An Ontology for Large Amplitude Oscillatory Shear Flow

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Abstract. Characterizing purely elastic or purely viscous rheological nonlinearities is straightforward. However, a comprehensive framework does not exist to characterize materials which exhibit both modes of nonlinearity simultaneously. We develop a descriptive language and set of unambiguous material measures for quantifying the nonlinear viscoelastic response of materials subjected to large amplitude oscillatory shear (LAOS) deformation, enabling us to develop a unique “rheological fingerprint” of an a priori unknown substance. We examine two representative soft materials with our framework; the new material measures clearly reveal properties such as local strain-stiffening which are obscured by conventional means. Our technique is universally applicable to any complex material and provides a test bed for new and existing constitutive models.

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Under small amplitude oscillatory shear (SAOS), a material can be characterized by the linear viscoelastic moduli \( G'(\omega), G''(\omega) \). However, these conventional viscoelastic moduli are not uniquely defined once the material response becomes nonlinear at sufficiently large strains [1, 2]. Interpretation of large amplitude oscillatory shear (LAOS) nonlinearities is difficult, and has been hindered because an appropriate and comprehensive framework does not yet exist. The most common method of quantifying LAOS tests is Fourier transform (FT) rheology [3]. For a sinusoidal strain input \( \gamma(t) = \gamma_0 \sin \omega t \), the stress response can be represented completely as a Fourier series of odd harmonics

\[
\sigma(t) = \gamma_0 \sum_{n \text{odd}} \left\{ G'_n(\omega, \gamma_0) \sin n \omega t + G''_n(\omega, \gamma_0) \cos n \omega t \right\}.
\] (1)

A viscous scaling may be obtained by factoring out \( \gamma_0 = \gamma_0 \omega \), giving the coefficients \( \eta'_n = G'_n/\omega \) and \( \eta''_n = G''_n/\omega \).

Although this FT framework is mathematically robust, it suffers from two drawbacks. First, the FT framework lacks a clear physical interpretation of the higher-order coefficients, and second, the use of \( G'_1 \) and \( G''_1 \) (the first harmonic coefficients) as viscoelastic moduli in the nonlinear regime is arbitrary and often fails to capture the rich nonlinearities that appear in the raw data signal [4]. Other methods have been used to quantify viscoelastic nonlinearities [5, 6, 7, 8]; however, these techniques either lack physical interpretation, cannot be calculated uniquely, or do not apply simultaneously to both elastic and viscous phenomena. It is therefore desirable to develop a set of unambiguous parameters and a descriptive language (an ontology) for interpreting nonlinear viscoelasticity in LAOS.

To demonstrate the strengths of our new framework, we apply it to experimental data from a wormlike micellar solution (prepared as in [9]) and a natural biopolymeric hydrogel, gastropod pedal mucus (collected as in [4]). All experiments were performed on a strain-controlled ARES rheometer (TA Instruments) at \( T = 22^\circ \text{C} \) using a solvent trap. The micellar solution was tested with a cone-plate geometry (diameter \( D = 50 \text{ mm} \), angle \( \alpha = 2.3^\circ \)). The mucus was tested with a plate-plate configuration (\( D = 8 \text{ mm} \) and gap \( h = 550 \mu\text{m} \)). To eliminate slip, the plate-plate surfaces were covered with adhesive-backed waterproof sandpaper, 600 grit (ARC Abrasives Inc.).

