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Cover letter

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June 30 , 2018

Dear Dr. Upponi,

Please find enclosed a manuscript entitled, “Measuring and understanding large amplitude oscillatory shear: A case study of concentrated polymeric systems” authored by Johnny Ching-Wei Lee, Jun Dong Park, and myself, which I submit to you for publication in the Journal of Visualized Experiments.

The paper contains original research on how to perform large amplitude oscillatory shear (LAOS) measurements using a TwinDrive MCR 702 rheometer from Anton Paar. Using this experimental equipment and procedure, we identify the sequence of processes undergone by two industrially and environmentally important concentrated polymer suspensions using a freely-available MATLAB-based software package based on the newly-published SPP framework. We describe in depth the instrument setup, the experimental procedure, and using the analysis software. We demonstrate a clear link between the results of the LAOS experiments and results obtained from other traditional rheological measurements, providing a generic approach to understanding the nonlinear rheology of concentrated polymer suspensions that can be applied by other researchers investigating other systems, which we think makes it a good fit for the Journal of Visualized Experiments.

I anticipate that this research will be of interest to the Journal of Visualized Experiments viewership as a collective, but more specifically to researchers interested in polymeric suspensions and transient nonlinear rheology.

I look forward to hearing from you regarding the publication of this manuscript.

Simon Rogers

TITLE:

Studying Large Amplitude Oscillatory Shear Response of Soft Materials

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KEYWORDS:
Rheology, LAOS, soft matter, viscoelastic, viscoplastic

SUMMARY:
We present a detailed protocol outlining how to perform nonlinear oscillatory shear rheology on soft materials, and how to run the SPP-LAOS analysis to understand the responses as a sequence of physical processes.

ABSTRACT:
We investigate the sequence of physical processes exhibited during large amplitude oscillatory shearing (LAOS) of polyethylene oxide (PEO) in dimethyl sulfoxide (DMSO) and xanthan gum in water — two concentrated polymer solutions used as viscosifiers in foods, enhanced oil recovery, and soil remediation. Understanding the nonlinear rheological behavior of soft materials is important in the design and controlled manufacturing of many consumer products. It is shown how the response to LAOS of these polymer solutions can be interpreted in terms of a clear transition from linear viscoelasticity to viscoplastic deformation and back again during a period. The LAOS results are analyzed *via* the fully quantitative Sequence of Physical Processes (SPP) technique, using free MATLAB-based software. A detailed protocol of performing a LAOS measurement with a commercial rheometer, analyzing nonlinear stress responses with the freeware, and interpreting physical processes under LAOS is presented. It is further shown that, within the SPP framework, a LAOS response contains information regarding the linear viscoelasticity, the transient flow curves, and the critical strain responsible for the onset of nonlinearity.

INTRODUCTION:

Concentrated polymeric solutions are used in a variety of industrial applications primarily to increase viscosity, including in foods[1] and other consumer products[2], enhanced oil recovery[3], and soil remediation[4]. During their processing and use, they are necessarily subjected to large deformations over a range of timescales. Under such processes, they demonstrate rich and complex nonlinear rheological behaviors that depend on the flow or deformation conditions[1]. Understanding these complex nonlinear rheological behaviors is essential for successfully controlling processes, designing superior products, and maximizing energy efficiency. Aside from the industrial importance, there is a great deal of academic interest in understanding the rheological behaviors of polymeric materials far from equilibrium.

Oscillatory shear tests are a staple component of every thorough rheological characterization because of the orthogonal application of strain and strain rate[5], and the ability to independently control the length and time scales probed by tuning the amplitude and frequency. The stress response to small amplitude oscillatory shear strains, which are small enough not to disturb a material's internal structure, can be decomposed into components in phase with the strain and in phase with strain rate. The coefficients of the components in phase with the strain and the strain rate are collectively referred to as the dynamic moduli[6,7], and individually as the storage modulus, G', and loss modulus, G''. The dynamic moduli lead to clear elastic and viscous interpretations. However, interpretations based on these dynamic moduli are valid only for small strain amplitudes, where the stress responses to sinusoidal excitations are also sinusoidal. This regime is generally referred to as the small amplitude oscillatory shear (SAOS), or the linear viscoelastic regime. As the imposed deformation becomes larger, changes are induced in the material microstructure, which are reflected in the complexity of the non-sinusoidal transient stress responses[8]. In this rheologically nonlinear regime, which more closely mimics industrial processing and consumer usage conditions, the dynamic moduli act as poor descriptions of the response. Another way to understand how concentrated soft materials behave out of equilibrium is therefore required.

