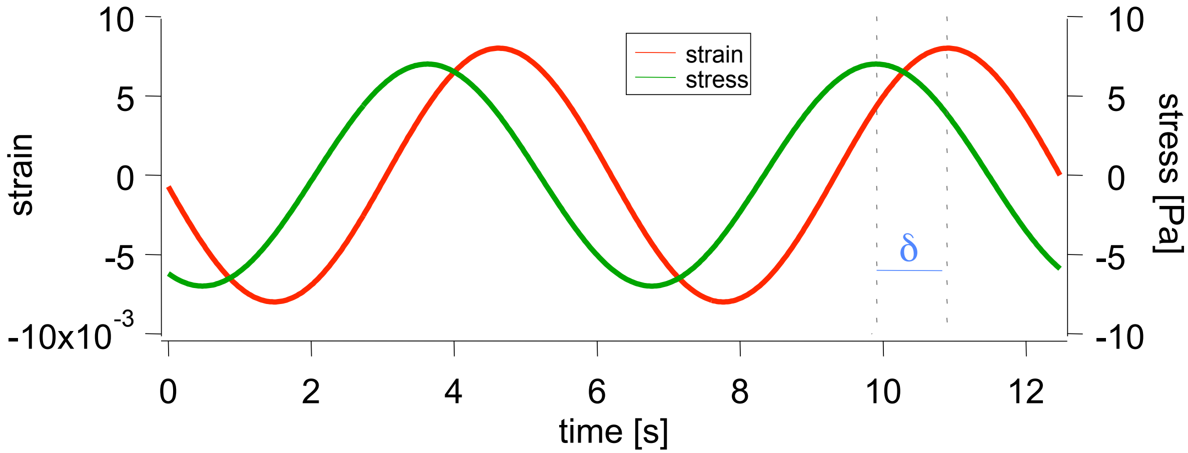


Introduction to Rheology

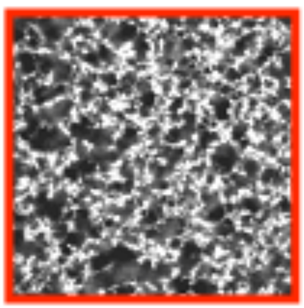
D. Vader, H.Wyss

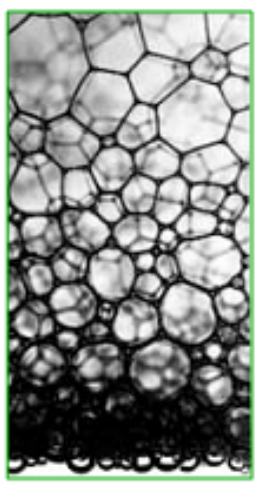
Weitzlab group meeting tutorial

What is rheology?

- Rheology is the study of the flow of matter: mainly liquids but also soft solids or solids under conditions in which they flow rather than deform elastically. It applies to substances which have a complex structure, including muds, sludges, suspensions, polymers, many foods, bodily fluids, and other biological materials.

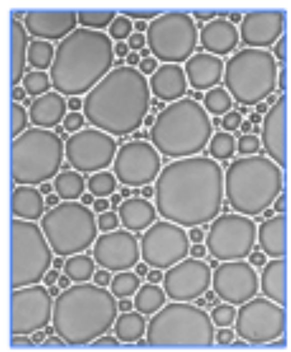
Cheese

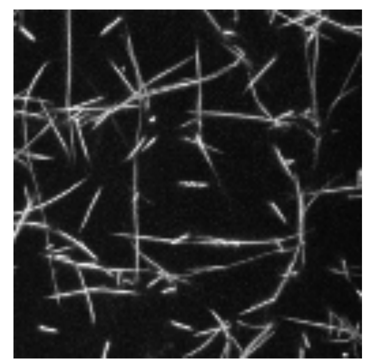




Foams

Emulsions



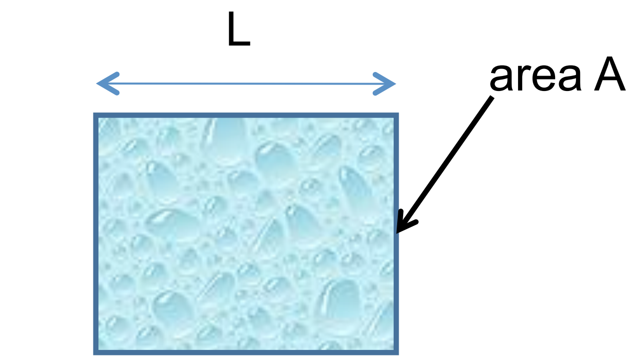


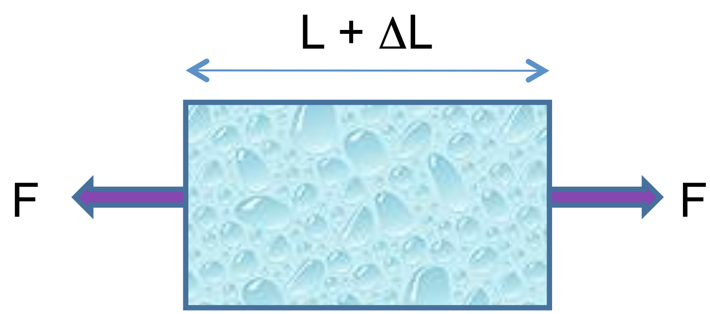
Biopolymers

What is rheology?

- The term rheology was coined in 1920s, and was inspired by a Greek quotation, "panta rei", "everything flows".
- In practice, rheology is principally concerned with extending the "classical" disciplines of elasticity and (Newtonian) fluid mechanics to materials whose mechanical behavior cannot be described with the classical theories.

