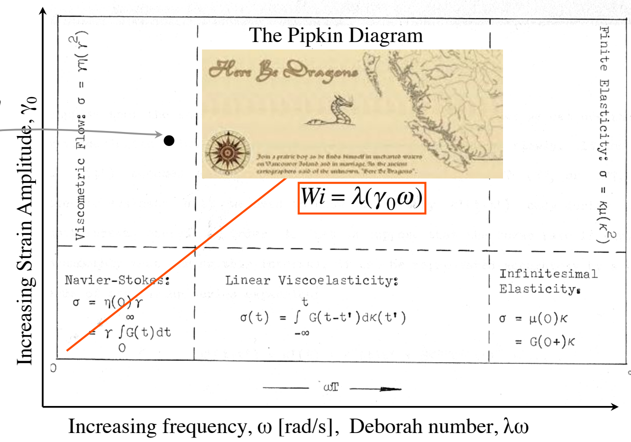
Motivation for LAOS

- 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, mucins, 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, New York (1972) 5

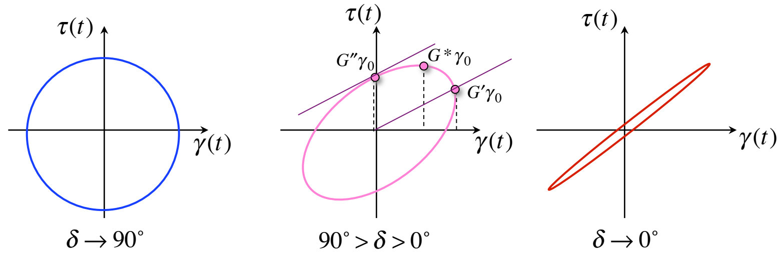
Linear Viscoelasticity & Ellipses

- 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.

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

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

Jules Lissajous (1822-1880)



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

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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 Natura Principia Mathematica*. At seventeen, he wrote a letter to a Harvard University professor pointing out an error in the *Principia*.…

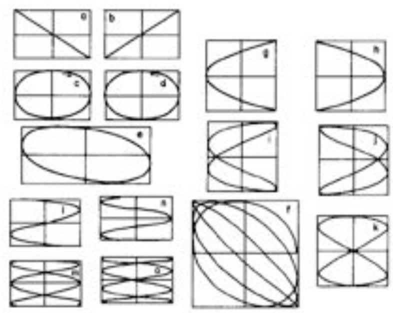


Fig. 3. Tracings of drawings of the orbits of two mutually orthogonal oscillations, published by N. Bowditch (Ref. 3). Drawings a, b, c, and d

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

Tools for Analyzing Nonlinear Oscillatory Rheology

- **Pipkin Space** Pipkin, 1972
- **Bowditch-Lissajous curves** W. Philippoff, *Trans Soc. Rheol*. **10,** 1964
  Dealy & Wissbrun *Melt Processing* 1990; Giacomin & coworkers
- **Fourier Transform Rheology** Dodge & Kreiger, *Trans Soc Rheol* 1972;
  Willhelm et al., *Macromol. Mater Eng*. 2002

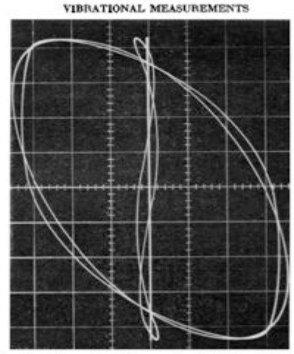
Curves Cho. Ahn et al.. *JoR* 2005

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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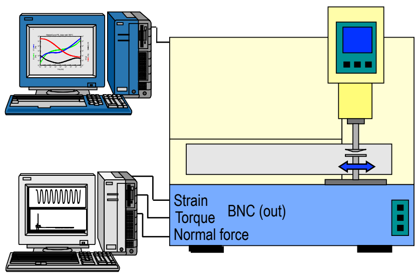
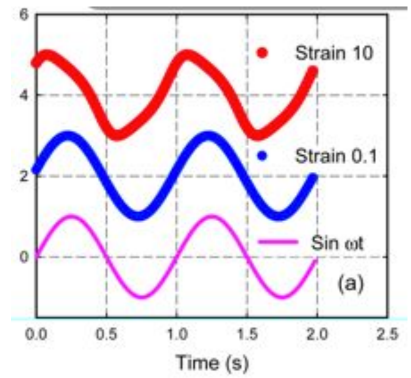
FT-Rheology and LAOS

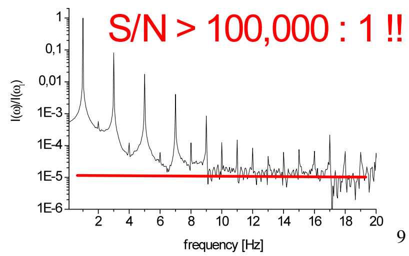
The picture:

The set up:



The data:





Ganeriwala & Rotz, Polym. Eng. Sci. **27** (1987)
M. Wilhelm; *Macromol. Mater. Eng.* **287** 83 (2002)

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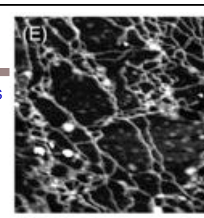
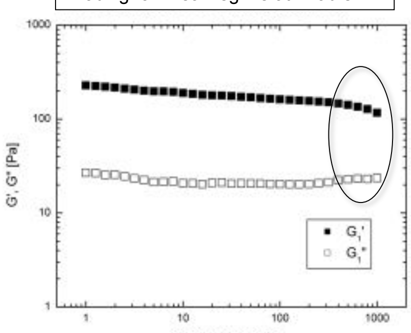
Linear Viscoelasticity of Mucin Gels



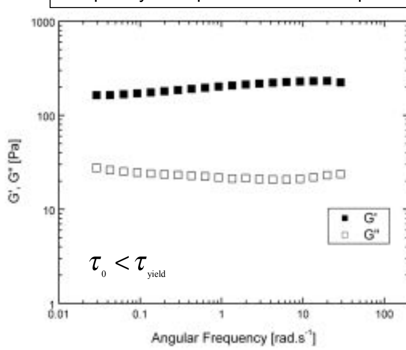
Miles & coworkers
Biophys. J., 2002

- The linear viscoelastic envelope is determined by performing an oscillatory stress sweep
- Elastic gel over a broad range of frequencies: $\xi \approx \left(k_B T / G'\right)^{1/3} \approx 30\text{nm}$

Probing for linear regime at 1 rad/s



Frequency sweep at 5 Pa stress amplitude



2cm steel plate, T=22°C, 200μm gap

$$\tau_y \approx \frac{Mg}{A_{contact}} \sim 100 - 200\,Pa$$

Ewoldt, Clasen, GHM; *Soft Matter* 2007

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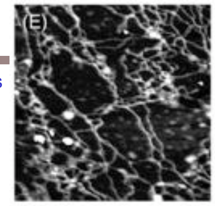
Linear Viscoelasticity of Mucin Gels



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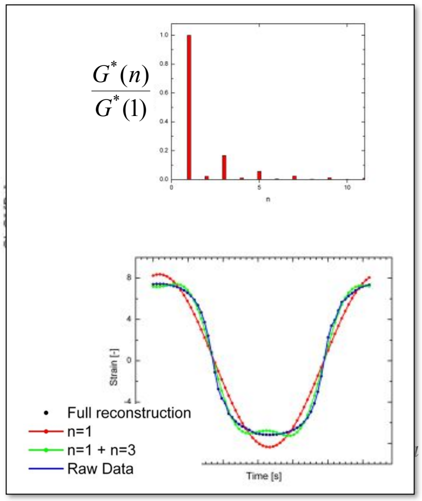
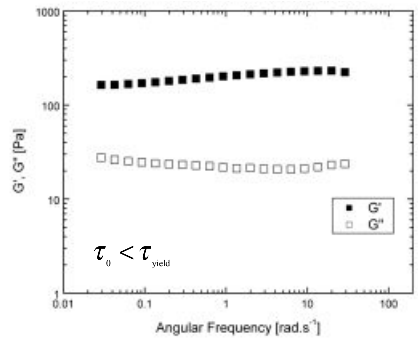


Frequency sweep at 5 Pa stress amplitude



2cm steel plate, T=22°C, 200μm gap

Ewoldt, Clasen, GHM; *Soft Matter* 2007

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Physical Interpretation of LAOS Deformations

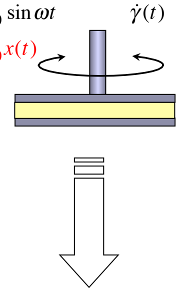
- General Fourier decomposition $\tau = \gamma_0 \sum_{n \text{ odd}} G_n'' \cos(n\omega t) + G_n' \sin(n\omega t)$

A New Approach

- Consider strain and strain rate as independent *orthogonal* inputs
  Cho, Hyun, Ahn, Lee, *J.Rheol.* **49** (2005).