A number of recent studies[9-16] have shown that materials pass through diverse intra-cycle structural and dynamical changes elicited by larger deformations in the medium amplitude oscillatory shear (MAOS)[15,17] and large amplitude oscillatory shear (LAOS) regimes. The intra-cycle structural and dynamical changes have different manifestations, such as breakage of microstructure, structural anisotropy, local rearrangements, reformation, and changes in diffusivity. These intra-cycle physical changes in the nonlinear regime lead to the complex nonlinear stress responses that cannot be simply interpreted with the dynamic moduli. As an alternative, several approaches have been suggested for the interpretation of the nonlinear stress responses. Common examples of this are Fourier transform rheology (FT rheology)[18], power series expansions[11], the Chebyshev description[19], and the sequence of physical processes (SPP)[5,8,13,14,20] analysis. Although all of these techniques have been shown to be mathematically robust, it is still an unanswered question as to whether any of these techniques can provide clear and reasonable physical explanations of nonlinear oscillatory stress responses. It remains an outstanding challenge to provide concise interpretations of rheological data that correlate to structural and dynamical measures.

In a recent study, the nonlinear stress response of the Soft Glassy Rheology (SGR) model[8] and a soft glass made of colloidal star polymers[7] under oscillatory shear was analyzed through the SPP scheme. Temporal changes in the elastic and viscous properties inherent in nonlinear stress responses were separately quantified by the SPP moduli, $G_t'(t)$ and $G_t''(t)$. Furthermore, the rheological transition represented by the transient moduli was accurately correlated to microstructural changes represented by the distribution of mesoscopic elements. In the study of the SGR model[8], it was clearly shown that rheological interpretation *via* the SPP scheme accurately reflects the physical changes under all oscillatory shear conditions in the linear and nonlinear regimes for soft glasses. This unique capability to provide accurate physical interpretation of nonlinear responses of soft glasses makes the SPP method an attractive approach for researchers studying out-of-equilibrium dynamics of polymer solutions and other soft materials.

The SPP scheme is built around viewing rheological behaviors as occurring in a three-dimensional space ($\mathbb{R}^3$) that consists of the strain (γ), strain rate ($\dot{\gamma}$), and stress (σ)[5]. In a mathematical sense, the stress responses are treated as multivariable functions of the strain and strain rate ($\sigma = f(\gamma, \dot{\gamma})$). As the rheological behavior is regarded as a trajectory in $\mathbb{R}^3$ (or a multivariable function), a tool for discussing the properties of a trajectory is required. In the SPP approach, the transient moduli $G_t'(t)$ and $G_t''(t)$ play such a role. The transient elastic modulus $G_t'(t)$ and viscous modulus $G_t''(t)$ are defined as partial derivatives of the stress with respect to the strain ($\frac{\partial \sigma}{\partial \gamma}$) and the strain rate ($\frac{\partial \sigma}{\partial \dot{\gamma}}$). Following the physical definition of differential elastic and viscous moduli, the transient moduli quantify the instantaneous influence of strain and strain rate on the stress response respectively, whereas other analysis methods cannot provide any information on elastic and viscous properties separately.

The SPP approach enriches the interpretation of the oscillatory shear tests. With the SPP analysis, the complex nonlinear rheological behaviors of concentrated polymeric solutions in LAOS can be directly related to the linear rheological behaviors in SAOS. We show in this work how the maximum transient elastic modulus ($G_t'_{\text{max}}$) near the strain extrema corresponds to the storage modulus in the linear regime (SAOS). Furthermore, we show how the transient viscous modulus ($G_t''(t)$) during a LAOS cycle traces the steady state flow curve. In addition to providing details of the complex sequence of processes that concentrated polymer solutions go through under LAOS, the SPP scheme also provides information regarding the recoverable strain in the material. This information, which is not obtainable through other approaches, is a useful measure of how much a material will recoil once stress is removed. Such behavior has impact on the printability of concentrated solutions for 3D printing applications, as well as screen printing, fiber formation, and flow cessation. A number of recent studies[5,8,13] clearly indicate that the recoverable strain is not necessarily the same as the strain imposed during LAOS experiments. For instance, a study of soft colloidal glasses under LAOS[13] found that the recoverable strain is only 5% when significantly larger total strain (420%) is imposed. Other studies[16,21-24] using the cage modulus[21] also conclude that linear elasticity can be observed under LAOS at the point close to the strain maxima, implying that the materials experienced relatively small deformation at those instants.

