

Rheological Fingerprinting of Complex Fluids using Large Amplitude Oscillatory Shear (LAOS) Flow

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ABSTRACT

We describe a new approach to understanding the progressive transition from linear to nonlinear rheological response in complex fluids and soft solids. Large amplitude oscillatory shear (LAOS) tests are carried out over a wide range of frequencies and strain amplitudes. The resulting material response to an oscillatory input can be represented in terms of Lissajous figures and can also be decomposed into purely viscous and purely elastic contributions. By plotting these contributions in the form of Pipkin diagrams a unique rheological fingerprint of a complex fluid can be constructed.

INTRODUCTION

Nonlinear rheological properties are often relevant in understanding the response of a material to its intended environment. For example, many gastropods crawl on a thin layer of pedal mucus using a technique called adhesive locomotion, in which the gel structure is periodically ruptured and reformed. The thin layer (typically 10-20 μm) of excreted mucus serves both as glue and lubricant allowing the animals to climb walls and crawl across ceilings as shown in Figure 1. Gastropods exert shear stresses on this thin layer of structurally-sensitive mucus that holds the organism to the substrate. Compression waves move toward the head (top of picture) during locomotion. Muscular contractions (see label 'a' below) compress the foot parallel to the substrate, creating an area of high shear stress which

ruptures the mucus network structure; an interwave of low stress (label 'b') allows the network structure to periodically reform into a solid-like material which glues the organism to the substrate¹.

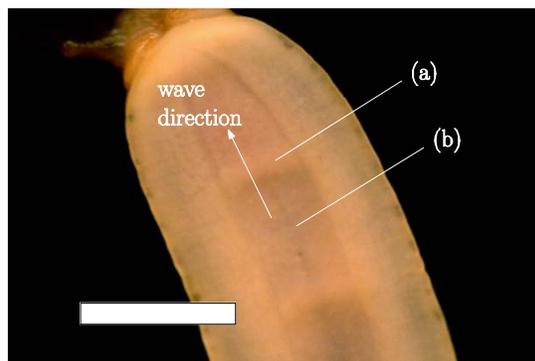


Figure 1 (a) Side view of common garden snails (*Helix aspersa*); (b) Bottom view of a crawling terrestrial slug (*Limax maximus*), 1 cm scale bar;

The thin pedal mucus film has an effective yield stress; at high applied stresses the network structure breaks, enabling the foot to glide forward over a fluid layer; whereas in regions of low applied stress the network structure reforms into a solid-like layer connecting the foot to the substrate¹.

The question arises of how best to probe the complex rheological response of such soft materials. The flow is neither a steady shearing flow nor a linear viscoelastic deformation with small strain amplitudes. Large amplitude oscillatory shear (LAOS)² provides a systematic framework to measure and quantify the progressive transition from linear to nonlinear rheological behaviour of such biological gels and we consider this deformation protocol in detail below.

LARGE AMPLITUDE OSCILLATORY SHEAR FLOW (LAOS)

For many complex materials the common practice of reporting just the “linear viscoelastic moduli” as calculated by commercial rheometers (or more accurately, the first harmonic coefficients $\{G'(\omega), G''(\omega)\}$ in a Fourier series) is insufficient and/or misleading for describing the nonlinear material response under deformation conditions characteristic of the actual process of interest. As an example, we show in Fig. 2 a stress sweep to probe the linear viscoelastic response of a mucin gel excreted by a crawling slug at a fixed frequency of $\omega = 0.5$ rad/s.

The material response is clearly that of a soft elastic solid with the magnitude of $G' > G''$. A weak degree of strain softening is observed as the stress amplitude is increased; however the response is otherwise unremarkable until the material suddenly ruptures and fails at a critical stress of ~ 600 Pa. Similar responses can be measured at different frequencies and the material exhibits the characteristic elastically-dominated frequency response of a soft gel [1],[3].

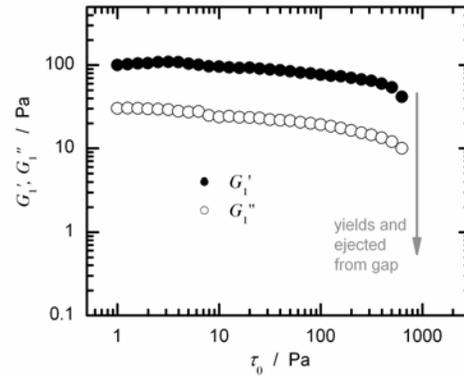


Figure 2: stress amplitude sweep showing the variation of the linear viscoelastic moduli of a pedal mucus film as the oscillatory stress amplitude is increased.