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

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



- Decompose output stress using symmetry arguments into 'elastic' (*x*) and 'viscous' (*y*) contributions
  - Point group symmetries & Frieze group analysis
    Rogers & Vlassopoulos, J. Rheol. **54** (2010).

- Represent the unknown material response or *Transfer Function* in terms of **Chebyshev polynomials** in x and y:

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

R.H. Ewoldt, A.E. Hosoi, GHM, *J. Rheology* **52** (2008)

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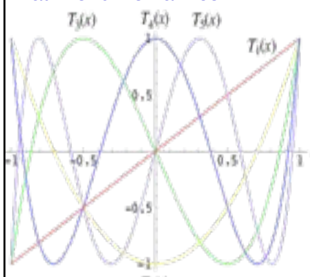
The Benefits of Chebyshev* polynomials

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

mathworld.wolfram.com



$T_0(x) = 1$
$T_1(x) = x$
$T_2(x) = 2x^2 - 1$
$T_3(x) = 4x^3 - 3x$
$T_4(x) = 8x^4 - 8x^2 + 1$
$T_5(x) = 16x^5 - 20x^3 + 5x$

BENEFITS

- Chebyshev polynomials are *orthonormal* 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

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

$T_i(y) \equiv T_i(\cos \omega t) = \cos(i\omega t)$

Example: $T_3(\cos z) \equiv \cos 3z = 4\cos^3 z - 3\cos z$
($i=3$; $z=\omega t$)

* Also transliterated as *Tschebychev*
* PhD Students of Tschebychev include Markov, Lyapunov…

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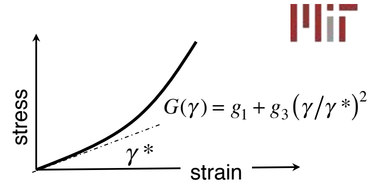
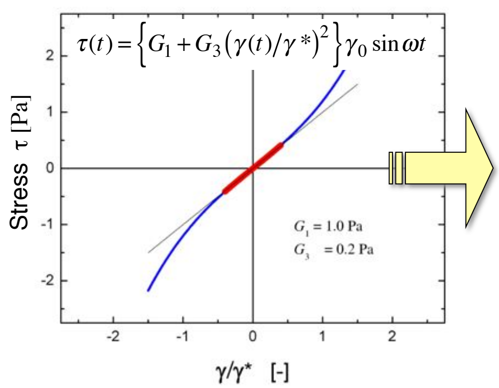
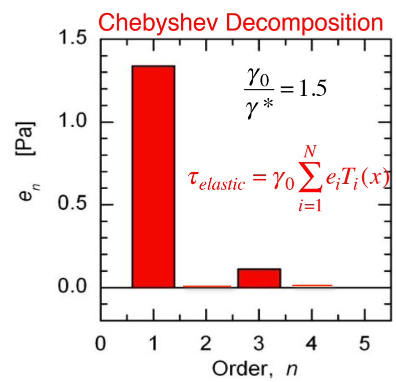
Example: Nonlinear Elastic Solid

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







- Material Moduli: $e_1 = G_1' = g_1 + \frac{3}{4}\left(\frac{\gamma_0}{\gamma^*}\right)^2 g_3$ $\quad e_3 = -G_3' = +\frac{1}{4}\left(\frac{\gamma_0}{\gamma^*}\right)^2 g_3$

Linear elastic limit *Direct measure of the nonlinearity*

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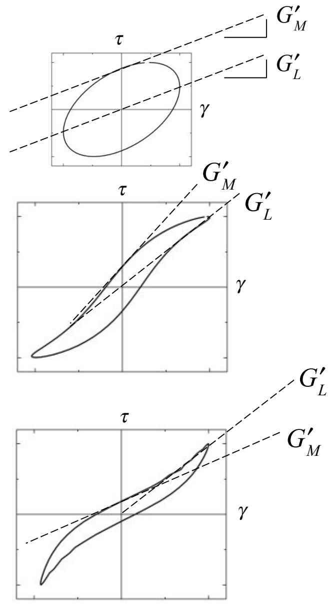
Additional Physical Quantifiers of Nonlinearity

Strain-stiffening index, S

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

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

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

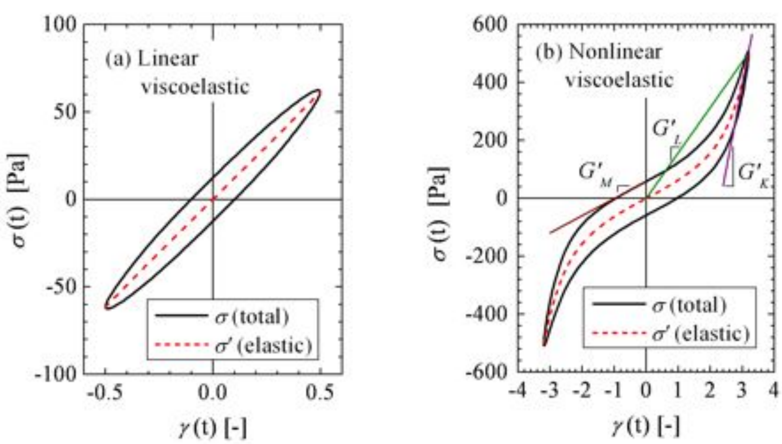


$$S = \frac{G'_L - G'_M}{G'_L} = 1 - \frac{\sum_{n=odd} nG'_n}{\sum_{n=odd} G'_n(-1)^{(n-1)/2}} = \frac{4e_3\ldots}{e_1 - 3e_3 + 5e_5\ldots}$$

- S = 0 for linear viscoelastic material
- S < 0 for *strain softening*
- S > 0 for *strain stiffening*

Ewoldt, Hosoi, GHM; *J. Rheol.* 2008 15

Example: Evaluating Measures of Nonlinear Moduli

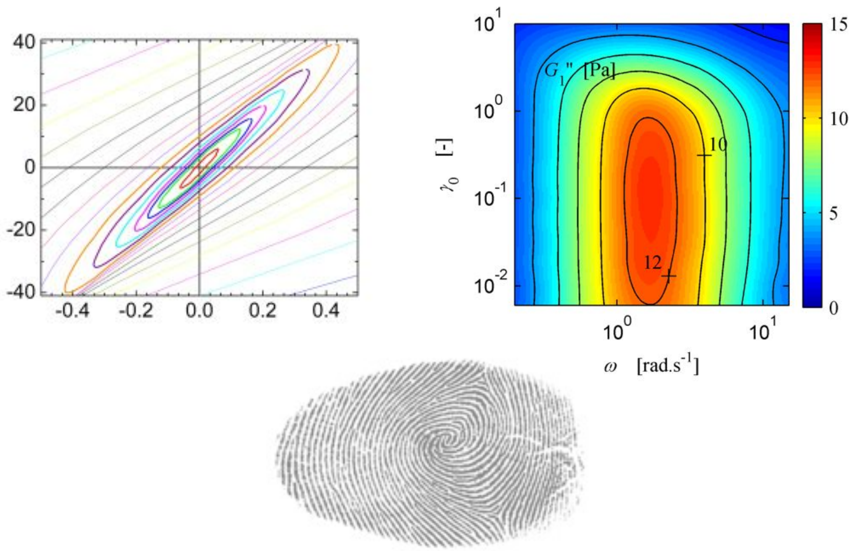


Snail Pedal Mucus
Roughened Plates
T = 25˚C

$\gamma_0 = 0.5$		$\gamma_0 = 3.2$	
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

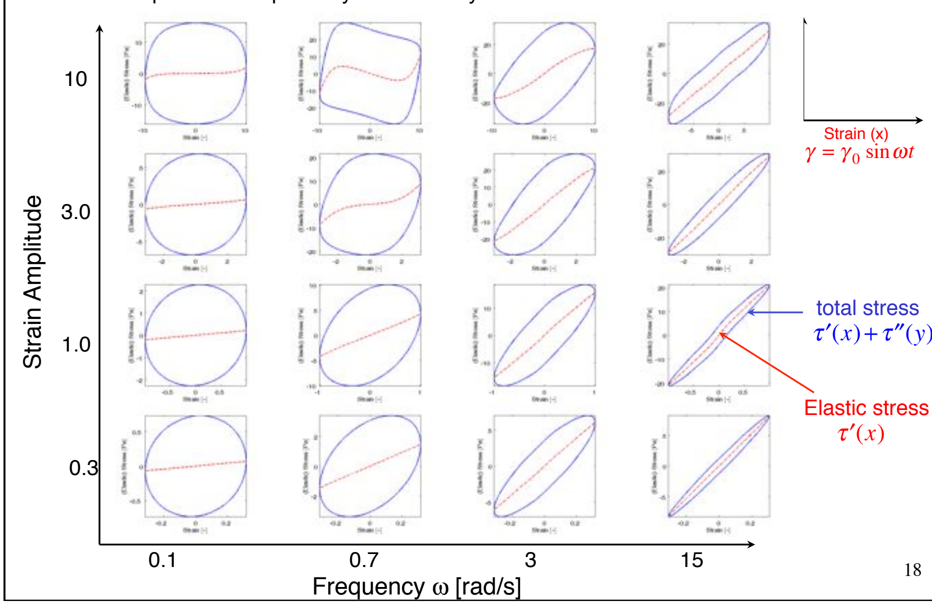
Ewoldt, Hosoi, GHM; *J. Int. Comp. Biol* . 2009