The SPP scheme is the only framework for understanding LAOS that accounts for a shift in the strain equilibrium that leads to a difference between the recoverable and the total strains.

This article aims to facilitate understandings and ease of use of the SPP analysis method by providing a detailed protocol for a LAOS analysis freeware, using two concentrated polymer solutions, a 4 wt% xanthan gum (XG) aqueous solution and a 5 wt% PEO in DMSO solution. These systems are chosen because of their broad range of application and rheologically interesting properties. Xanthan gum, a natural high-molecular-weight polysaccharide, is an exceptionally effective stabilizer for aqueous systems and commonly applied as a food additive to provide desired viscosification or in oil drilling to increase viscosity and yield points of drilling muds. PEO has a unique hydrophilic property and is often used in pharmaceutical products and controlled release systems as well as soil remediation activities. These polymeric systems are tested under various oscillatory shear conditions that are intended to approximate processing, transport, and end-use conditions. Although these practical conditions may not necessarily involve flow reversal as in oscillatory shear, the flow field can be easily approximated and tuned with the independent control of applied amplitude and imposed frequency in an oscillatory test. Furthermore, the SPP scheme can be used as described here to understand a broad range of flow types, including those that do not include flow reversals such as the recently-proposed UD-LAOS[25], in which large amplitude oscillations are applied in one direction only (leading to the moniker "uni-directional LAOS"). For simplicity, and for illustrative purposes, we restrict the current study to traditional LAOS, which does include periodic flow reversal. The measured rheological responses are analyzed with the SPP approach. We demonstrate how to use the SPP software with simple explanations on salient calculation steps to improve readers' understanding and usage. A legend for interpreting the SPP analysis results is introduced, according to which the type of rheological transition is identified. Representative SPP analysis results of the two polymers under various oscillatory shear conditions are displayed, in which we clearly identify a sequence of physical processes that contains information on the material's linear viscoelastic response as well as the steady-state flow properties of the material.

This protocol provides salient details of how to accurately perform nonlinear rheological experiments, as well as a step-by-step guide to analyzing and understanding rheological responses with the SPP framework, as shown in **Figure 1**. We begin by providing an introduction to the instrument setup and calibrations, followed by specific commands for making a commercially-available rheometer collect high-quality transient data. Once the rheological data have been obtained, we introduce the SPP analysis freeware, with a detailed manual. Further, we discuss how to understand the time-dependent response of the two concentrated polymer solutions within the SPP scheme, by comparing the results obtained from LAOS with the linear-regime frequency sweep and the steady-state flow curve. These results clearly identify that the polymer solutions transition between distinct rheological states within an oscillation, allowing for a more detailed picture of their nonlinear transient rheology to emerge. These data can be used to optimize processing conditions for product formation, transport, and use. These time-dependent responses further provide potential pathways to clearly form structure-property-processing relationships by coupling the rheology with microstructural information obtained

from small-angle scattering of neutrons, X-rays, or light (SANS, SAXS, and SALS, respectively), microscopy, or detailed simulations.

PROTOCOL:

1. Rheometer Setup

1.1. With the rheometer configured in the SMT mode (see note), attach the upper and lower drive geometries. To maintain as close to a homogeneous shear field as possible, use a 50 mm plate (PP50) as the lower fixture, and a 2-degree cone (CP50-2) for the upper fixture.

Note: The rheometer we use (see the **Table of Materials**) can be configured in either a combined motor-transducer (CMT) or separate motor transducer (SMT) mode. With only a single motor integrated in the rheometer head, it acts as a traditional CMT stress-controlled rheometer and the data obtained require inertia corrections. With two motors incorporated in a SMT mode, the upper motor operates solely as a torque transducer and the bottom motor acts as a drive unit thus converting the rheometer into a typical strain-controlled rheometer.

1.1.1. Attach the bottom and top geometries.

1.1.2. Click the **zero-gap** button in the control panel.

1.1.3. Navigate to **start service function** under the **Measuring set** tab on top. Run the inertia calibrations for the upper and lower measuring systems, found in the dropdown menu.

1.1.4. Run adjustments for the upper and lower motors.

1.1.5. Specify the desired temperature in the **control panel**.

Note: The measurements at which experiments on XG and PEO solutions are performed are 25 ± 0.1 °C and 35 ± 0.1 °C, respectively.

1.2. Load the material of interest on top of the bottom geometry with a spatula or pipette, ensuring no air bubbles are entrained in the sample.