A closer examination of the individual raw waveforms however shows that the material response is actually very rich. A convenient way of representing this information is in the form of *Lissajous figures*² in which the time varying stress $\sigma(t)$ is plotted as a function of the oscillating strain $\gamma(t) = \gamma_0 \sin \omega t$, or as a function of the instantaneous shear rate $\dot{\gamma}(t) = \gamma_0 \omega \cos \omega t$. A representative plot for the gastropod mucin film is shown in Figure 3:

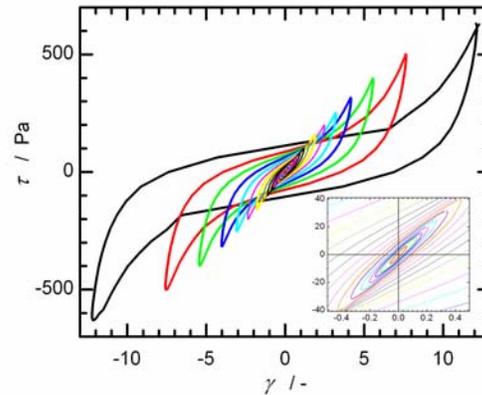


Figure 3. Lissajous figures of the oscillatory stress in a gastropod mucin film as a function of increasing strain amplitude at a fixed frequency of $\omega = 0.5$ rad/s.

At small strains (see inset) the response is linearly viscoelastic and the trajectories are elliptical which can be analyzed to extract values of G' & G'' respectively. A perfectly elastic material response would appear as a straight line in Fig. 3, and conversely a purely viscous fluid response would correspond (when appropriately scaled) to a circular trajectory. However as the strain amplitude increases this rheological test highlights two distinguishing features of such soft viscoelastic gels: firstly, a gradual softening with increasing strain-amplitude indicated by the clockwise rotation of curves; and secondly, a distortion from elliptical shape indicative of strain-stiffening at large strains. Nonlinear responses have been documented in a large number of other soft solids and biopolymer gels^{3,4}. The question then arises as to how to quantify this nonlinear material response.

One natural and rigorous approach is to represent the material response as a Fourier series⁵:

$$\tau(t; \omega, \gamma_0) = \gamma_0 \left\{ \sum_i G_i'' \cos(i\omega t) + G_i' \sin(i\omega t) \right\} \quad (1)$$

Although the higher Fourier harmonics $\{G_i', G_i''\}$ of the material response capture the mathematical structure of the measured waveform, they lack a clear physical interpretation. We thus seek to develop a framework for physically interpreting deviations from linearity which considers the 2D space of frequency and strain-amplitude first discussed by Pipkin to generate a unique ‘rheological fingerprint’ of a complex fluid.

We build on the earlier geometrical interpretation of Cho *et al.* (2005)⁶ which decomposes a nonlinear stress response into elastic and viscous stress contributions using symmetry arguments so that the stress in eq. (1) is given by:

$$\tau(t; \omega, \gamma_0) \equiv \tau_{even}(\gamma(t)) + \tau_{odd}(\dot{\gamma}(t)) \quad (2)$$

We then use Chebyshev polynomials of the first kind as orthonormal basis functions to further decompose each of these two stresses into harmonic representations

$$\tau_{even} = \gamma_0 \sum_{i=1}^N e_i T_i(x) \quad (3)$$

$$\tau_{odd} = \gamma_0 \omega \sum_{i=1}^N v_i T_i(y) \quad (4)$$

where the elastic and viscous material coefficients are e_i and v_i respectively, the (scaled) strain is $x \equiv \gamma(t)/\gamma_0 = \sin \omega t$ and the shear rate is $y \equiv \dot{\gamma}(t)/(\gamma_0 \omega) = \cos \omega t$. From symmetry arguments regarding the form of the stress we expect all even coefficients ($i = 2, 4, \dots$) in these expansions to be identically zero.

The motivation behind this representation is three fold: firstly at each order i of approximation, the Chebyshev polynomials are orthogonal – fitting the material data to a higher order N thus does not change the lower order coefficients for $i = 1, \dots, N-1$. This is in contrast to other polynomial representations used in the past⁶. Secondly, in the linear domain the material response is elliptic and can be completely described by the leading order coefficients; *i.e.* $e_1 \rightarrow G'(\omega)$ and $v_1 \rightarrow G''(\omega)$. Finally, the temporal response of the system can be readily reconstructed if desired through the following identity for Chebyshev polynomials: $T_i(y) \equiv T_i(\cos \omega t) = \cos i\omega t$.

RESULTS

We first apply these ideas to model hypothetical systems such as a neo-Hookean elastic solid or a generalized Newtonian fluid (*e.g.* a Carreau fluid) to show that a strain-stiffening elastic response is indicated generically by a positive 3rd order elastic Chebyshev coefficient, $e_3 > 0$, whereas shear-thinning is always indicated by a

negative 3rd order viscous Chebyshev coefficient, $v_3 < 0$.