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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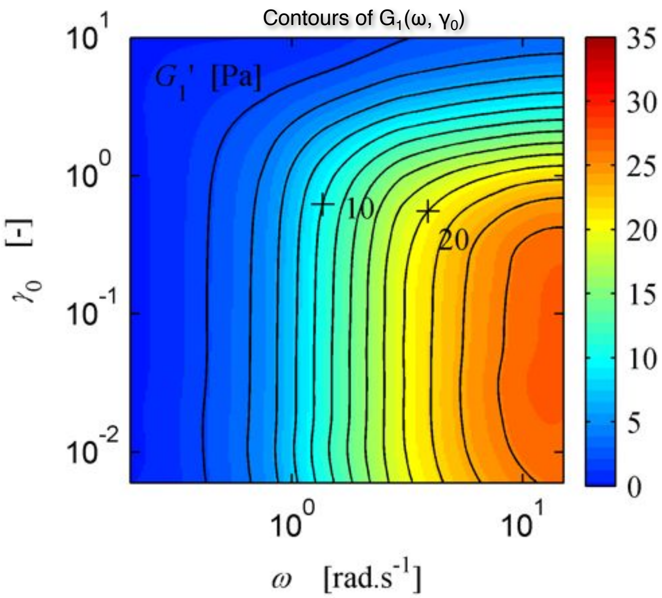
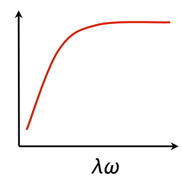
Example: Wormlike Micellar Fluid (CpyCl/NaSal)

- Contours of the first harmonic component: the linear elastic modulus



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



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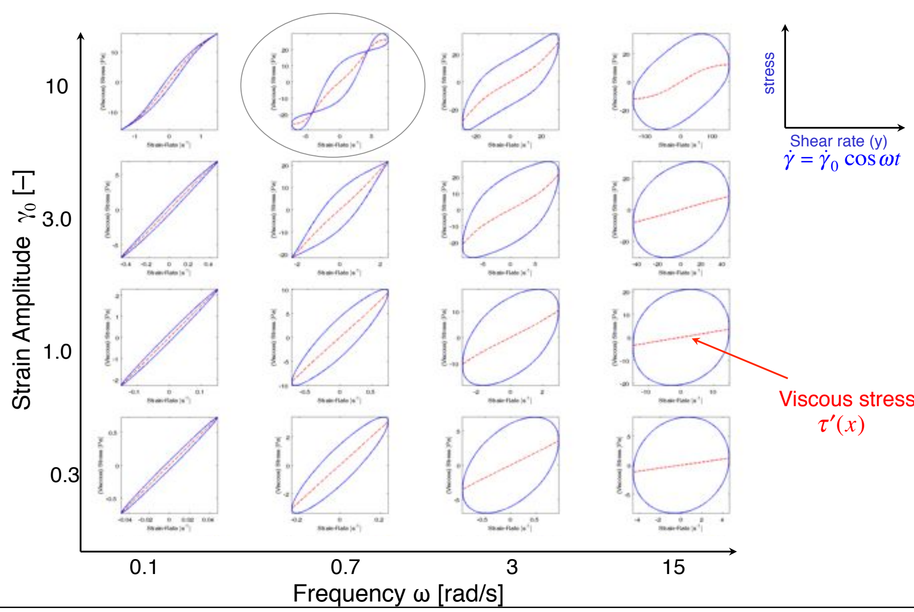
Example: Wormlike Micellar Fluid

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



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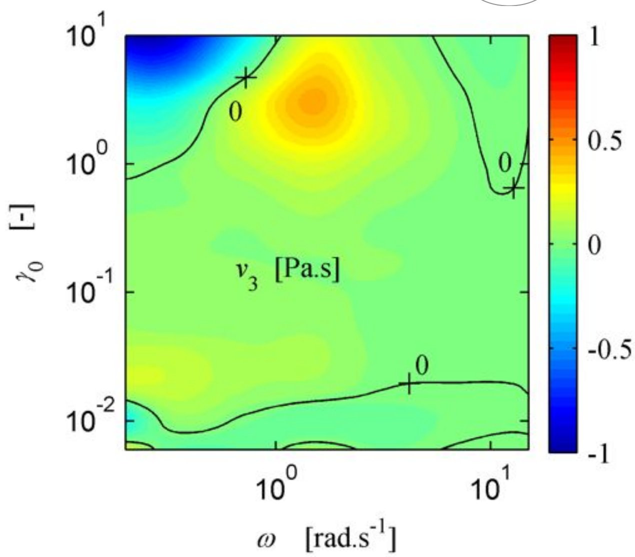
Example: Wormlike Micellar Fluid

- 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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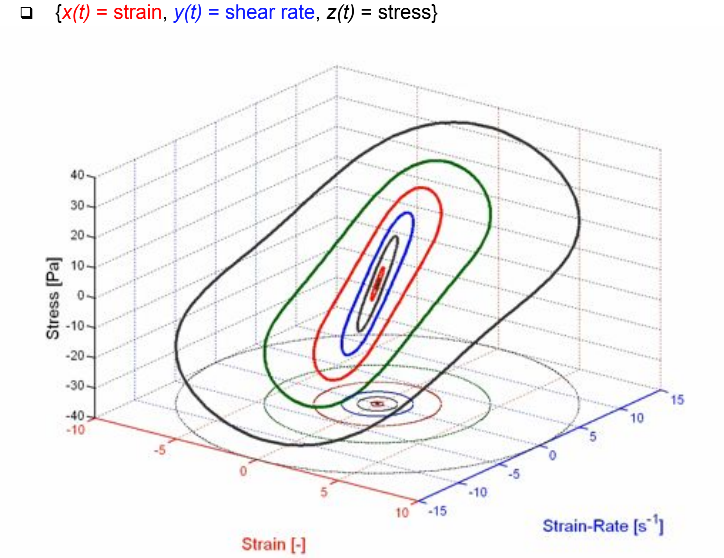
Phase Plane Portrait

- 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}



For a discussion on "loops" see Ewoldt & GHM., *Rheol.Acta, 2010*

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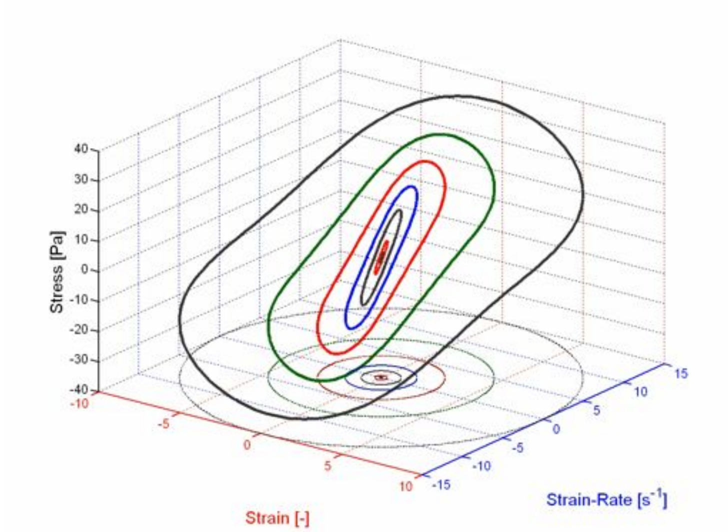

For a discussion on "loops" see Ewoldt & GHM., *Rheol. Acta, 2010*

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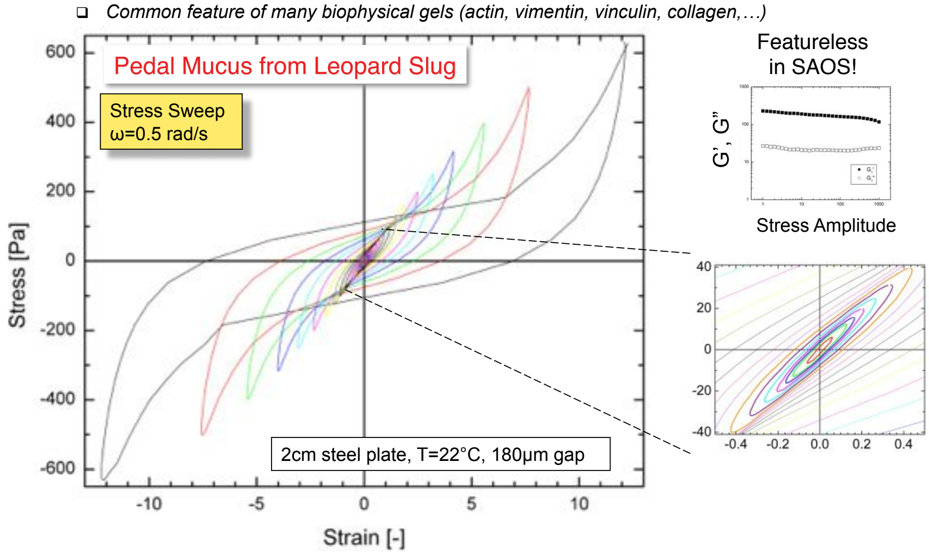
LAOS Measurements of Mucin Slime Film

- Progressive transition from linear viscoelasticity to nonlinear viscoelastic solid
- Strain-hardening at large strains enables traction and *adhesive locomotion*
  - *Common feature of many biophysical gels (actin, vimentin, vinculin, collagen,…)*



Ewoldt, Hosoi, McKinley, *Soft Mat.* **3**(5) 2007.