Basic concepts

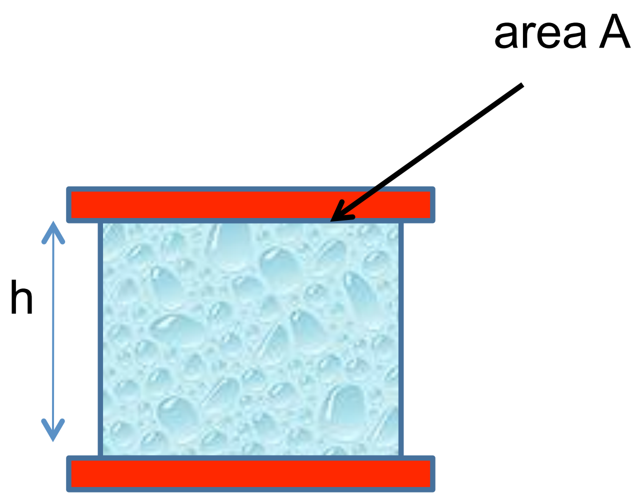


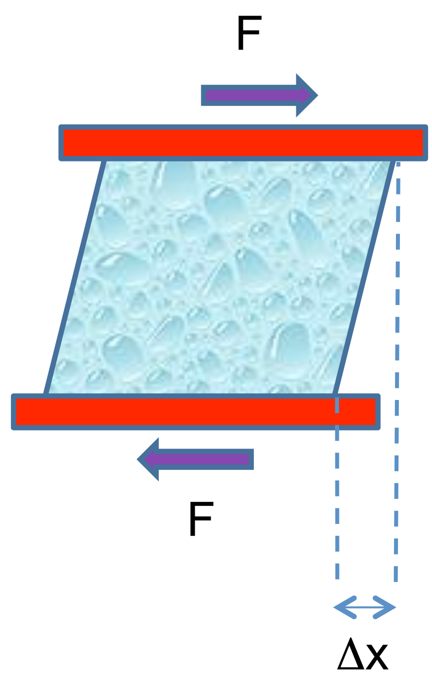


$$\varepsilon = \frac{\Delta L}{L}$$

$$\sigma = E\varepsilon$$

$$\boxed{\sigma = \frac{F}{A}}$$





$$\gamma = \frac{\Delta x}{h}$$

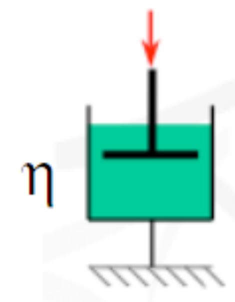
$$\sigma = G'\gamma$$

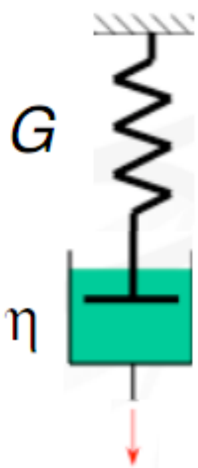
$$\sigma = G''\dot{\gamma}$$

Simple mechanical elements

Elastic solid: force (stress) proportional to strain

Viscous fluid: force (stress) proportional to strain rate



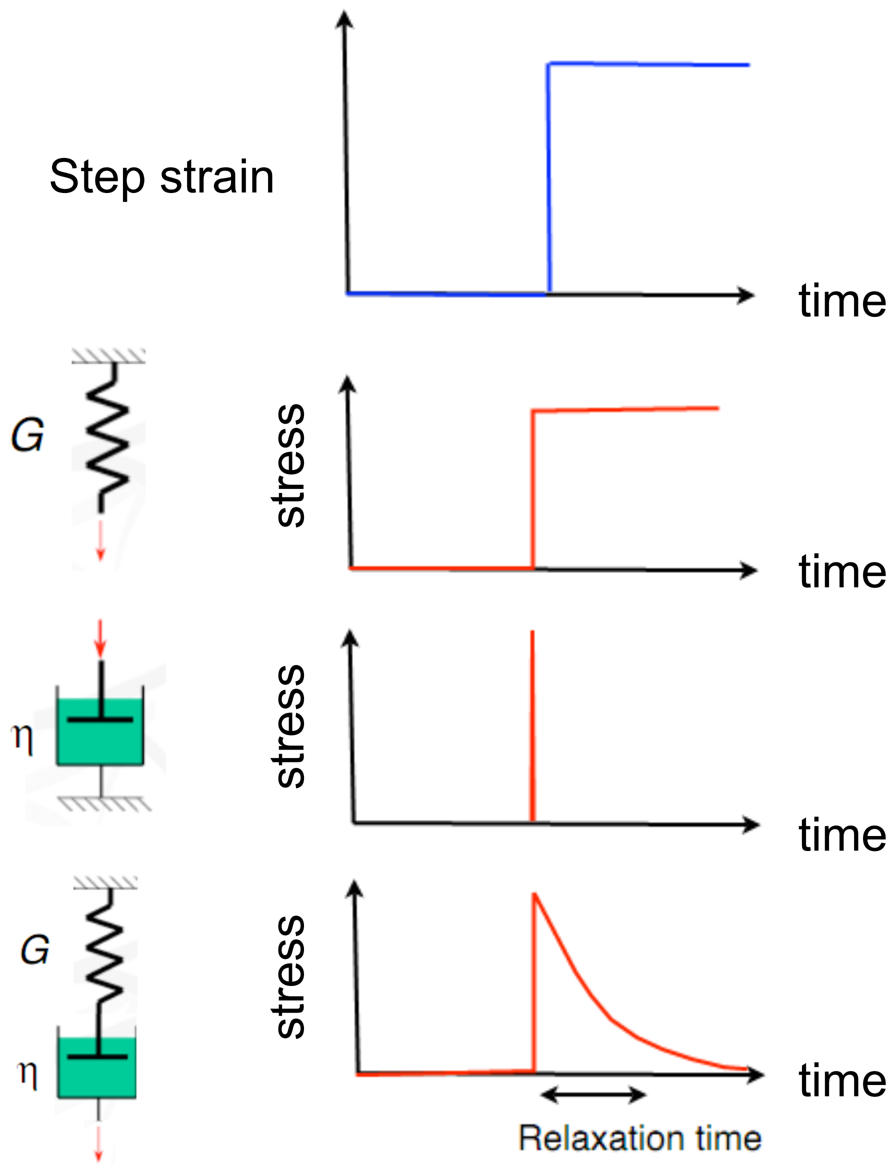


Viscoelastic material: time scales are important

Fast deformation: solid-like
Slow deformation: fluid-like

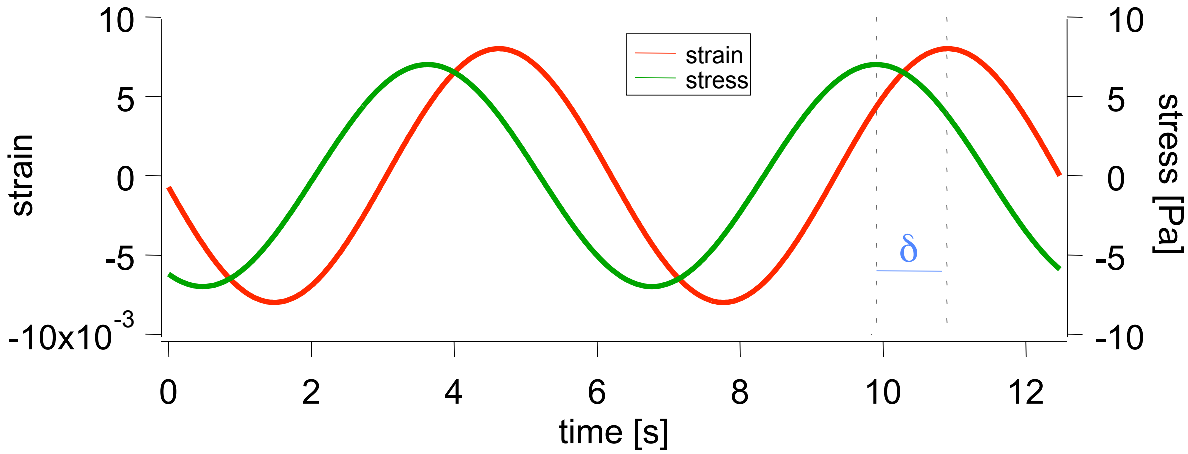
$$\tau = \frac{\eta}{G}$$

Response to deformation



$$\tau = \frac{\eta}{G}$$

Oscillatory rheology



Elastic solid: $\boxed{\sigma = G\gamma}$ Stress and strain are in phase

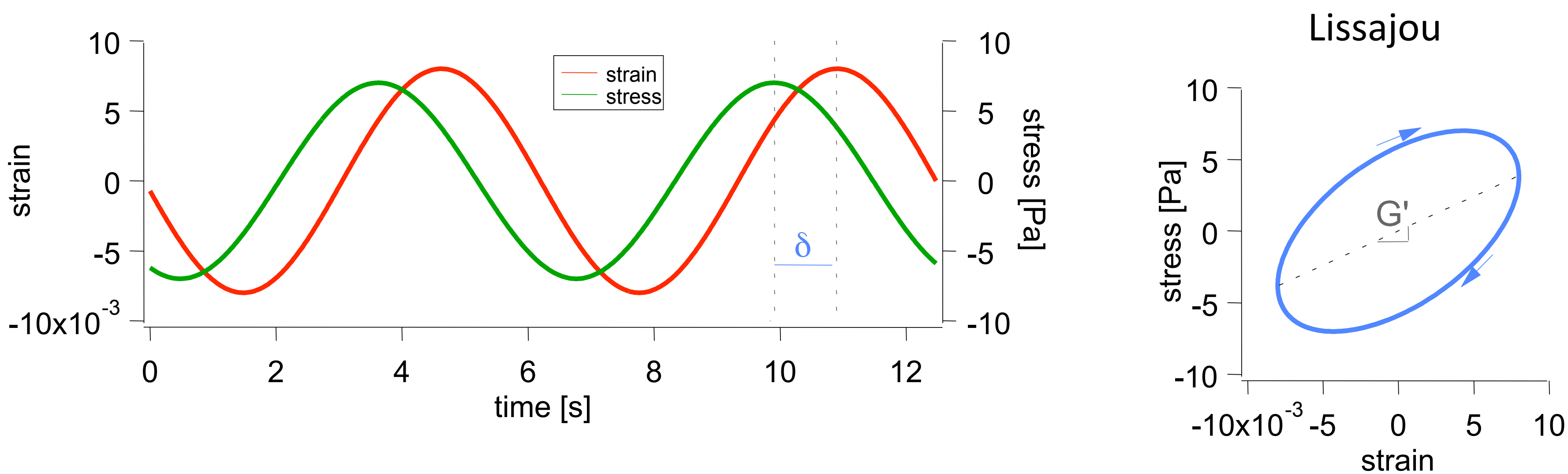
Viscous fluid: $\boxed{\sigma = \eta\dot{\gamma}}$ Stress and strain are out of phase

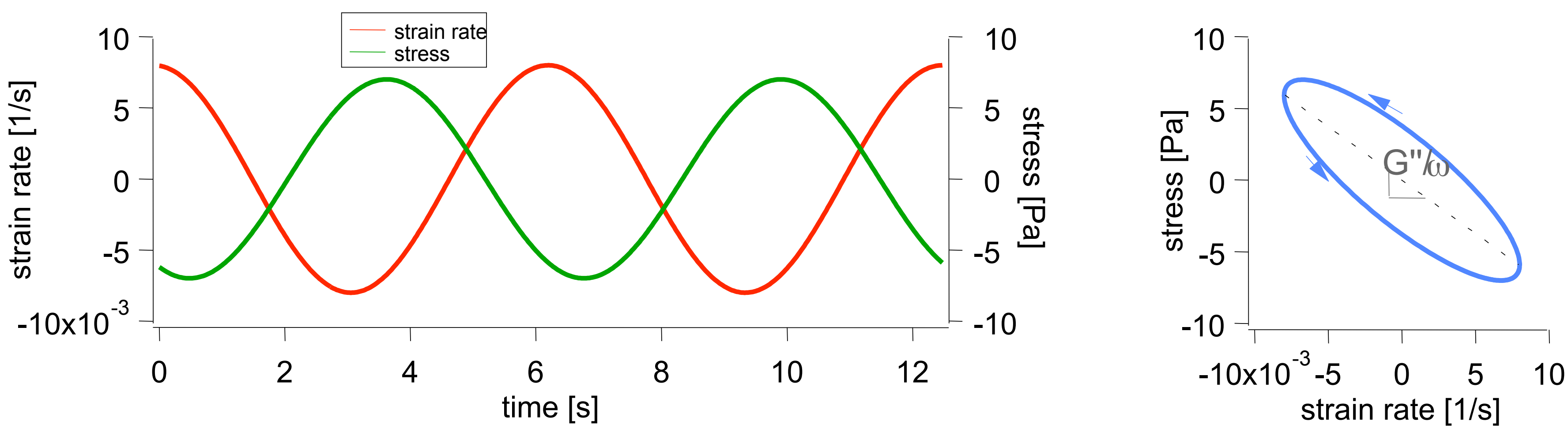
Viscoelastic material, use: $\gamma(\omega, t) = \gamma_0 \sin(\omega t)$

$$\sigma(\omega, t) = \boxed{G' \cdot \gamma_0 \cdot \sin(\omega t)} + \boxed{G'' \cdot \gamma_0 \cdot \cos(\omega t)}$$