Sample experimental results for the response of a mucin film at $\omega = 1$ rad/s and a strain amplitude of $\gamma_0 = 3$ are shown in Fig. 4. The measured response is shown in the time domain by the solid blue line, and the elastic contribution to the stress $\tau_e(\gamma)$ is shown by the red line. The nonlinear regime is clearly identified in the spectral domain by the presence of higher order Chebyshev coefficients.

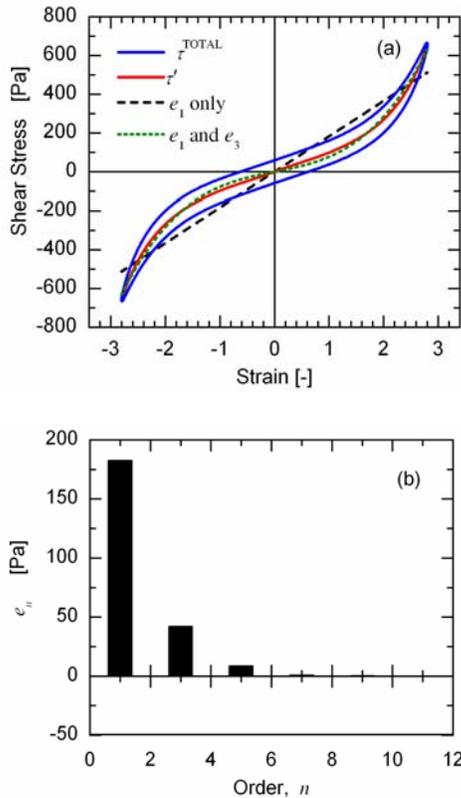


Figure 4. (a) Lissajous figure of the total stress (shown in blue) as a function of the oscillatory strain amplitude together with the elastic contribution to the stress (solid red line); (b) modal decomposition of the individual Chebyshev contributions (e_i) to the elastic stress τ_e .

A simple linear fit to this data (*i.e.* the first harmonic contribution calculated by standard rheometer software) is shown by

the broken line and is clearly an inadequate representation of the material response. The sign of e_3 shows that the gel is strain stiffening and the magnitude of e_3/e_1 provides a quantitative measure of the degree of nonlinearity. The two mode reconstruction of the material response (shown by the green dotted line) provides a very good description of the actual material response.

In general, this new elastic/viscous modal decomposition is invaluable for characterizing and for verbally describing the nonlinear rheological response in a wide range of materials including biopolymer gels, regenerative polymer networks, entangled melts and micellar solutions.

The Pipkin Diagram

The nonlinear material response can be measured over a range of frequencies and strain amplitudes to generate values of $e_i(\omega, \gamma_0)$ and $v_i(\omega, \gamma_0)$. The remaining question then becomes: *how best to represent the wealth of material information that comprises the distinct rheological signature of a given material in large amplitude oscillatory shear flow?* One approach we have found especially useful is to represent the responses in the form of a *Pipkin diagram*⁷ in which the variation in the material response with imposed frequency (or Deborah number) and with strain amplitude are represented on the abscissa and ordinate axes respectively. We demonstrate this approach graphically in Fig. 5 (overleaf) using data for a wormlike micellar fluid (consisting of 100 mM cetylpyridinium chloride in salicylic acid). Each individual curve corresponds to a Lissajous figure at a specified pair of coordinate values $[\omega, \gamma_0]$. Each Lissajous curve can also be analyzed to extract the viscous and elastic stress contributions. The individual Chebyshev contributions to the elastic stress and the viscous stress can also be obtained as described above. These values can then be represented in terms of

contour plots of $e_i(\omega, \gamma_0)$ and $v_i(\omega, \gamma_0)$ if desired.