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Using LAOS to Evaluate Constitutive Models

- Use LAOS fingerprints to evaluate nonlinear coefficients of constitutive models for complex fluids and compare with experiments

❑ The Q-Parameter (Hyun, Wilhelm)

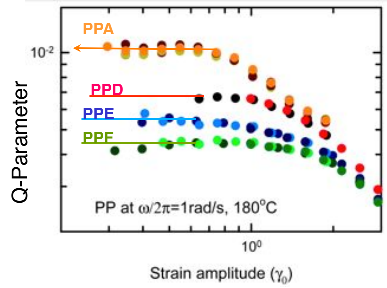
$$\lim_{\gamma_0\to 0}\frac{I_3}{I_1} \equiv \lim_{\gamma_0\to 0} I_{3/1} = Q(\omega)\gamma_0^2 + O(\gamma_0^4)\ldots$$

Remember: $\sin x \approx x - \frac{1}{3}x^3 \ldots \Rightarrow I_{3/1} \sim x^2$

❑ Loss of phase information… (also have to monitor phase angle δ_3)

$$\frac{I_3}{I_1} = \frac{\sqrt{e_3^2 + (v_3\omega)^2}}{\sqrt{e_1^2 + (v_1\omega)^2}}$$

- Other general representations of linear and nonlinear viscoelastic response: $R'(\omega,\gamma_0)$, $R''(\omega,\gamma_0)$ (Rogers, JoR **56**(5), 2012)



Commercial PP (linear chain structure)

Sample	Mn	Mw	MWD	
PP-A	106k	460k	4.3	Linear
PP-D	37k	270k	7.3	Linear
PP-E	50k	240k	4.8	Linear
PP-F	57k	230k	4	Linear
PP-G	76k	220k	3.9	Linear

K. Hyun, M. Willhelm; *Macromolecules* **42** 411 (2009) 25

The Reptation Model in LAOS

Behavior of Concentrated Polystyrene Solutions in Large-Amplitude Oscillating Shear Fields

DALE S. PEARSON and WILLIE E. ROCHEFORT, *Bell Laboratories, Murray Hill, New Jersey 07974*

$$\sigma_{xy}(t) = \gamma_0[G'_{11}(\omega)\sin\omega t + G''_{11}\cos\omega t] + \gamma_0^3[G'_{31}(\omega)\sin\omega t + G''_{31}\cos\omega t + G'_{33}(\omega)\sin 3\omega t + G''_{33}\cos 3\omega t] + O(\gamma_0^5) \quad (14)$$

where

$$G'_{31} = -\frac{3}{14}\frac{\rho kT}{N_e}\sum_{p,\text{odd}}\frac{8}{\pi^2 p^2}\left(\frac{2\omega^2\tau_d^2}{p^4+\omega^2\tau_d^2} - \frac{2\omega^2\tau_d^2}{p^4+4\omega^2\tau_d^2}\right) \quad (15a)$$

$$G''_{31} = -\frac{3}{14}\frac{\rho kT}{N_e}\sum_{p,\text{odd}}\frac{8}{\pi^2}\left(\frac{\omega\tau_d}{p^4+\omega^2\tau_d^2} - \frac{\omega\tau_d}{p^4+4\omega^2\tau_d^2}\right) \quad (15b)$$

$$G'_{33} = \frac{3}{28}\frac{\rho kT}{N_e}\sum_{p,\text{odd}}\frac{8}{\pi^2 p^2}\left(\frac{\omega^2\tau_d^2}{p^4+\omega^2\tau_d^2} - \frac{4\omega^2\tau_d^2}{p^4+4\omega^2\tau_d^2} + \frac{3\omega^2\tau_d^2}{p^4+9\omega^2\tau_d^2}\right) \quad (16a)$$

$$G''_{33} = \frac{3}{28}\frac{\rho kT}{N_e}\sum_{p,\text{odd}}\frac{8}{\pi^2}\left(\frac{\omega\tau_d}{p^4+\omega^2\tau_d^2} - \frac{2\omega\tau_d}{p^4+4\omega^2\tau_d^2} + \frac{\omega\tau_d}{p^4+9\omega^2\tau_d^2}\right) \quad (16b)$$

All the sums in these equations can be evaluated, leaving analytical expressions for G_{31} and G_{33} (see Appendix A).

(a)

(b)

(c)

Journal of Polymer Science: Polymer Physics Edition, Vol. 20, 83–98 (198
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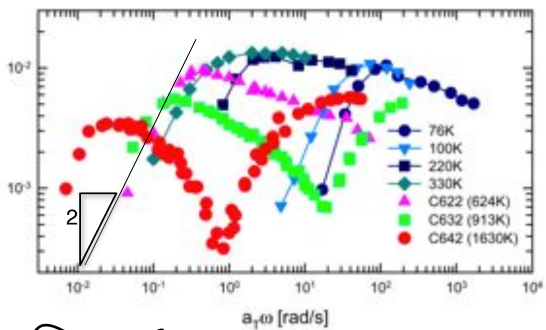
The Reptation Model in LAOS

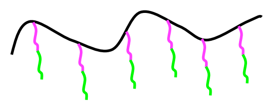
- Evaluating the Q parameter for the DE model gives:

$$\lim_{\omega \to 0} Q_0(\omega) = \frac{1}{3}(\lambda_d \omega)^2$$

Reptation time

	M_b	M_a
76K	75.9	-
100K	100	-
220K	214	-
330K	330	-
C632	275	**25.7**
C622	275	**11.7**
C642	275	**47**





Effect of Chain-Branching on Nonlinearity in LAOS

❑ Comb PS with **entangled branches** displays two relaxation processes, one corresponding to **the branches'** disentanglements and one due to the **backbone chain**.

K. Hyun, M. Willhelm; *Macromolecules* **42** 411 (2009)
K. Hyun et al. *Prog Polym Phys.* (2011)

27

Comparison of LAOS Data with MSF Model

- Molecular Stress Function model of M.H. Wagner & coworkers

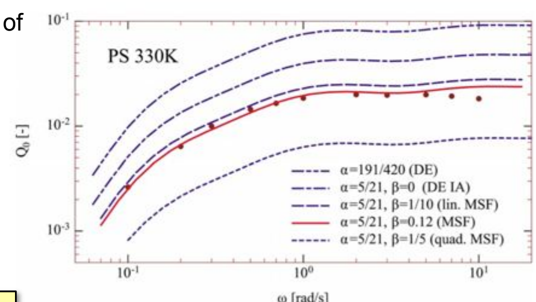
Chain orientation *Chain stretching*

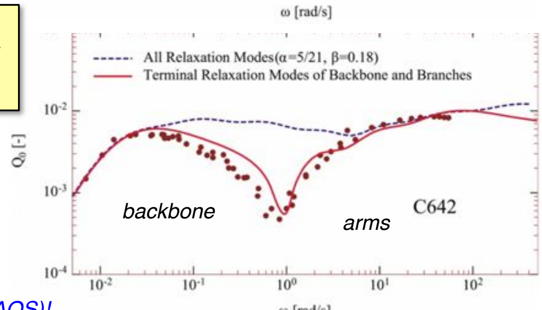
$$I_{3/1} = \frac{|G_{33}^*|}{|G_{11}^*|}\gamma_0^2 \propto (\alpha - \beta)\gamma_0^2$$

$$\lim_{\omega \to 0} Q_0(\omega) = \frac{3}{2}(\alpha - \beta)(\lambda_d \omega)^2$$

α = 5/21 : Doi-Edwards; IAA

β = 1/5 : Quadratic MSF





Moderate Amplitude Oscillatory Shear (MAOS)!
M. H. Wagner, et al.; *J. Rheol.* **55** 495 (2011)

28

Fluids with Yield Stresses/Critical Stresses

How "yield-stressy" is a given fluid?