Rich nonlinear viscoelastic behavior is apparent in the LAOS results from the wormlike micelle solution shown in Fig. 1. The periodic stress response \( \sigma(t; \omega, \gamma_0) \) at steady state is plotted against either \( \gamma(t) \) or \( \dot{\gamma}(t) \), the simultaneous orthogonal inputs. The individual orbits (or Lissajous curves) are arranged in Fig. 1 so that they are centered about the independent coordinates \( \{ \omega, \gamma_0 \} \) to form a Pipkin diagram [10] of the material response. To interpret the data, we extend the method of orthogonal stress decomposition [7], which uses symmetry arguments to decompose the generic nonlinear stress response into a superposition of an elastic stress \( \sigma'(x) \), where \( x = \gamma/\gamma_0 = \sin \omega t \), and viscous stress \( \sigma''(y) \) where \( y = \gamma/\gamma_0 = \cos \omega t \). Thus, in contrast to the closed loops formed by the total stress \( \sigma \) vs. \( \gamma \) or \( \sigma \) vs. \( \dot{\gamma} \) (solid lines in Fig. 1), plotting \( \sigma' \) vs. \( x \) (Fig. 1a dashed lines) or \( \sigma'' \) vs. \( y \) (Fig. 1b dotted lines) produces single-valued functions of strain or strain-rate respectively. The intra-cycle elastic and viscous nonlinearities (i.e. nonlinearities within a given steady state cycle) are therefore related to the nonlinearity of these functional forms. We argue that these curves are best represented by the set of orthogonal Chebyshev polynomials of the first kind. Using this basis
for reporting the viscous or dissipative response: graphically as shown in Fig. 2(i)b by the broken lines. The measures are deliberately chosen such that both converge interpret any initial deviation from linearity, i.e. the order polynomial we define a set of elastic moduli and derive their relation to the Chebyshev and Fourier coefficients, distinctly represent the local elastic response of the system at small and large strains. To capture this local behavior, where the total stress \( \sigma = \sigma' + \sigma'' \), and \( T_n(x) \) are the \( n \)th-order Chebyshev polynomials of the first kind. We refer to \( e_n \) as the elastic Chebyshev coefficients and \( v_n \) as the viscous Chebyshev coefficients.

In the linear regime, Eq. 2 recovers the linear viscoelastic result such that \( e_1 \rightarrow G' \) and \( v_1 \rightarrow \eta' = G''/\omega \). We interpret any initial deviation from linearity, i.e. the \( n = 3 \) harmonic, as follows. A positive contribution of the third-order polynomial \( T_3(x) = 4x^3 - 3x \) results in a higher stress at maximum strain, \( x \rightarrow 1 \), than represented by the first-order contribution alone. Thus, \( e_3 > 0 \) corresponds to \( \text{intra-cycle stress-stiffening} \) of the elastic stress, whereas \( \eta_3 < 0 \) indicates strain-softening. Similarly, a positive value for \( v_3 \) represents \( \text{intra-cycle shear-thickening} \) and \( v_3 < 0 \) describes shear-thinning. These physical interpretations are not apparent in the time-domain (Fourier coefficients) but become immediately apparent from the sign of the Chebyshev coefficients.

Our deliberate use of Chebyshev polynomials allows the coefficients \( e_n \) and \( v_n \) (Eq. 2) to be calculated from the familiar Fourier coefficients (Eq. 1). Using the identity \( T_n(\cos \theta) = \cos(n \theta) \) gives \( e_n = G_n(-1)^{(n-1)/2} / \omega = \eta_n' \) (for \( n \) odd). When applied to the micelle data of Fig. 1, the Chebyshev coefficients offer physical insight to the \( \text{intra-cycle stress-stiffening} \) in the elastic response (\( e_3 > 0 \)) combined with \( \text{intra-cycle shear-thickening} \) in the viscous response (\( v_3 < 0 \)). This demonstrates a physically meaningful interpretation of higher-order coefficients.

We now address the issue of reporting first-order (linear) viscoelastic moduli in the \( \text{nonlinear} \) regime. The first-harmonic FT coefficients are an arbitrary choice, and we define alternative, physically meaningful measures of first-order moduli. The nonlinear behavior of the physically cross-linked mucus gel is used as an example. The “elastic modulus” of the gel, as reported by a rheometer (i.e. the first harmonic elastic modulus, \( G_1' \)), decreases slightly with strain amplitude (Fig. 2(ii)a), implying minor strain-softening. However, the raw data in the form of elastic Lissajous curves (Fig. 2(ii)b) reveals a strong nonlinear response evocative of strain-stiffening. This paradoxical behavior is not unique to pedal mucus but appears to be common in soft biological materials.