$$\eta = \frac{G''}{\omega} \qquad \tan(\delta) = \frac{G''}{G'}$$

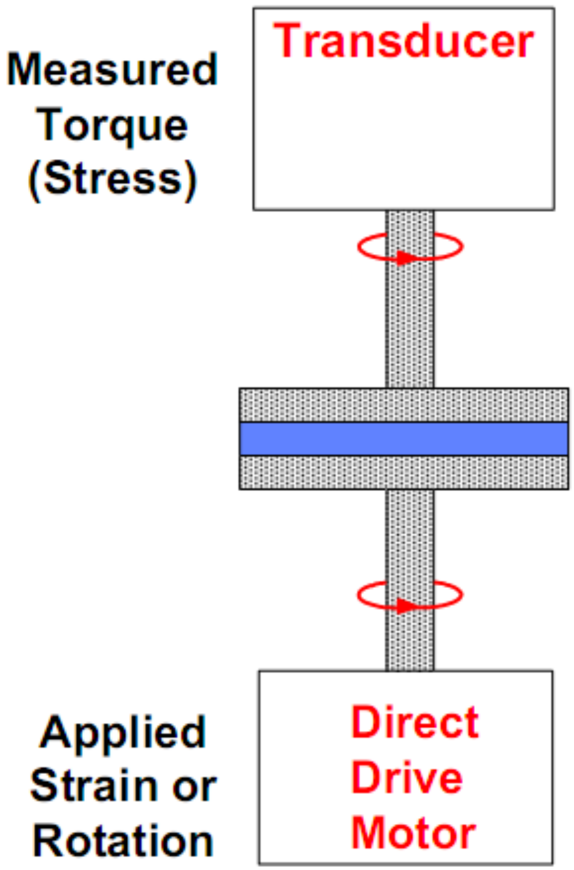
Lissajou plots





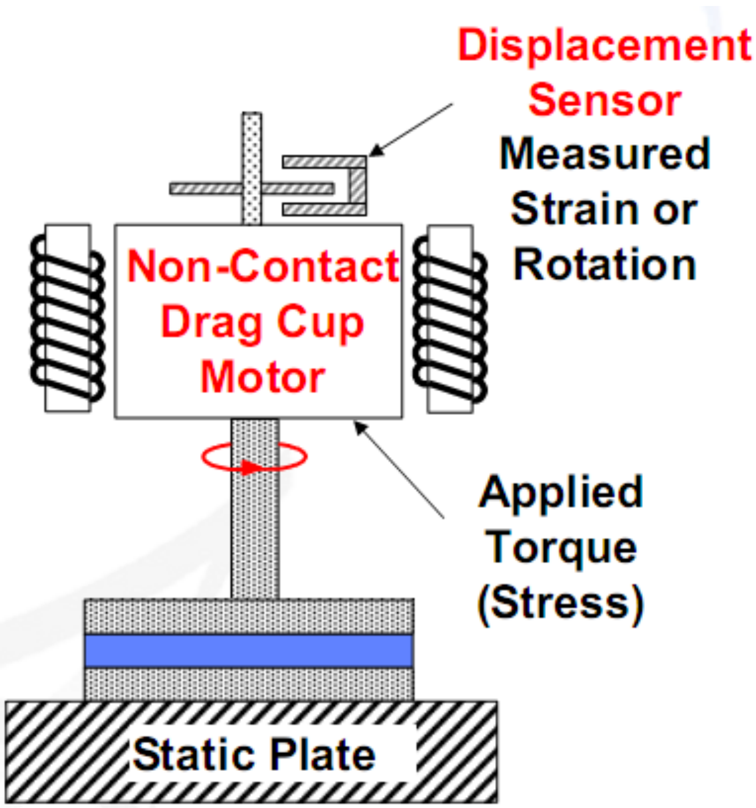
Strain-control vs stress-control

Strain-controlled



ARES

Stress-controlled



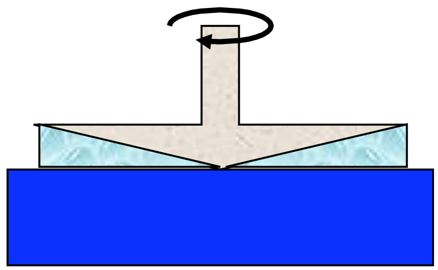
Bohlin, AR-G2, Anton Paar

Strain-control vs stress-control

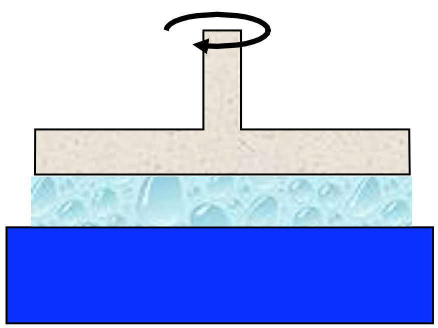
- *Strain-controlled state typically considered better defined*
- Stress-controlled rheometers have better torque sensitivity
- Strain-controlled rheometers can probe higher frequencies
- BUT… nowadays, feedback loops are fast enough that most rheometers can operate OK in both modes

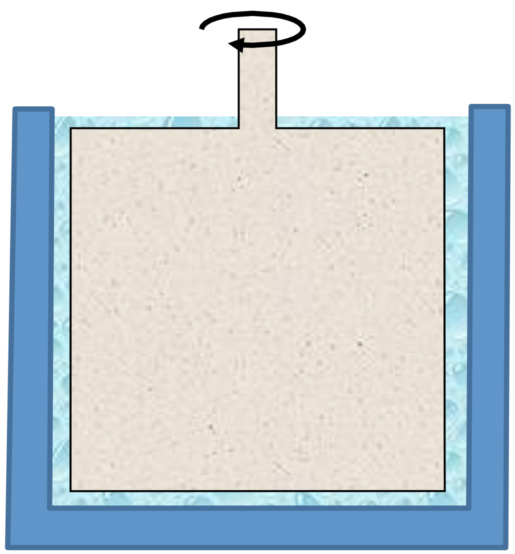
Rheometer geometries

- ❑ Cone-plate
  - uniform strain / strain-rate
  - fixed gap height



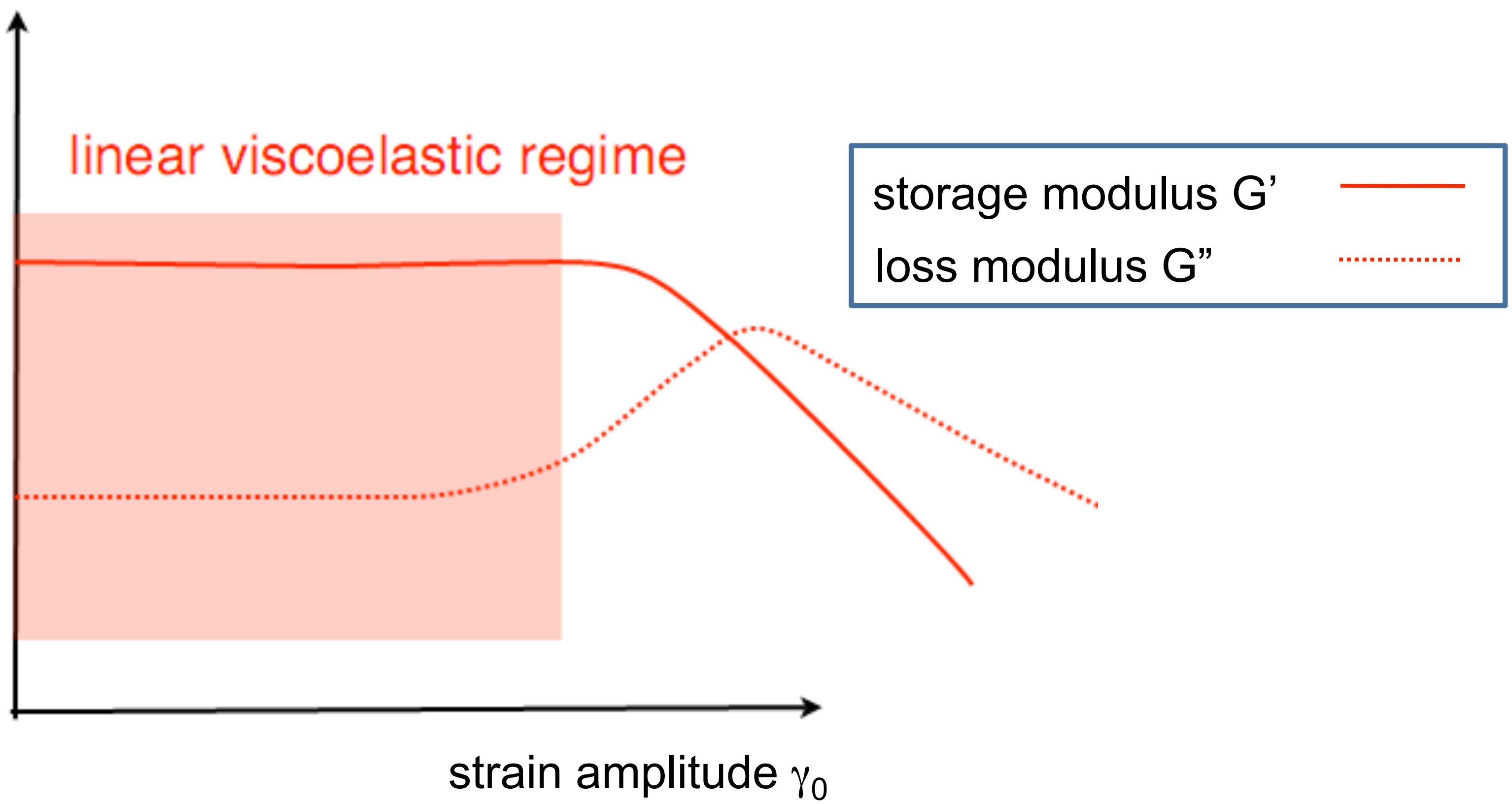
- ❑ Plate-plate
  - non-uniform strain
  - adjustable gap height
  - good for testing boundary effects like slip
- ❑ Couette cell
  - good sensitivity for low-viscosity fluids





Linear viscoelasticity

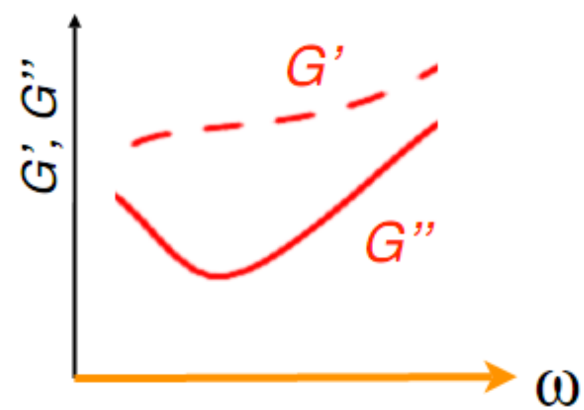
Acquire data at constant frequency, increasing stress/strain