Most common rheometric tests

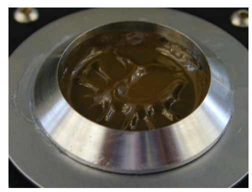
- Steady flow: steady state nonlinear viscous properties $\eta(\dot{\gamma})$
- Thixotropic loops: time-dependent viscous properties $\eta(\dot{\gamma}_{\mathrm{up}}), \eta(\dot{\gamma}_{\mathrm{down}})$
- Linear viscoelasticity: $G'(\omega), G''(\omega)$

A more-complete characterization?

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

Carbopol Gel
W. Hartt, P&G

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



Ewoldt, Winter, Maxey, McKinley, *Rheol. Acta.* ***49****(2), 2010; Dimitriou et al., JoR 2012 submitted.*

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Stress-Controlled Experiments: LAOStress

- For many foods and consumer products it is more common to perform stress-controlled experiments.
- *LAOStress* is a great experimental methodology to probe differences between yielded/unyielded regime as well as limitations of constitutive models
- Decompose strain into an elastic component and a viscoplastic component
  - Describe in terms of models that naturally capture '*sequence of physical processes*' for elastic strain, yielding, viscoplastic flow

Normalized Input sinusoidal stress: $x(t) = \frac{\tau(t)}{\tau_0} = \cos\omega t$

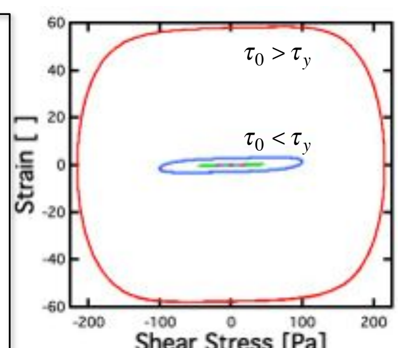
Fourier series representation of strain:

$$\gamma(t) = \tau_0 \sum_{n\ odd} J_n' \cos n\omega t + J_n'' \sin n\omega t$$

Chebyshev representation:

$$\gamma_e(t) = \tau_0 \sum_{n\ odd} J_n' \cos n\omega t = \tau_0 \sum_{n\ odd} c_n T_n(x) \quad \text{compliances}$$

$$\dot{\gamma}_p(t) = -\tau_0 \sum_{n\ odd} n\omega J_n'' \cos n\omega t = \tau_0 \sum_{n\ odd} \phi_n T_n(x) \quad \text{Fluidities}$$



Lauger & Stettin, Rheol. Acta 2010
S. Rogers & coworkers, J. Rheol. 2011, 12

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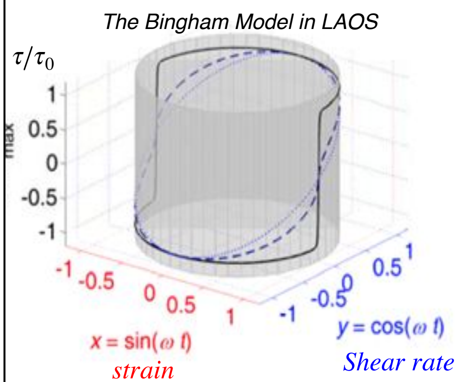
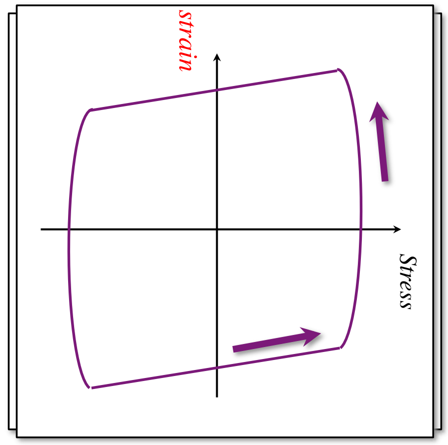
The Basic Anatomy of a Lissajous Figure in LAOStress

- Input is an oscillating stress field $\tau(t;\omega) = \tau_0 \cos\omega t$ => output is the strain $\gamma(t;\omega,\tau_0)$
- Shear strain and shear rate are no longer orthogonal variables
- How do I traverse this trajectory in 3-dimensional space?
- How do I describe it quantitatively?





Ewoldt, Winter, Maxey, GHM, *Rheol. Acta.* **49**(2), 2010; *Dimitriou et al., JOR 2012 submitted.*

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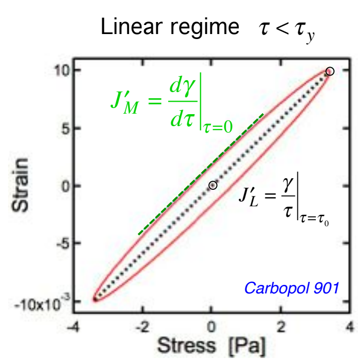
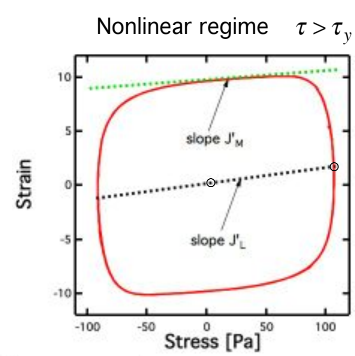
Graphical Definitions of Nonlinear Compliances





Nonlinear compliance measure: (non-locally computed!)

$$J'_M = \left.\frac{d\gamma}{d\tau}\right|_{\tau=0} = c_1 - 3c_3 + 5c_5 \ldots$$

$\tau_0 = 4$ Pa		$\tau_0 = 100$ Pa
2.9×10^{-3}	J'_1 (Pa^{-1})	5.7×10^{-3}
2.9×10^{-3}	J'_M (Pa^{-1})	7.0×10^{-3}
2.9×10^{-3}	J'_L (Pa^{-1})	13.9×10^{-3}

- For yielding materials, elastic LAOStress measures are typically more effective at quantifying nonlinear elastic behavior
- Typical yielding material retain some (measurable) elasticity even under flow

Lauger & Stettin, Rheol. Acta 2010; Dimitriou et al., JOR 2012

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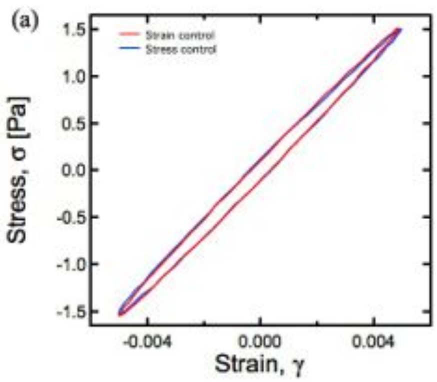
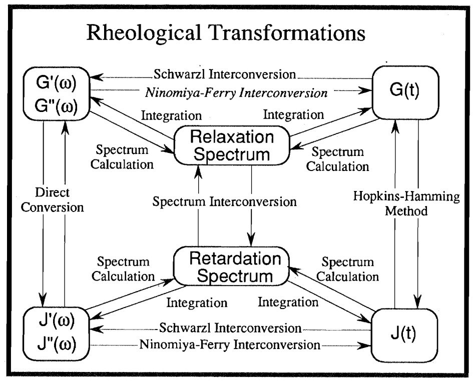
LAOStress vs. LAOStrain

- In the linear regime the two techniques yield the same information
  - ❑ Linear viscoelastic moduli and compliances are interchangeable $G^*(\omega)\,J^*(\omega)=1$





J. D. Ferry, Viscoelastic Properties of Polymers (1980)

- Energy dissipated in cycle (per unit volume) is always represented by area enclosed by the corresponding Bowditch-Lissajous curve:

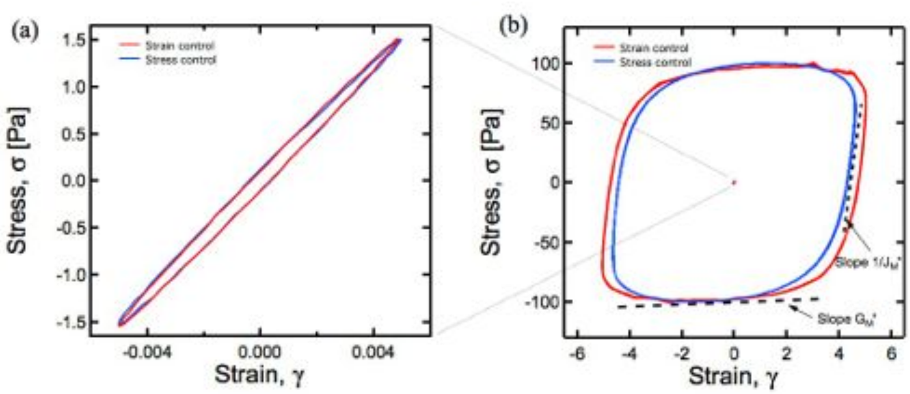
$$E_d = \oint \tau(t)\dot{\gamma}(t)\,dt$$

33

LAOStress vs. LAOStrain

- In the linear regime the two techniques yield the same information
  - ❑ Linear viscoelastic moduli and compliances are interchangeable $G^*(\omega)\,J^*(\omega)=1$

….this is NOT true in the nonlinear regime!