We resolve this apparent contradiction by first recognizing that \( G_1' \) represents a sine transform, \( G_1' = \omega / (\pi G_0') \int \sigma(t) \gamma(t) dt \), which is a measure of the average elasticity in the material response, and is unable to distinctly represent the local elastic response of the system at small and large strains. To capture this local behavior, we define a set of elastic moduli and derive their relation to the Chebyshev and Fourier coefficients,

\[
G_1' = \left. \frac{d \sigma}{d \gamma} \right|_{\gamma=0} = \sum_{n \text{ odd}} n G_n e_1 = e_1 - 3e_3 + ... \]  \quad \text{and} \quad G_L' = \left. \frac{\sigma}{\gamma} \right|_{\gamma=0} = \sum_{n \text{ odd}} G_n (-1)^{(n-1)/2} = e_1 + e_3 + ... \]  

where \( G_1' \) is the \( \text{minimum-strain modulus} \) and \( G_L' \) is the \( \text{large-strain modulus} \). These measures can be visualized graphically as shown in Fig. 2(ii)b by the broken lines. The measures are deliberately chosen such that both converge to the linear elastic modulus \( G' \) in the limit of small strains (\( e_3/e_1 \ll 1 \)). We also define a set of dynamic viscosities for reporting the viscous or dissipative response: \( \eta_1' = \left. \frac{d \sigma}{d \gamma} \right|_{\gamma=0} = v_1 - 3v_3 + ... \), and \( \eta_L' = \left. \frac{\sigma}{\gamma} \right|_{\gamma=0} = v_1 + v_3 + ... \)
FIGURE 2. Oscillatory strain sweep of pedal mucus from *Limax maximus* at a frequency $\omega = 3$ rad s$^{-1}$. (i) Conventional data output from a rheometer (a) Fluid viscoelasticity as parameterized by the first-harmonic Fourier moduli. (b) Plotting the raw data from every-other point as $\sigma(t)$ vs. $\gamma(t)$, with graphical representation of the new measures $G'_M, G'_L$ for $\gamma_0 = 2.8$. (ii) Analysis of material response using the new LAOS framework: (a) Elastic moduli (b) Dynamic viscosities (c) Elastic nonlinearity measures indicate *intra*-cycle strain-stiffening (d) Viscous nonlinearity measures indicate *intra*-cycle shear-thinning.

The *intra*-cycle nonlinearities which distort the familiar linear viscoelastic ellipse can also be quantified by comparing these local moduli. Here we define the strain-stiffening ratio as $S \equiv (G'_L - G'_M)/G'_L$ where $S = 0$ for a linear elastic response, $S > 0$ indicates *intra*-cycle strain-stiffening, and $S < 0$ corresponds to *intra*-cycle strain-softening. We similarly define the shear-thickening ratio as $T \equiv (\eta'_L - \eta'_M)/\eta'_L$ where $T = 0$ indicates a single harmonic linear viscous response, $T > 0$ represents *intra*-cycle shear-thickening, and $T < 0$ *intra*-cycle shear-thinning.

The *inter*-cycle variation of these new measures (i.e. the dependence on imposed strain $\gamma_0$) is reported in Fig. 2(ii). Here $G'_M$ decreases with $\gamma_0$, whereas $G'_L$ first decreases then increases, i.e. the large-strain elasticity of the network softens then stiffens (see Fig. 2(ii)a). This rich behavior is revealed and physically described only by the use of the present framework. The *intra*-cycle nonlinearities of the pedal mucus gel are quantified in Fig. 2(ii)c,d. Both $S$ and $\epsilon_3$ are positive at the largest strain amplitudes, indicating strain-stiffening, while the nonlinear viscous measures $T$ and $\nu_3$ are both negative at large strain amplitudes, indicating *intra*-cycle shear-thinning. The true rheological behavior of this nonlinear viscoelastic biopolymer gel could only be fully ascertained by using the present decomposition scheme.

This framework serves as a complement to the familiar and successful linear viscoelastic framework embodied in $G'(\omega)$ and $G''(\omega)$, and is robustly applicable to any complex material or constitutive model which can be tested in oscillatory shear.$^\dagger$ These new measures will provide a more rigorous test of constitutive models, and serve as a sensitive probe for comparing the true nonlinear rheological properties of different materials.

REFERENCES


$^\dagger$ Software to analyze raw measurement of $\{\gamma(t), \sigma(t)\}$ is available from the authors or from [http://web.mit.edu/nnf/](http://web.mit.edu/nnf/)