Typical protocol

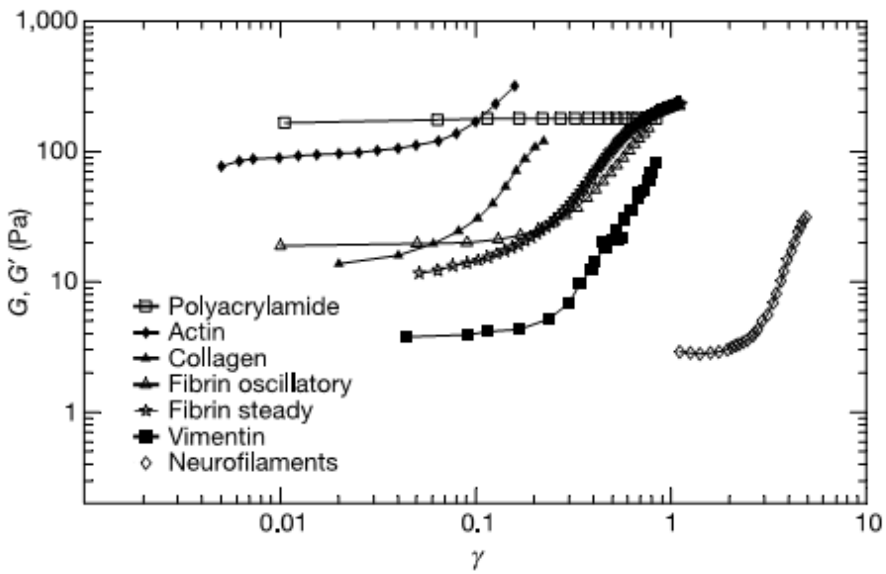
- Limits of linear viscoelastic regime in desired frequency range using amplitude sweeps

  => yield stress/strain, critical stress/strain
- Test for time stability, i.e time sweep at constain amplitude and frequency
- Frequency sweep at various strain/stress amplitudes within linear regime
- Study non-linear regime

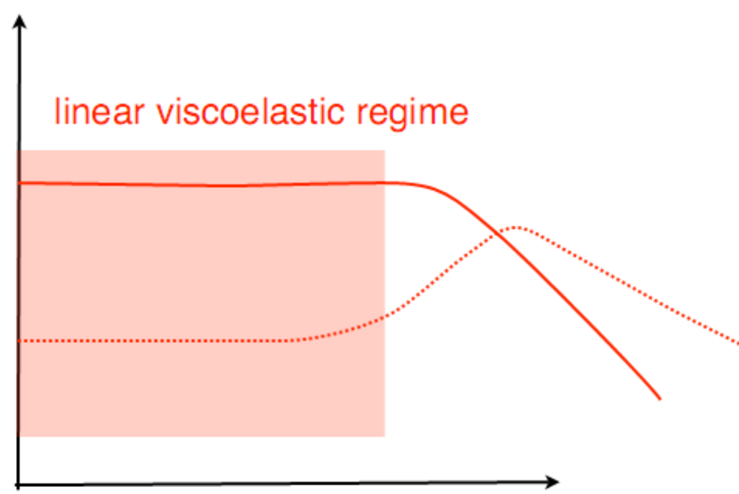


Nonlinear rheology (of biopolymers)

- *"Unlike simple polymer gels, many biological materials—including blood vessels, mesentery tissue, lung parenchyma, cornea and blood clots—stiffen as they are strained, thereby preventing large deformations that could threaten tissue integrity."* (Storm *et al.*, 2005)