- Energy dissipated in cycle (per unit volume) is always represented by area enclosed by the corresponding Bowditch-Lissajous curve:

$$E_d = \oint \tau(t)\dot{\gamma}(t)\,dt$$

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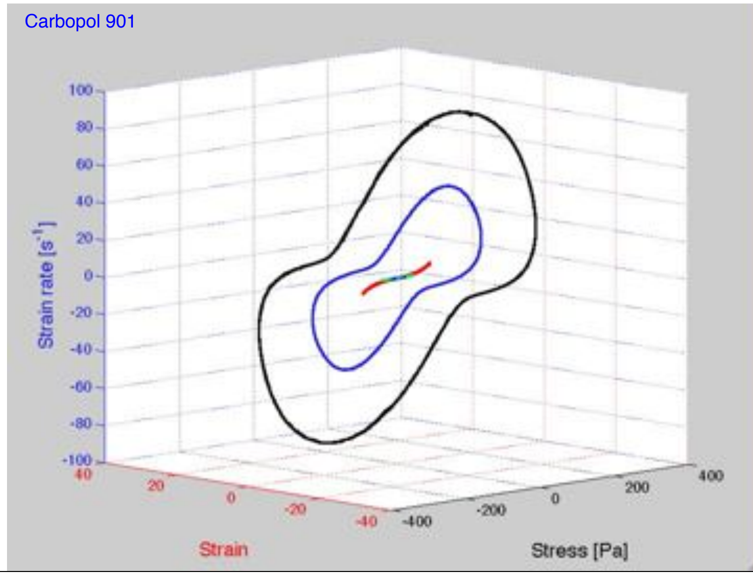
LAOStress: Yielding in Three-Dimensions

- Visualize the yielding surface as a function of stress amplitude and frequency
  - Remember shear strain and shear rate are no longer orthogonal!



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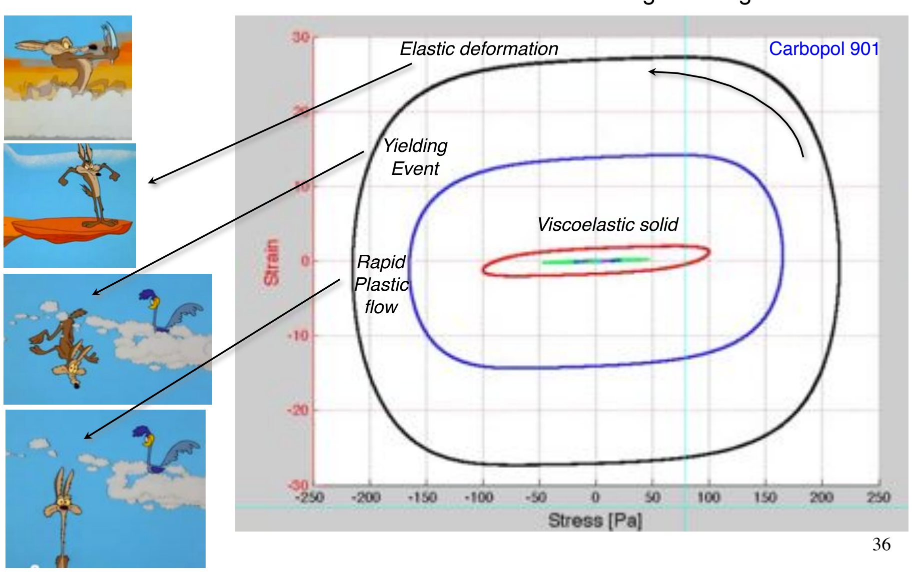
LAOStress: Yielding Signature in a Lissajous Figure

- Visualize the yielding surface as a function of stress amplitude and frequency
  - Also: remember shear strain and shear rate are no longer orthogonal!



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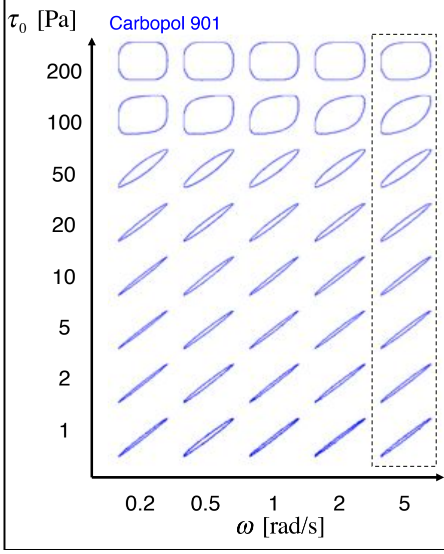
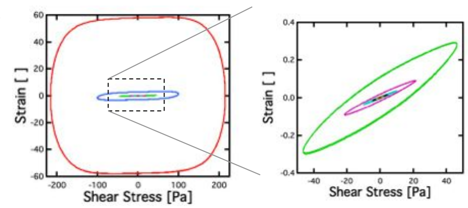
Bowditch-Lissajous Figures in LAOStress

- Help visualize the transition between an viscoelastic solid below a critical stress to a visco-elasto-plastic material at high stresses
- Yielding transition is time-scale dependent

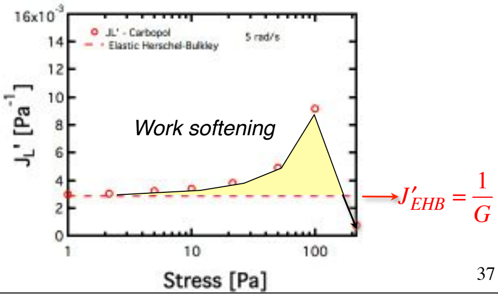




Quantify using corresponding nonlinear *compliance* measures:

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

$$J'_L = \frac{\gamma}{\tau}\Big|_{\tau=\tau_0}$$



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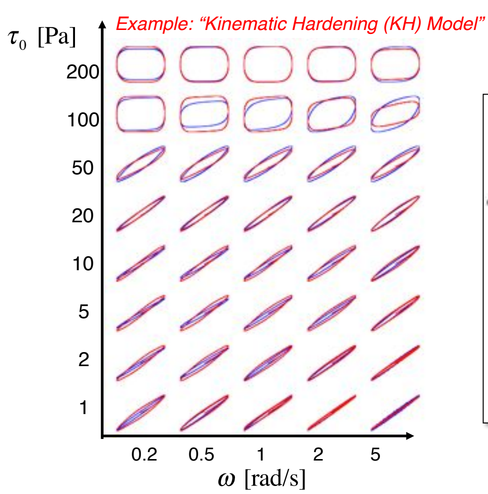
Using LAOS to Fit Constitutive Models

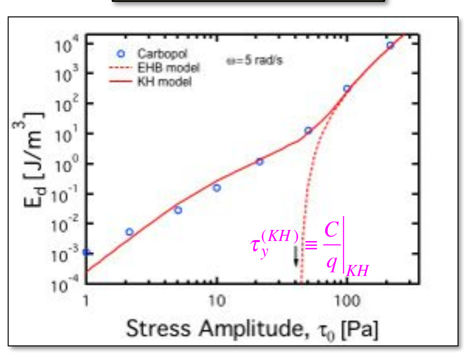
- LAOStress tests provide a systematic test protocol for fitting model parameters in visco-elasto-plastic constitutive models
- Yielding is a gradual (freq. dependent) process!



$G = 350$ Pa; $k = 26$ Pa.s^n; $n = 0.43$; $q = 12$; $C = 540$ Pa.

Energy Dissipation During a Loop

$$E_d = \int_0^{2\pi/\omega} \tau\dot{\gamma}\,dt = \tau_0^2 J_1'' \pi$$



Data: Carbopol 901; T = 25˚C, 25mm C&P

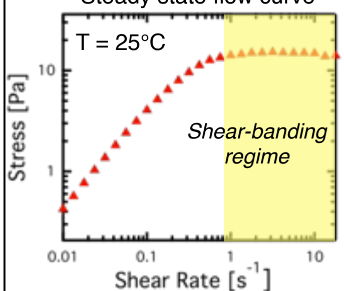
Dimitriou, Ewoldt, GHM JoR 2012 submitted. 38

What's Going On Inside?

