**Rheological Fingerprinting of Complex Fluids and Soft Solids**

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Large amplitude oscillatory shear (LAOS) is used increasingly as a tool to measure the nonlinear viscoelastic responses of soft solids and complex fluids. For many material systems the common practice of reporting only “viscoelastic moduli” as calculated by commercial rheometers (typically corresponding to the first harmonic Fourier coefficients ) is insufficient and/or misleading in describing the nonlinear phenomena. The mathematical structure of the nonlinear response is fully captured by the higher Fourier harmonics, but these coefficients lack a clear physical interpretation. We describe a framework for quantifying and physically interpreting deviations from linearity that considers the 2D space of frequency and strain-amplitude first discussed by Pipkin to generate a unique ‘rheological fingerprint’ of a viscoelastic material.

We build on the earlier geometrical interpretation of Cho et al. [1] that decomposes a nonlinear stress response into elastic and viscous stress contributions using symmetry arguments. We then use Chebyshev polynomials as orthonormal basis functions to further decompose these stresses into harmonic components having physical interpretations. This framework naturally generates alternative measures of viscoelastic moduli, all of which reduce to G' & G" in the linear regime, but offer different physical insight into the distinctive nonlinear response of a material [2]. LAOS fingerprinting is invaluable for both characterizing and describing the nonlinear rheological response of a wide range of materials including biopolymer gels, regenerative polymer networks, entangled melts and micellar solutions. Illustrative examples drawn from the recent literature will be used to demonstrate the range of studies that are possible.

 The great majority of work to date has focused on the use of strain and strain rate as the orthogonal input variables (and might thus be more completely termed *LAOStrain*), in conjunction with an additive decomposition of the stress into viscous and elastic components. However for many rheologically-complex materials – especially those with a critical stress or with yield-like characteristics – imposing a large amplitude oscillatory stress is both easier experimentally and more instructive [3]. We therefore outline an ontology for imposing *LAOStress* protocols that decomposes the rheometer output into an elastic strain and a viscoplastic strain rate and provides quantitative elasto-visco-plastic material parameters. Finally we use this framework to investigate the nonlinear properties of a representative gel-like system and determine its characteristic rheological fingerprint.

1. Cho, K.S., K.H. Ahn, and S.J. Lee, A Geometrical interpretation of Large Amplitude Oscillatory Shear Response*.* *J. Rheol.*, 2005. **49**(3): p. 747-758.

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

3. Läuger, J. and H. Stettin, Differences between Stress and Strain-Control in the Nonlinear Behavior of Complex Fluids*.* *Rheol. Acta*, 2010. **49**: p. 909-930.