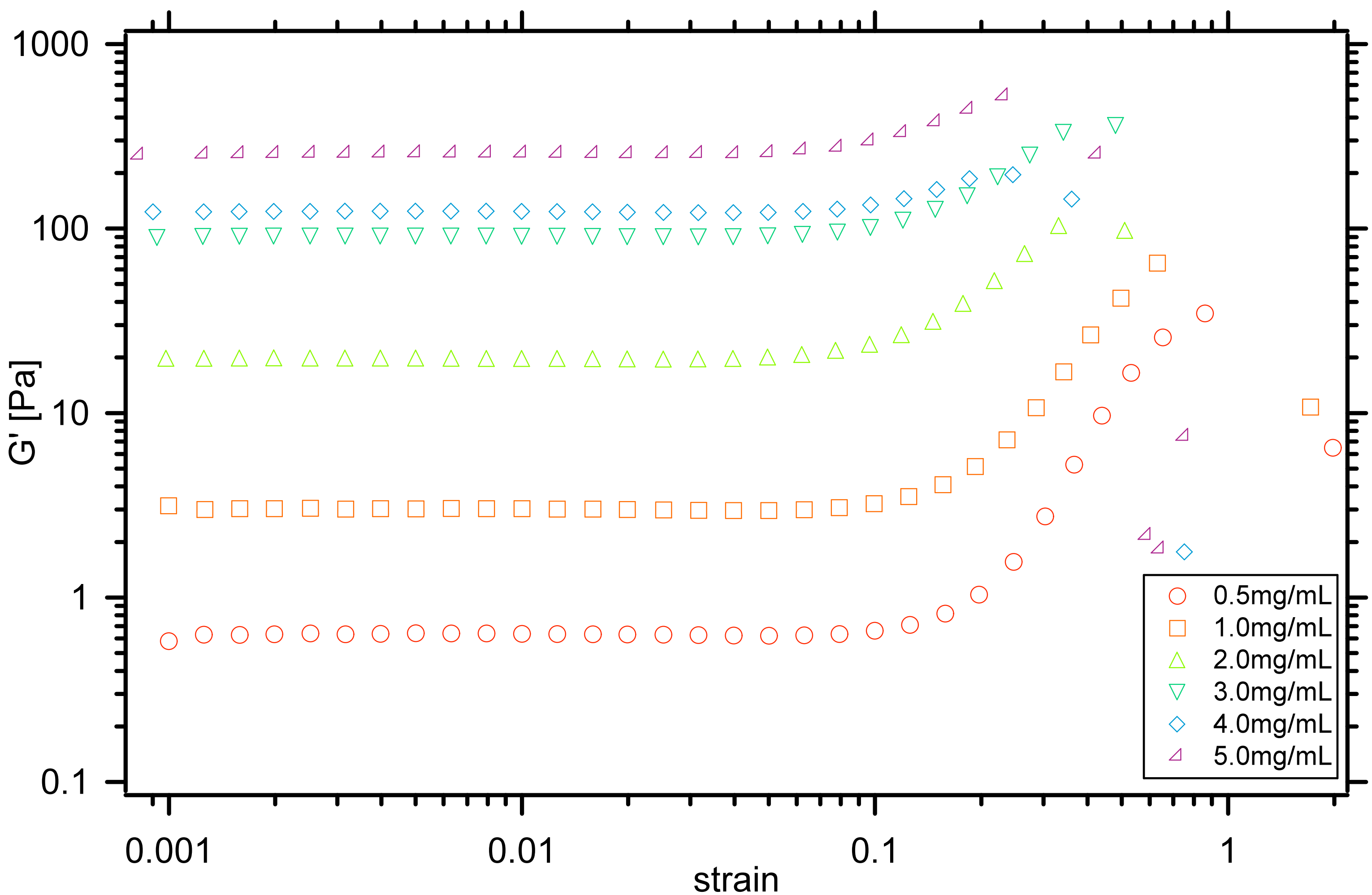


stiffening

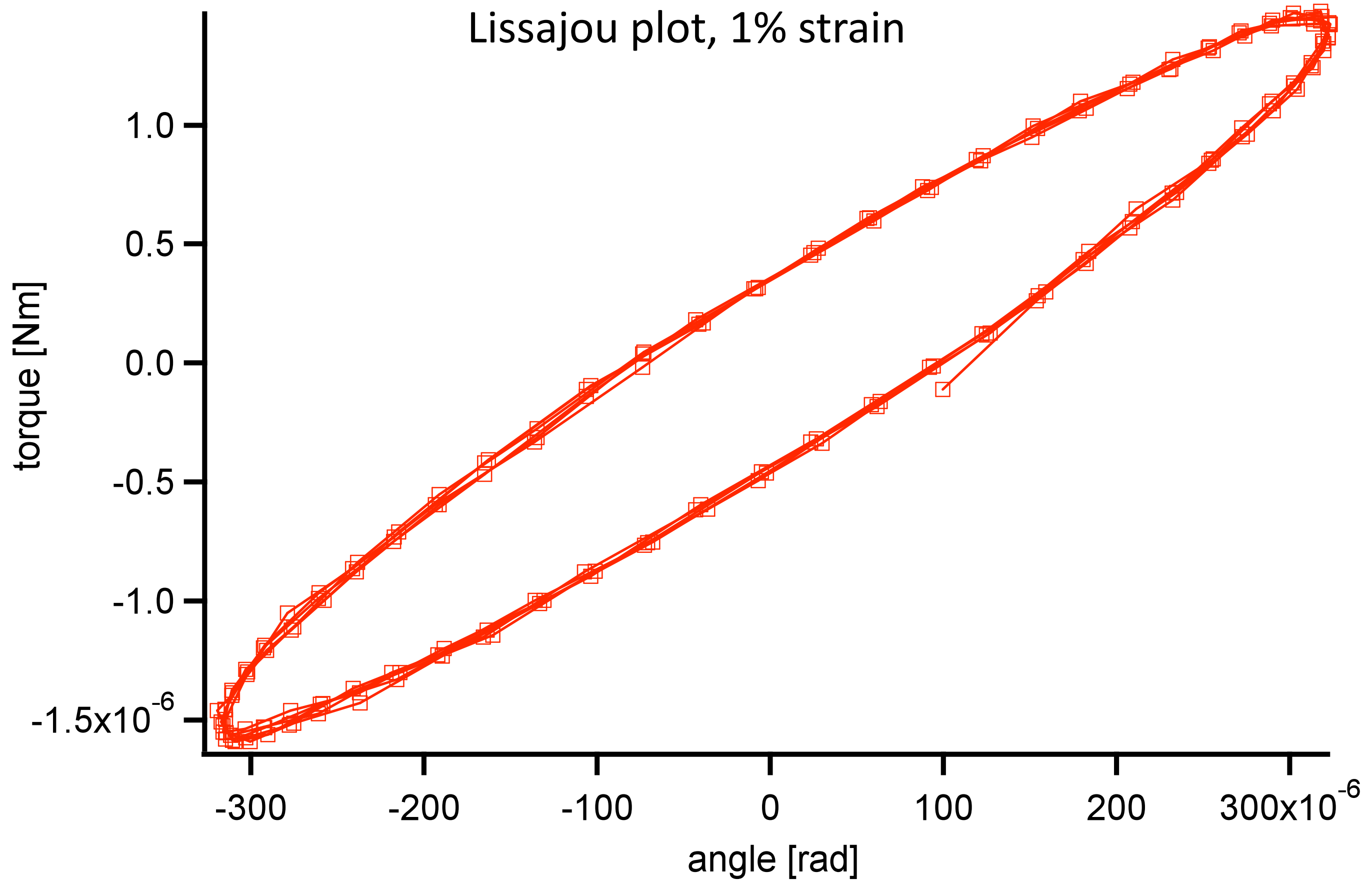


weakening

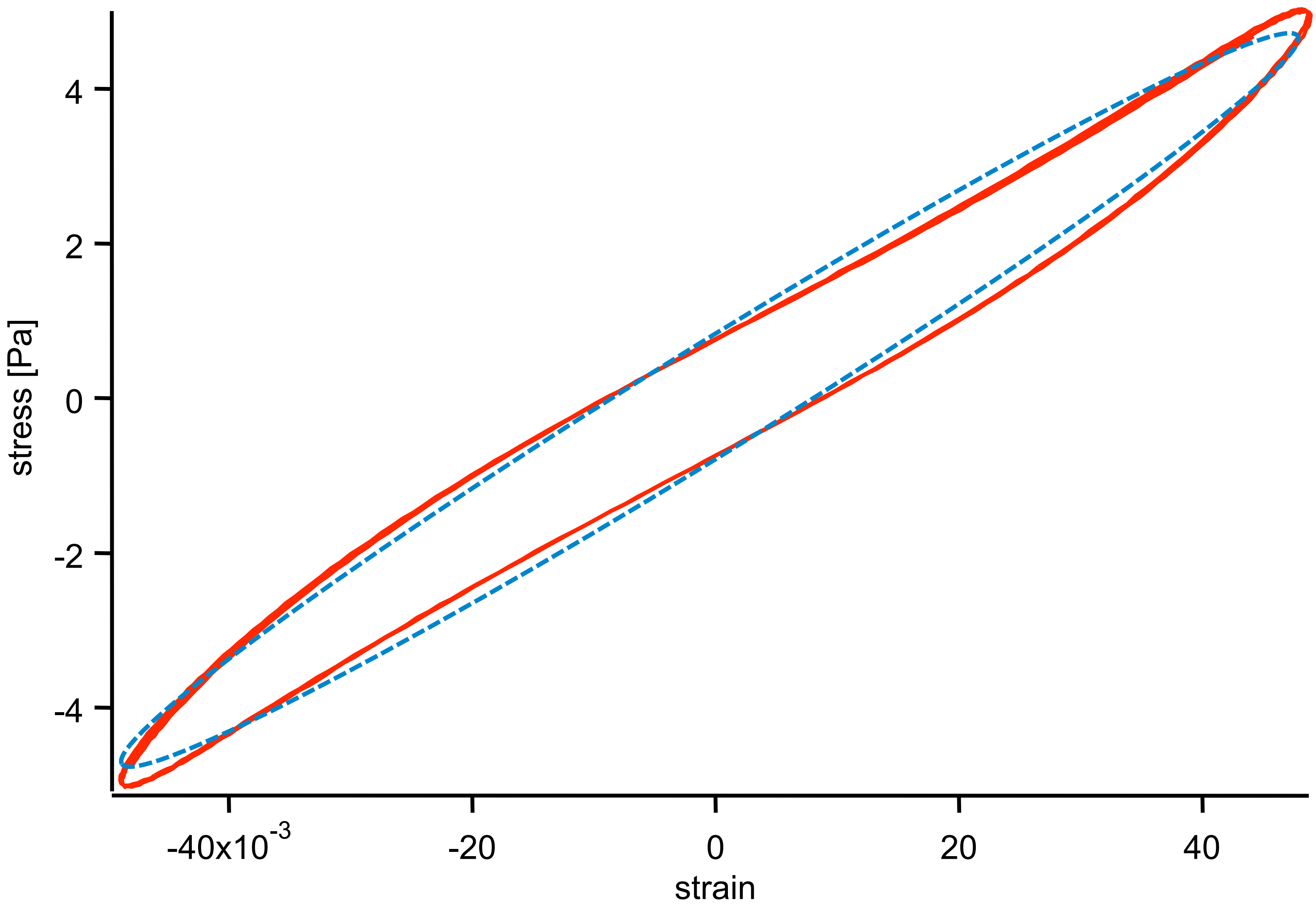
Oscillatory strain sweeps (collagen gels)



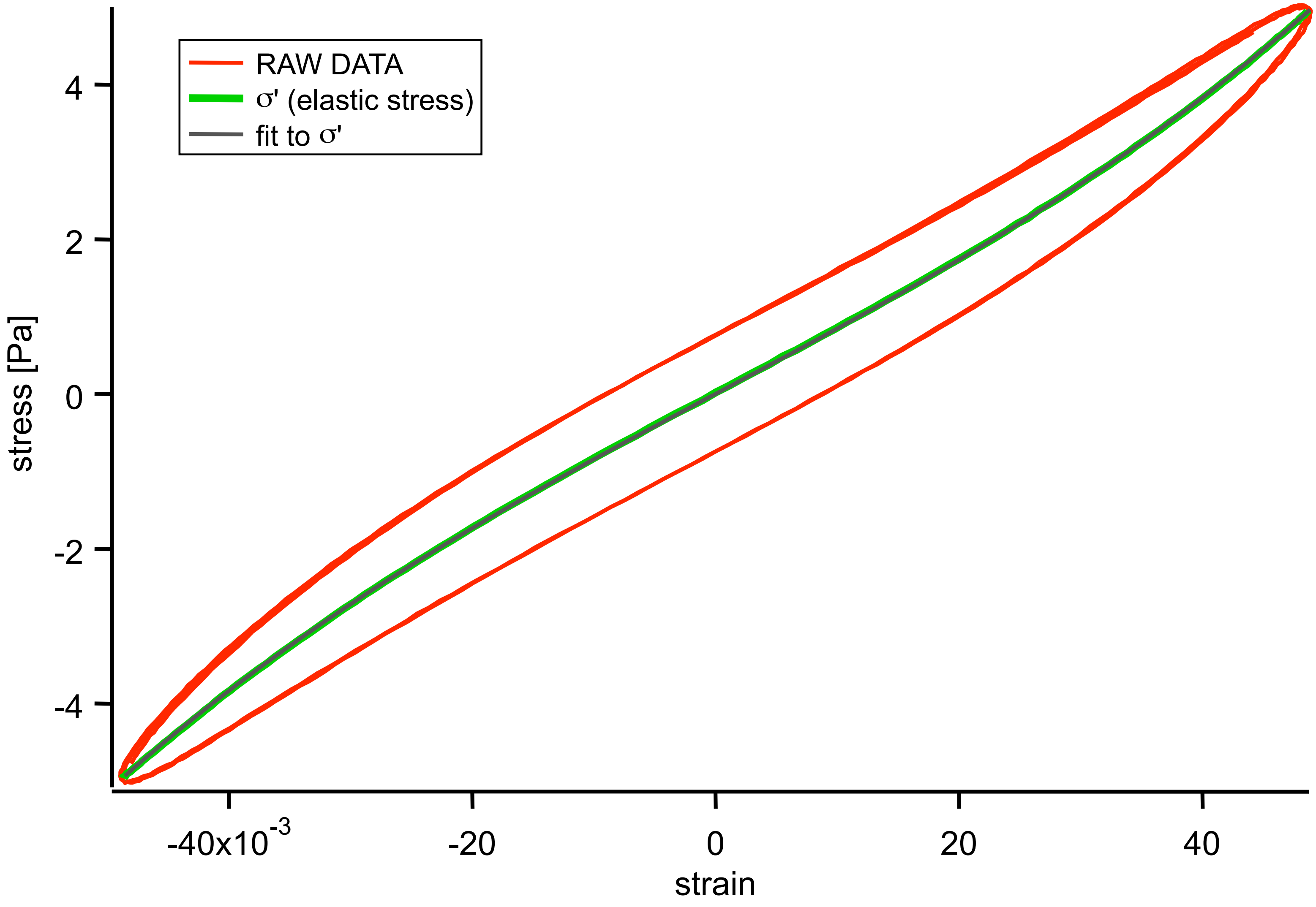
Lissajou plots from the G2 Raw data tool