In-Situ Rheo-PIV, Rheo-PTV, Rheo-NMR, Ultrasound…

- Validate the assumption of homogeneous shearing flow
- Investigate slip at boundaries
- Investigate internal fracture/"shear-banding"

Steady state flow curve



Rheo-SANS, Rheo-XRAY…

- Investigate deformation of microstructure and compare with microstructural models
- Mapping of local concentration variations under imposed steady shear

Challenge: achieve temporal and spatial resolution of oscillatory flow dynamics…

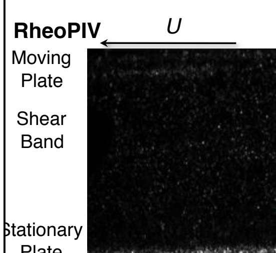
Example: Model Entangled Worm-like Micellar Fluid (CPyCl/NaSal) in LAOS

Rehage & Hoffmann, Molecular Physics. **74**(5): 933-973 (1991) 39

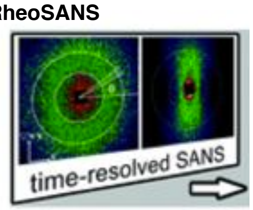
Pipkin Diagram for LAOS of a Shear-Banding Material

- Constitutive Modeling:
  - Rolie-Poly Model for monodisperse entangled polymer melts; Adams, Fielding, Olmsted
  - Two-species VCM model, (& Larson PEC model) for micellar networks; Zhou, Cook, GHM

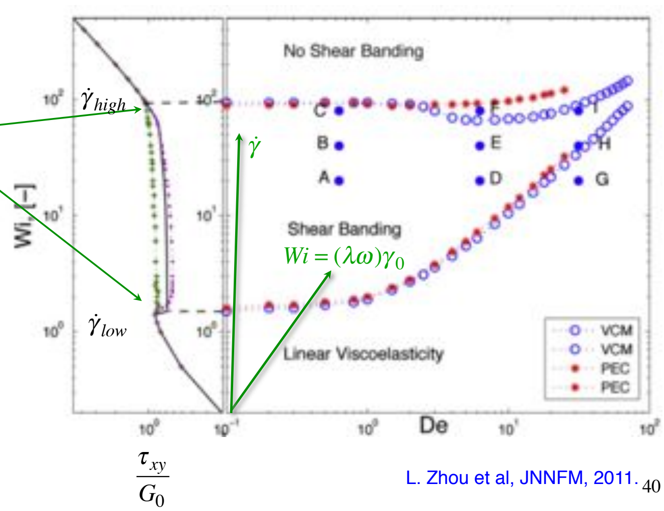
RheoPIV



RheoSANS



Rogers, Kohlbrecher, Lettinga, *Soft Matter* **8** (2012)

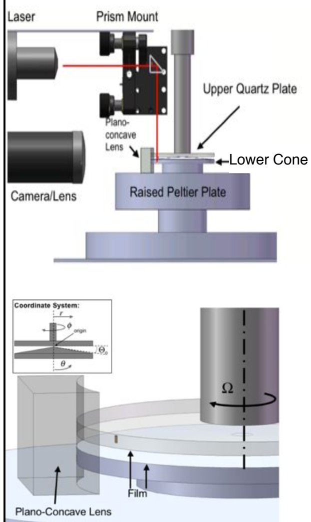


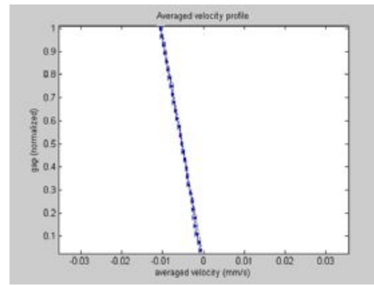
L. Zhou et al, JNNFM, 2011. 40

Rheo-PIV of WLM in Oscillatory Shear

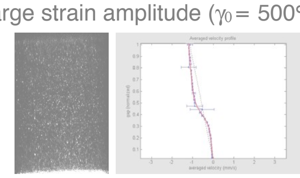
- In SAOS velocity gradient field is homogeneous as expected

Small strain amplitude (γ_0=10%): $v_x(y,t) = \gamma_0 \omega (y/H) \cos \omega t$





Large strain amplitude (γ_0= 500%):



Dimitriou *et al.* Energy & Fuels, **25**, 2012

Dimitriou *et al.* Rheol. Acta. **51**(5), 2012

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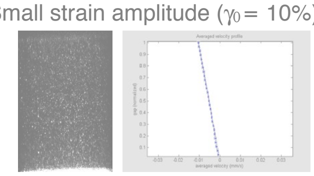
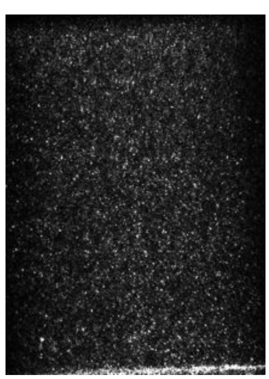
Rheo-PIV of WLM in Oscillatory Shear

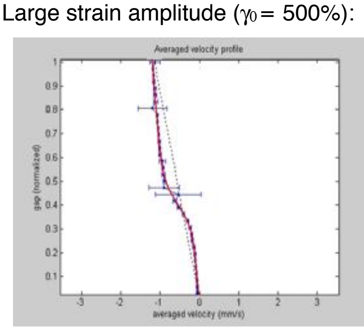
Small strain amplitude (γ_0= 10%):



- In LAOS the velocity profile exhibits a kink in the center of the gap

Large strain amplitude (γ_0= 500%):





Dimitriou *et al.* Rheol. Acta. **51**(5), 2012

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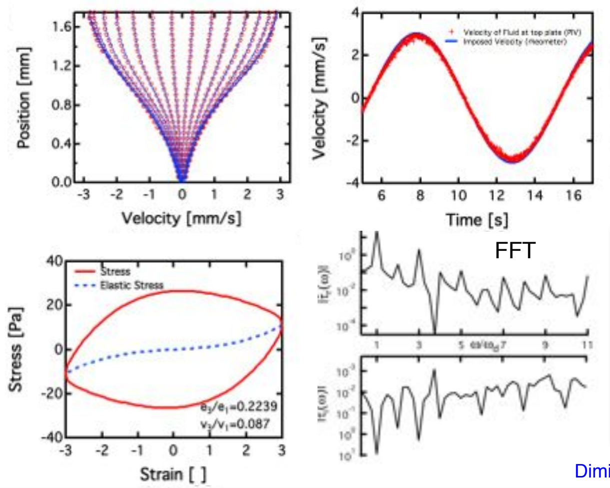
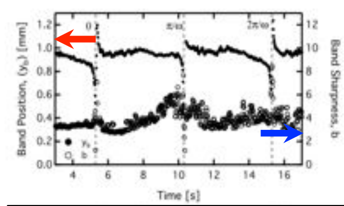
Shear Banding in Micellar Fluids - Nonlinear Regime

- Very pronounced banding and strong nonlinearities in stress signal
  =>No slip condition preserved at the plate boundary by a transparent optical film
- Interesting dynamics can be observed in shear band structure & position

Strain amplitude of γ_0 = 300% (*De* = 0.91, *Wi* = 2.73)



Band Dynamics



Need to be careful in Interpreting growth of higher harmonics: they can arise from:
– slip at the plate/sample
– internal shear-banding/fracture
– true nonlinear rheol. behavior

Dimitriou, *et al.* Rheol. Acta. **51**(5), 2012

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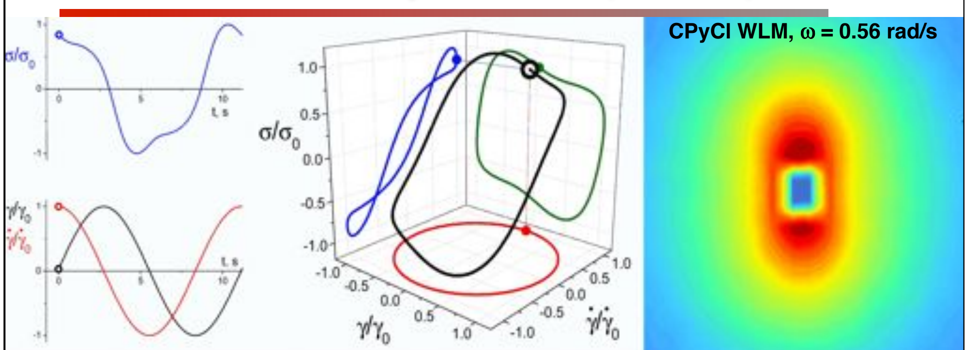
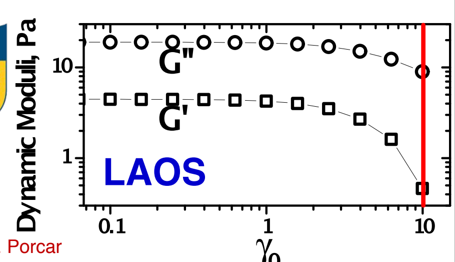
Time-resolved Oscillatory rheo-SANS (tOrSANS)