Strain-Amplitude $\gamma_0 = [0.1, 0.316, 1, 3.16, 10]$

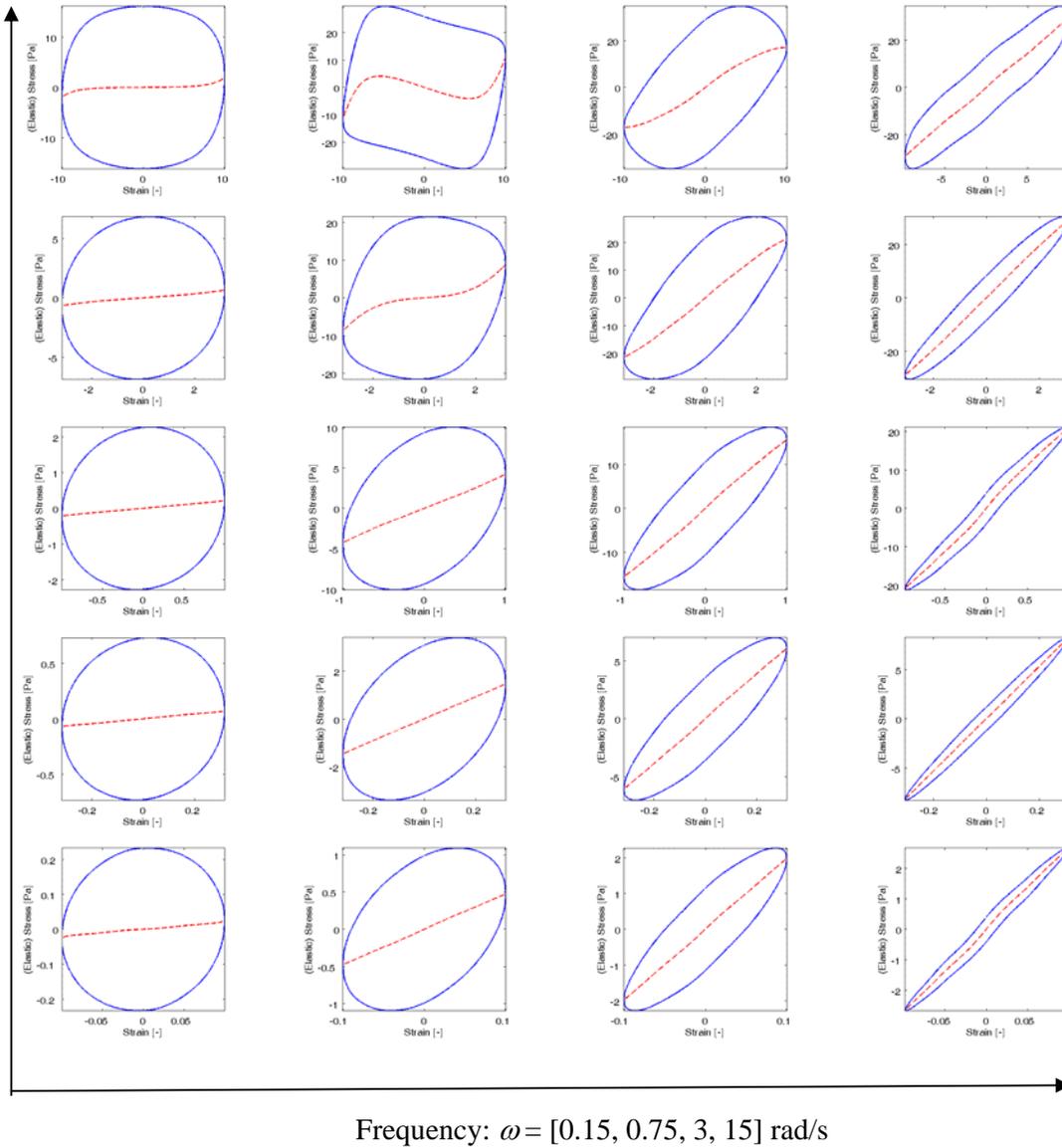


Figure 5. A Pipkin diagram showing the evolution of the material response in LAOS for a wormlike micellar fluid (CPyCl/NaSal) as a function of test frequency and strain amplitude.

The blue lines in Fig. 5 show the total oscillating stress $\tau(t; \omega, \gamma_0)$ and the red broken lines represent the elastic contribution to the stress. The viscous

contribution can of course be found from the difference between these two curves.

The familiar linear viscoelastic response of the system corresponds to small strain

amplitudes ($\gamma < 1$) and in this regime the material trajectories in each Lissajous figure are purely elliptical. As the imposed test frequency increases, the material shows the expected transition from the response of a viscously-dominated fluid (circular trajectory) to an elastically-dominated gel. As the strain amplitude increases the material response becomes more complex and the stress shows both strain-stiffening at moderate strains and also strain-softening characteristics at very high strains. The same information can also be plotted in terms of stress vs. shear rate to reveal the rate-dependence in the material response.

CONCLUSION

We have presented a new framework for systematically decomposing and analyzing the linear and nonlinear material responses of complex fluids and soft solids such as biopolymer gels. This framework considers the stress to be composed of a purely elastic and purely viscous term and then represents each contribution in terms of a series of orthogonal Chebyshev polynomials. This framework is consistent with earlier approaches such as Fourier decomposition, but offers the additional benefit of ascribing a clear physical significance to each Chebyshev coefficient. The resulting material response can be compactly represented by contour plots of the coefficients or by arrays of Lissajous figures in a two-dimensional Pipkin space. Every nonlinear viscoelastic material exhibits a unique response in this Pipkin space, and these images thus represent a distinct *rheological fingerprint* characterizing the material.

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