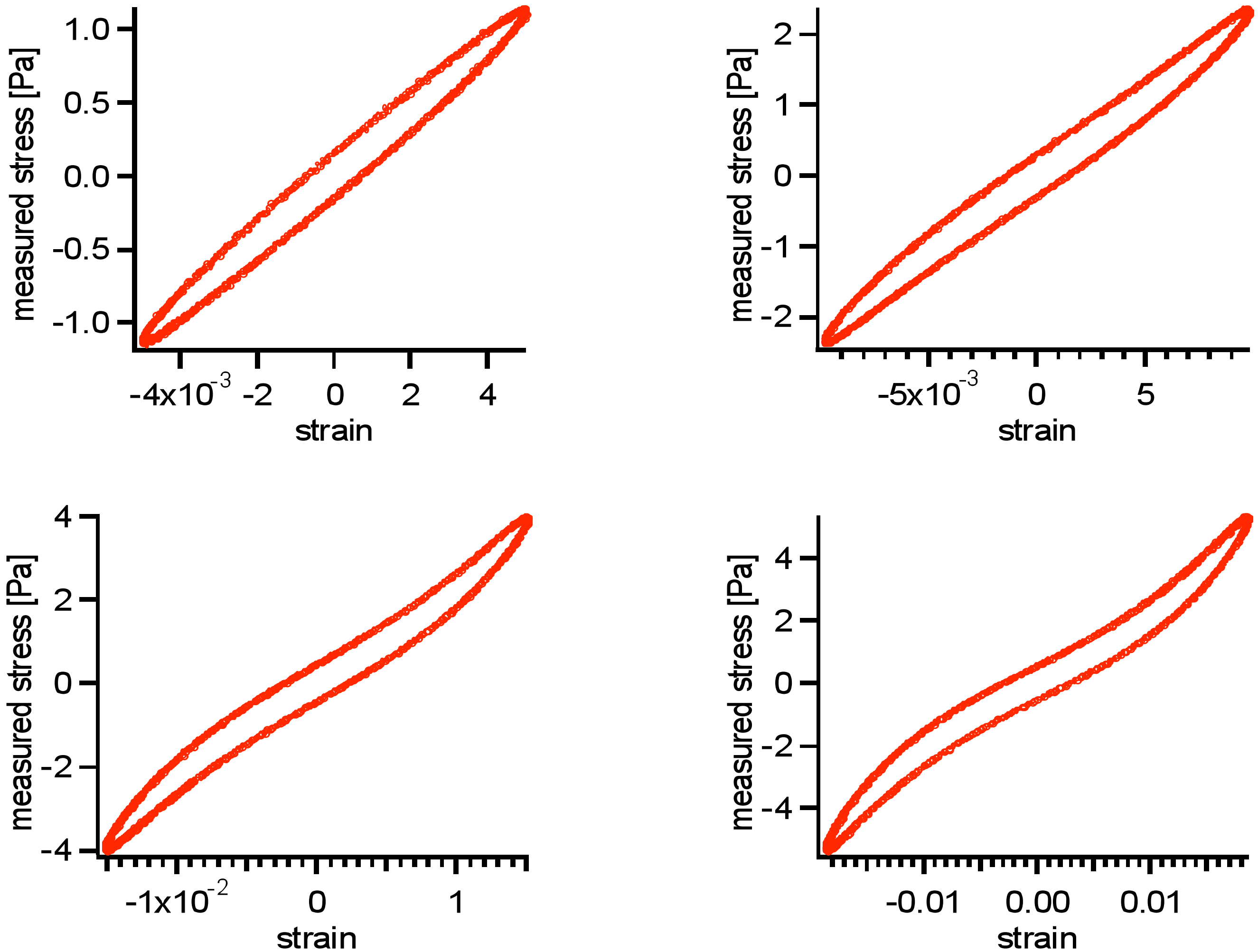
Nonlinear Lissajou plot



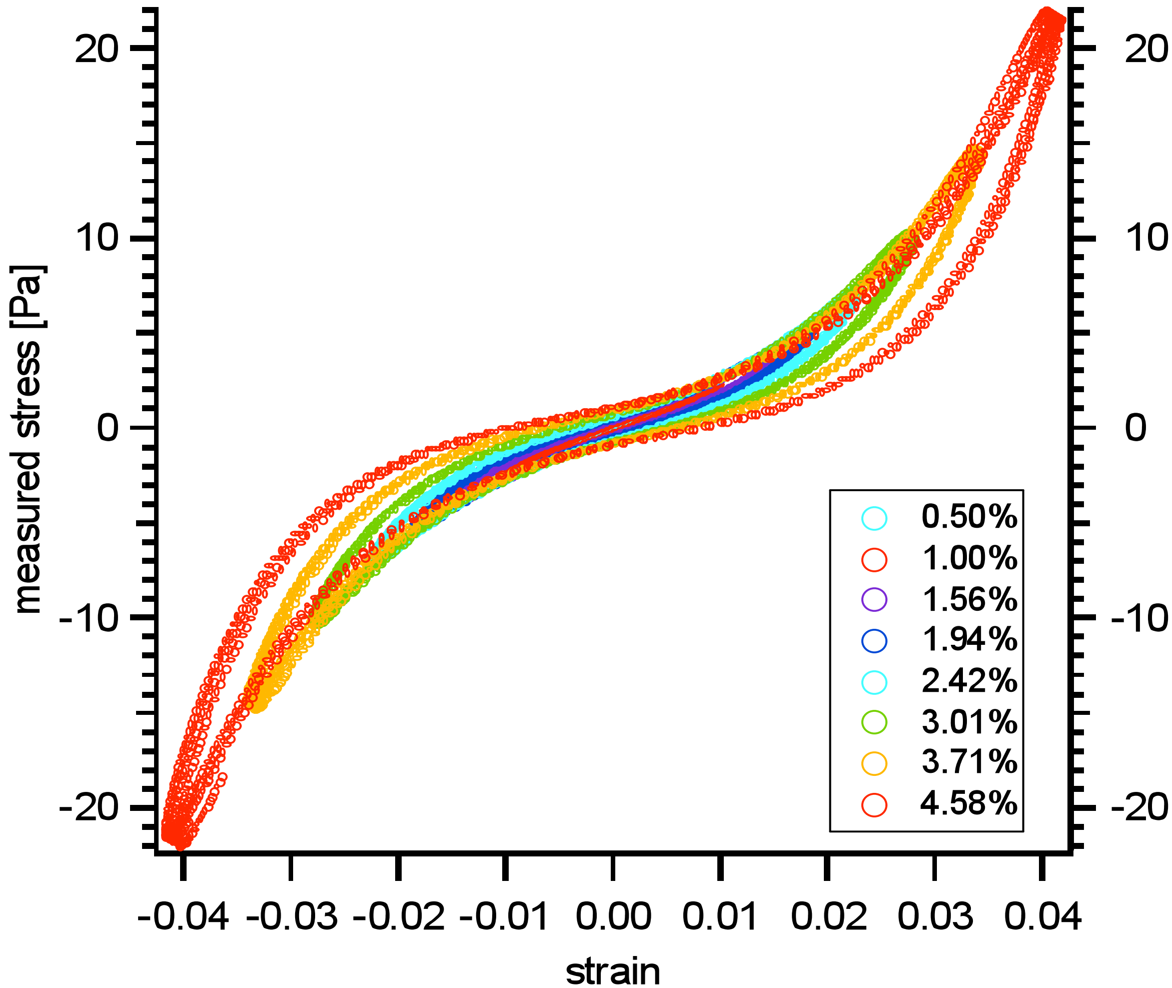
Nonlinear Lissajou plot



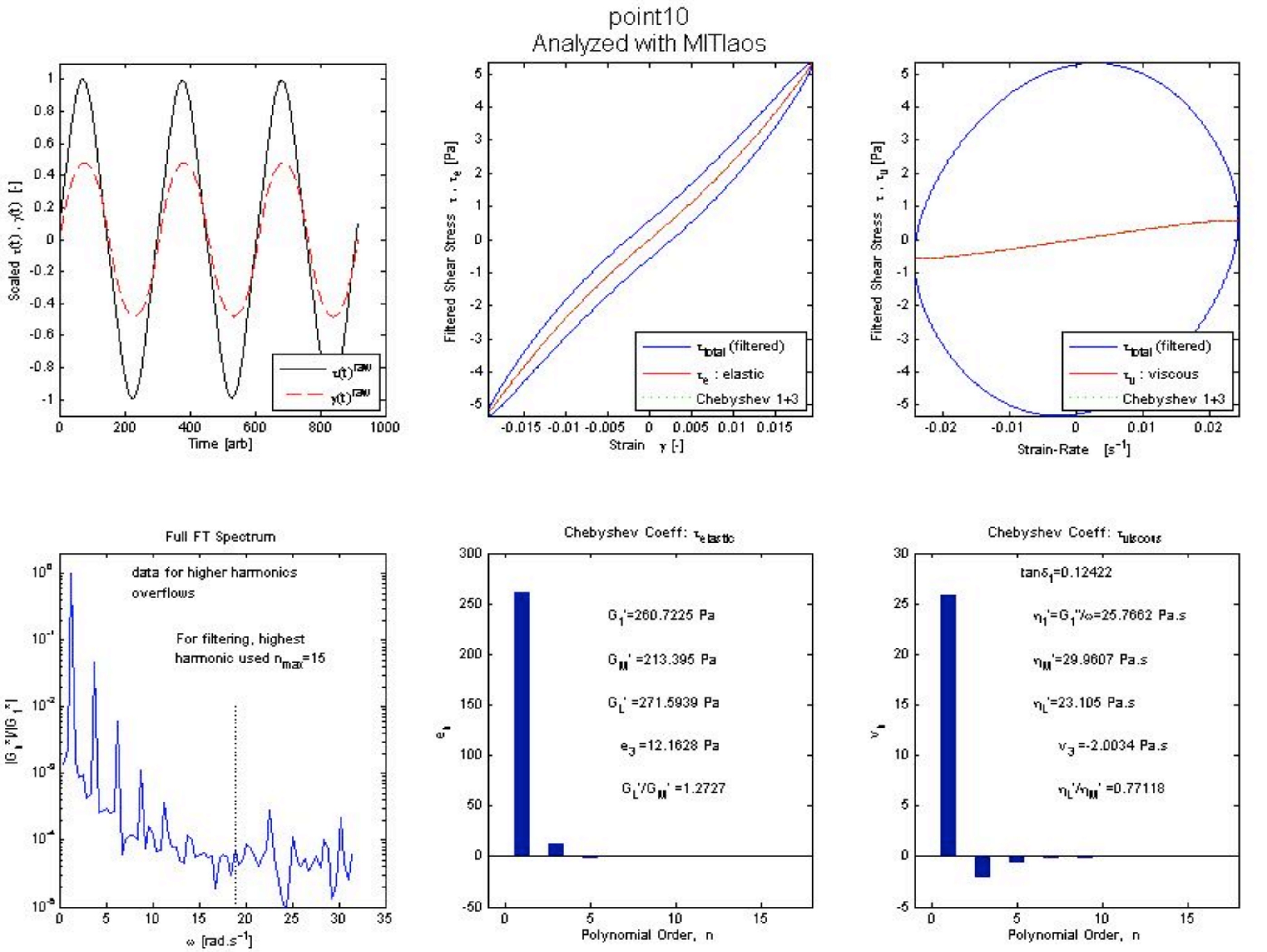
2.4mg/mL cone-plate



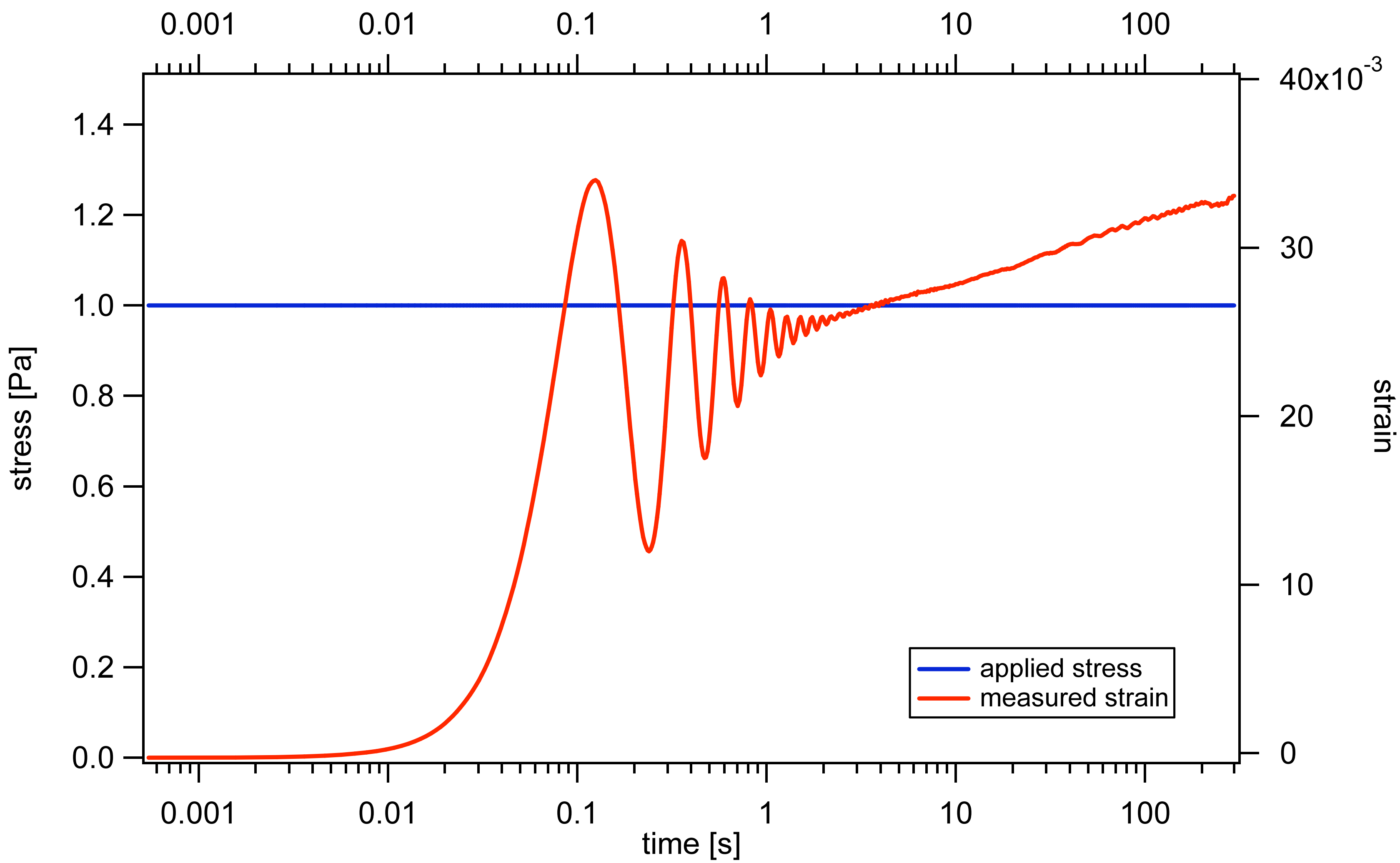
2.4mg/mL cone-plate



MIT LAOS MATLAB package

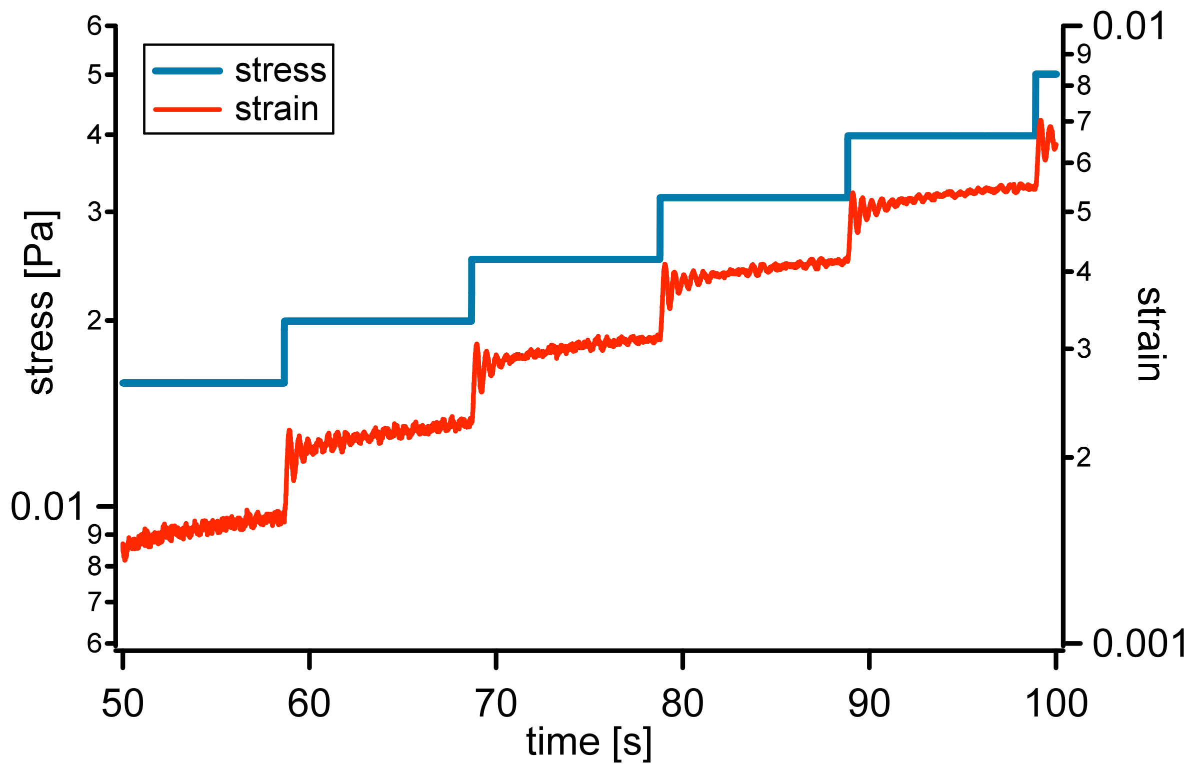