See ICR Presentation
"Understanding the Nonlinear Dynamics of Polymer-like Micelles by Combined time-resolved small angle neutron scattering (SANS) and large amplitude Oscillatory Shear (LAOS) rheology"



N.J. Wagner, A.K. Gurnon, C.R. López-Barrón, A. Eberle, L. Porcar

See also: *Day of LAOS* report; SOR Rheology Bulletin, July 2012

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CSI: Lisbon

* *CSI = Controlled Stress Investigation*

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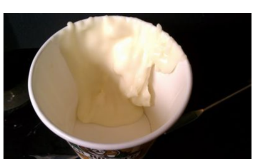
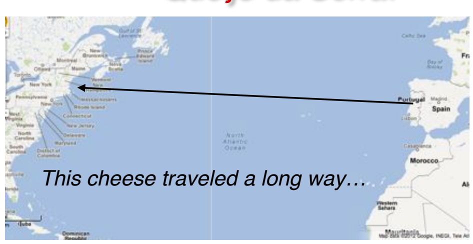
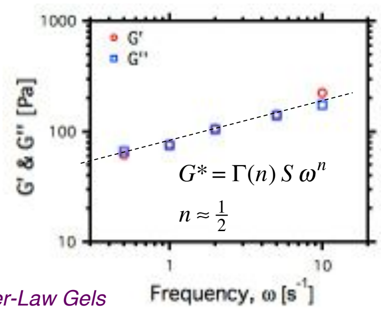
CSI: Lisbon

Queijo da Serra!







- Cheese: the famous "Queijo da Serra"
- LVE: Very close to a critical gel with G' = G"
- What about the nonlinear behavior?
- Use LAOStress to study it…

Fractional Calculus for Power-Law Gels

K. Song et al. *Korea-Aust Rheol. Journal*, **18** (2006)

A. Jaishankar & GHM, *Proc. Roy. Soc. A* (2012), in press

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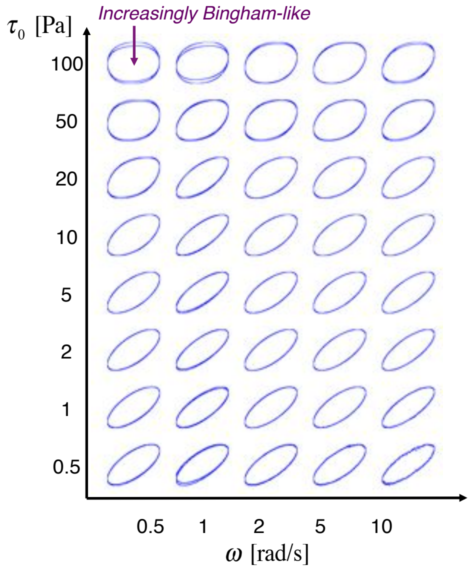
Nonlinear Rheology (LAOStress) of Queijo da Serra

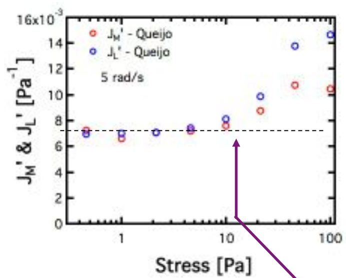


$$\tau(t) = \tau_0 \cos \omega t$$

$$\gamma(t) = \sum_{n \text{ odd}} \{\tau_0 J'_n \cos n\omega t + \tau_0 J''_n \sin n\omega t\}$$

$$J'_M \equiv \left.\frac{d\gamma}{d\tau}\right|_{\tau=0} = \sum_{n \ odd} (-1)^{(n-1)/2} n J'_n$$

$$J'_L \equiv \left.\frac{\gamma}{\tau}\right|_{\tau=\tau_0} = \sum_{n \ odd} J'_n$$



For an LVE material $J'_M = J'_L$

Onset of softening / yield like behavior

- Material stress softens around $\tau \approx 10$ Pa
- Relatively featureless in frequency (critical gel)

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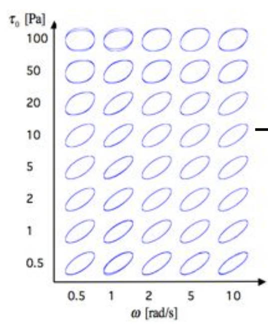
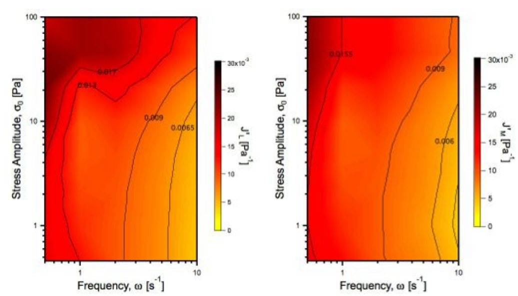
Fingerprinting

- Plot contours of the nonlinear measures..



Compute J_L'& J_M'



Loss of Evidence…

- There was not much of it left after a few days…

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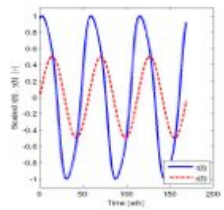
Summary of *Rheological Fingerprinting*

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

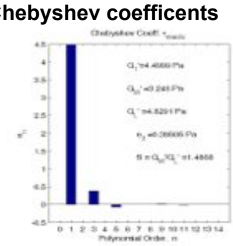
Time Series



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

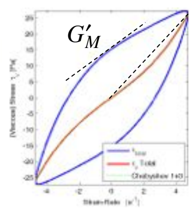
$$y = \frac{\dot{\gamma}(t)}{\gamma_0 \omega}$$

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

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

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

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

Ewoldt, et al. *Rheol. Acta*, **49**(2), 2010; Dimitriou, Ewoldt, GHM, *J. Rheol.* In prep

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SAOS

MAOS

LAOStrain, LAOStress

….what's next….?

Perhaps: Complete Harmonic Analysis of Oscillating Shear ??

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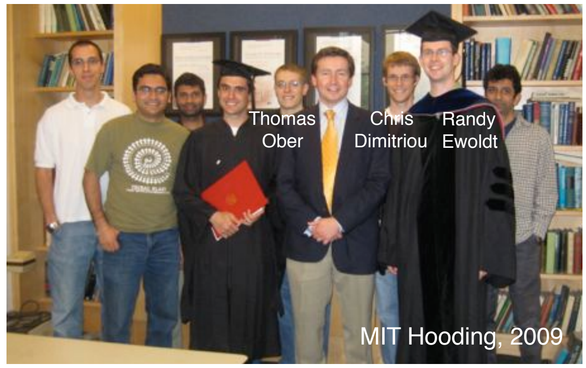

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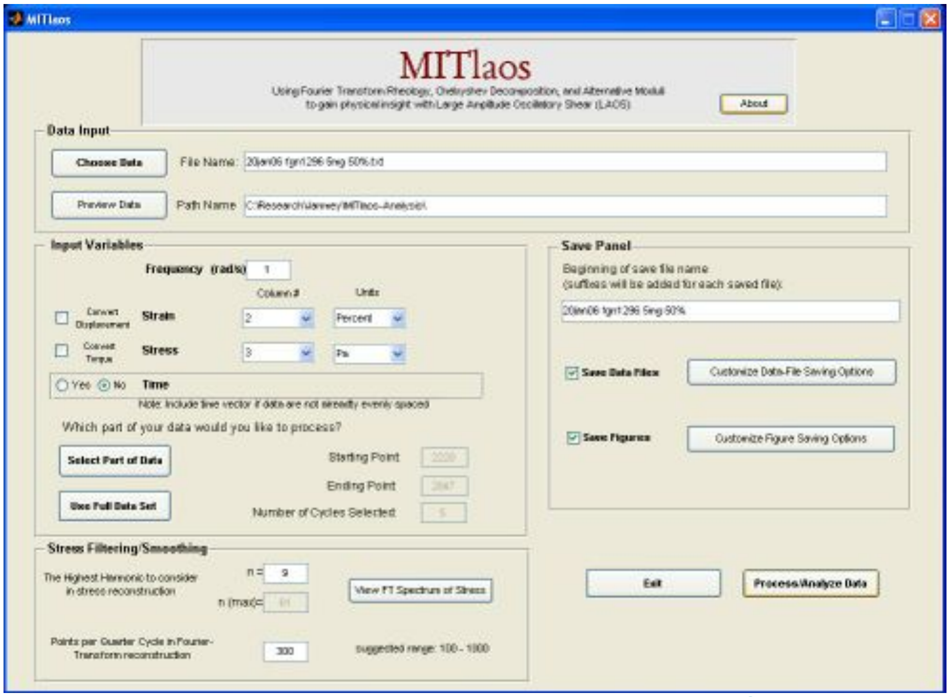

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