Creep-ringing



Creep-ringing

- Norman & Ryan's work here (fibrin, jamming)
- Good tutorial by Ewoldt & McKinley (MIT)



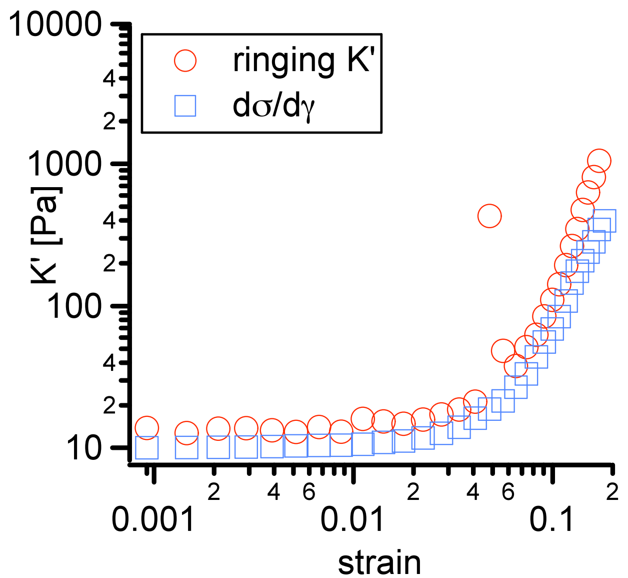
$$G' \approx \frac{I\omega^2}{b}\left(1 + \left(\Delta/2\pi\right)^2\right)$$

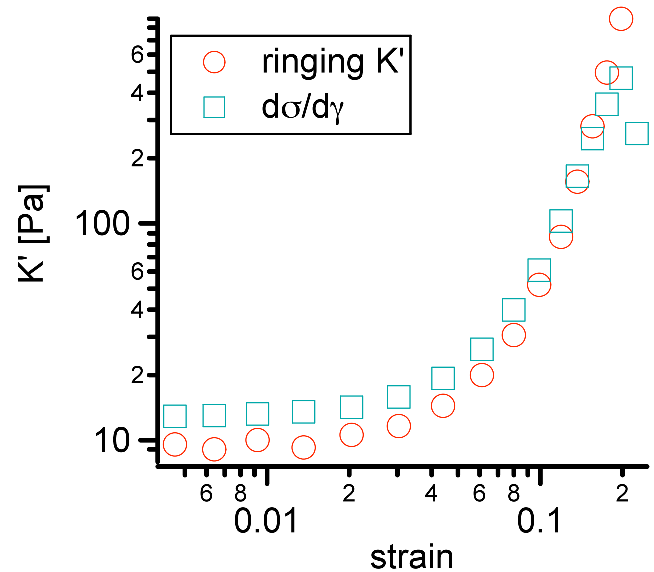
$$G'' \approx \frac{I\omega^2}{b}\left(\Delta/\pi\right)$$

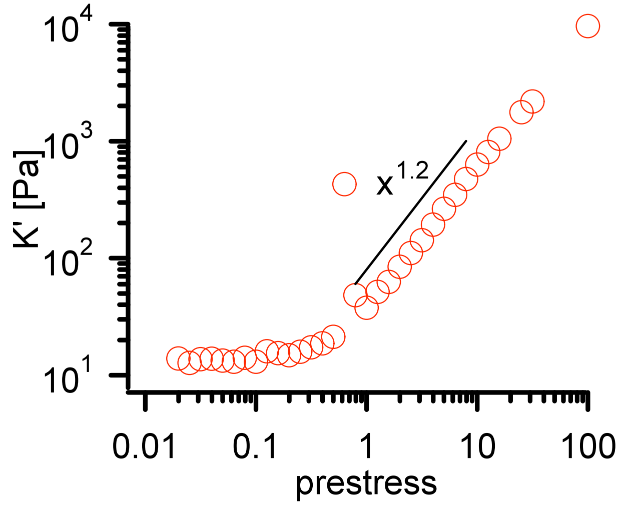
$$\Delta = \frac{1}{n}\ln\left(\frac{A_1}{A_{n+1}}\right)$$

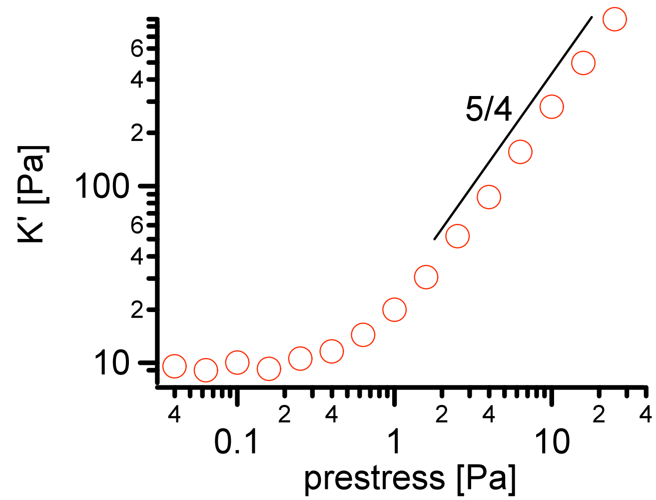
$$b = \frac{2\pi \cdot R^3}{3\tan\theta}$$

Creep-ringing results



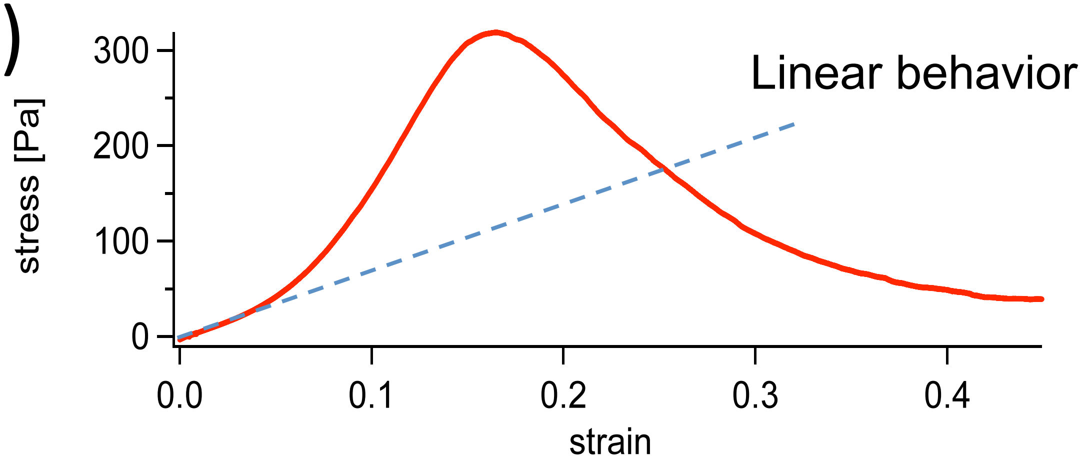






More nonlinear rheology

- Stress/strain ramps with constant rate
- Pre-stress measurements, i.e. small stress oscillations around a constant (pre-)stress
- Pre-strain measurements
- Transient responses in LAOS (talk to Stefan)
- Fourier domain analysis
- SRFS (talk to Hans)



Origin of nonlinear behavior

- Distribution of length-scales / inhomogeneities
- Rearrangement of particles / filaments
- Non-affine motion

- How do we find out?

Observation at the microscopic scale:
- Microrheology
- Microscopy

Microrheology basics

- General idea: look at the thermally-driven motion of micron-sized particles embedded in a material
- Mean-square displacement of particles as a function of time provides microscopic information on local elastic and viscous material properties as a function of frequency
- Mason and Weitz, PRL, 1995

Short and long timescales

Short time scales:
diffusive

$$\mathrm{MSD}(\tau) \equiv \left\langle \left(r_{t+\tau} - r_t \right)^2 \right\rangle_t \sim 4D\tau$$

$$D \sim \frac{k_B T}{6\pi \cdot a \cdot \eta}$$

r: position vector
D: diffusion constant
τ: lag time
kT: thermal energy
a: particle size
η: viscosity

Long time scales:
spring-like

$$\frac{1}{2} K \cdot \mathrm{MSD}(\tau) \sim \frac{1}{2} k_B T$$

K: effective spring-constant, linked to elastic properties

What about intermediate times?

Generalized Stokes-Einstein

$$D \sim \frac{k_B T}{6\pi \cdot a \cdot \eta} \quad \Rightarrow \quad \eta \sim \frac{k_B T}{6\pi \cdot a \cdot D} \sim \frac{k_B T \cdot 4\tau}{6\pi \cdot a \cdot MSD(\tau)}$$

$$\boxed{\eta(\tau) \sim \frac{\tau}{MSD(\tau)}}$$

Take Laplace transform of $\eta(\tau)$ numerically, to get $\eta(s)$ – with $s=i\omega$.
From earlier, we know:

$$G''(\omega) \sim \eta(\omega) \cdot \omega$$

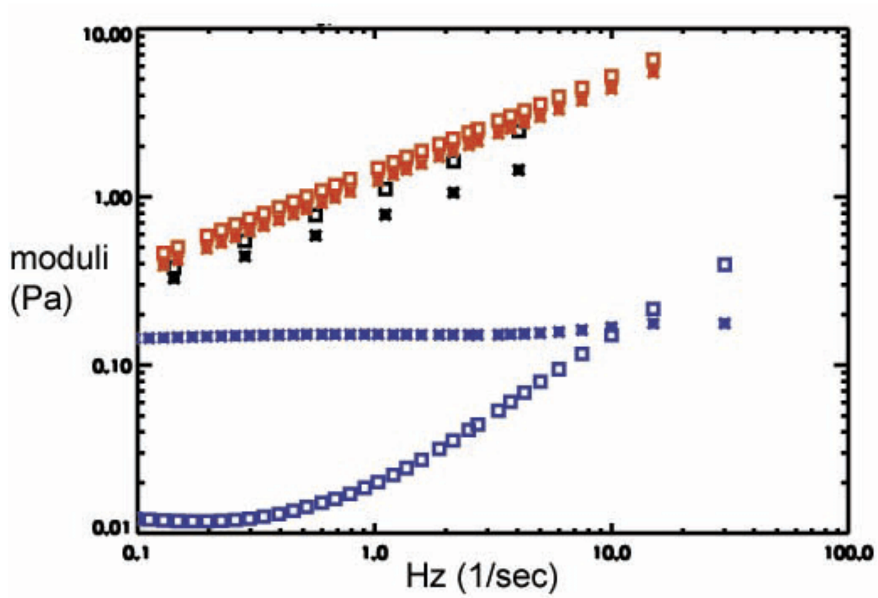
We can then get the generalized complex modulus, by analytically extending:

$$G''(s) \sim \eta(s) \cdot s$$

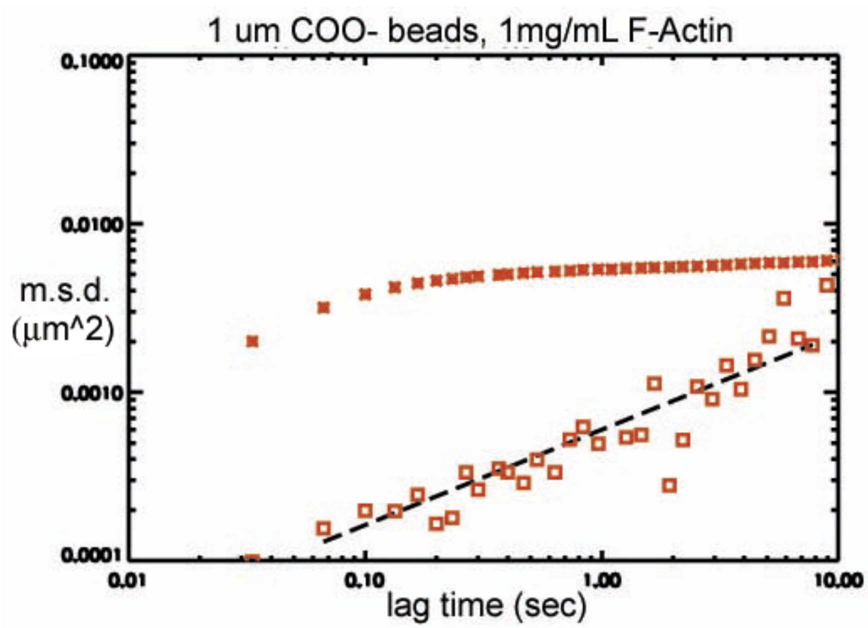
i.e. $$\boxed{G^*(i\omega) \sim \eta(i\omega) \cdot i\omega}$$

2-point vs 1-point microrheology

2-point microrheology calculates a mean-square displacement from the correlated pair-wise motion of particles, rather than the single-particle MSD.



Black: bulk rheology
Red: 2-point microrheology
Blue: 1-point microrheology
Open symbols: G”



Other considerations

- Non-linear regime non-trivial, but more interesting.
- Surface effects can be important.
- Imaging to figure out mechanisms.
- Richness of effects, mechanisms, time-, length- and energy- scales present in soft matter / complex fluids.
- More to explore on Weitzlab webpage.
- More at ComplexFluids meetings.