Note: Approximate volumes of material required to completely fill a geometry are provided in the rheometry software under **Setup** | **Measuring Systems**.

1.2.1. Load 1.14 mL to fill the cone-and-plate geometry. Load higher viscosity samples with a spatula, and less viscous materials with a pipette.

Note: A spatula is used to load the polymer solutions.

1.2.2. Command the measuring system to **trim gap** and gently trim the excess material at the edge of geometry with a square-ended spatula, ensuring the spatula remains perpendicular to the axis of the rheometer.

Note: The quality of material loading will affect the rheological results significantly and any apparent under- or over-filling should be avoided.

1.2.3. Press the **continue** button in the rheometry software to move to the **measurement gap**.
Note: A complete loading process is illustrated in **Figure 2**.

2. Running Oscillatory Shear Tests

Note: Two ways of running oscillatory shear tests are introduced. The first approach is designed for sinusoidal stresses and strains only and was used to collect the data we report here. The second method allows for arbitrary stress or strain schedules to be set.

2.1. Sinusoidal oscillatory shear

2.1.1. Navigate to **Large amplitude oscillatory shear-LAOS** under **My apps** in the software. Go to the **Measurement** box and click **strain** variable.

2.1.3. Specify the initial (1%) and final values (4000%) of a strain amplitude sweep. Specify the imposed frequency of 0.316 rad/s. Define the desired total number of strain amplitudes as 16 in the specified amplitude range, which results in the point density of 5 points per decade.

2.1.6. Check the **Get waveform** box at the top to collect transient responses.

2.1.7. Click the **start** button at the top to start the experiments and the raw data will be displayed in the rheometry software automatically.

2.2. Arbitrary Stress or Strain Schedules

2.2.1. To impose arbitrary-defined deformation, click **Waveform sine generator** under **My apps** in the software.

2.2.2. Define a list of strain values that correspond to the function that is to be applied (not restricted to sinusoidal waveform). Generate the value list in an external program.

2.2.3. Click **edit** under the strain value in the measurement box. Copy and paste these numbers into the **value list**.

2.2.5. Specify the number of data points, point duration, and interval time to adjust the imposed frequency. For instance, specify the number of data points and the interval time as 512 points

and 6.2832 s, respectively, if a cycle of sinusoidal strain is pasted into strain value list with 512 points and the frequency of 1 rad/s is desired.

Note: This approach is not recommended for running sinusoidal oscillatory shear due to the limited number of oscillatory cycles, and also due to the fact that automatic corrections which are enabled in an oscillatory test mode on the rheometer are disabled in this mode. Nonetheless, because there are no assumptions of sinusoidal strain built into the SPP framework, one can arbitrarily define imposed strain functions according to the processing conditions or end use the materials may experience, and the SPP framework remains applicable to analyze the rheological response.

2.2.6. Check the **Get waveform** box at the top. Then click the **start** button at the top to start the experiments.

3. Performing SPP analysis (SPP-LAOS software)

Note: The SPP analysis software is a MATLAB-based freeware package for analyzing rheological data with the SPP framework and is attached as **Supplementary Files 1–6**[21].

3.1. Format the data files to be tab-delimited text (.txt) consisting of four columns in the order of {Time (s), Strain (-), Rate (1/s), Stress (Pa)}.

Note: Users may need to modify the number of header lines in the function files to be able to process their data. See sample data files (**Supplementary Files 7–9**).

3.2. To run SPP-LAOS software, open the m-file named **RunSPPplus_v1.m** in MATLAB.

Note: While RunSPPplus_v1.m is the main script to run the analysis, the package contains other function files that will be called from the main script, including SPPplus_read_v1.m, SPPplus_fourier_v1.m, SPPplus_numerical_v1.m, SPPplus_print_v1.m and SPPplus_figure_v1.m.

3.3. Navigate to the section labeled **User-defined variables**, and specify the following variables.

3.3.1. Filename: Specify the name of .txt file that will be used for the SPP analysis.

Note: The file must match the above format requirement.

3.3.2. Run state: Place the vector as [1, 0] to run Fourier analysis mode for regular oscillatory shear response.

Note: The software employs two different methods of calculating the instantaneous SPP moduli, $G_t'(t)$ and $G_t''(t)$, based on Fourier transformation and numerical differentiation. The Fourier transform approach is designed for periodic input, such as oscillatory shear tests. Arbitrary time-

dependent tests, which include, but are not limited to sinusoidal protocols, can be analyzed with the numerical differentiation approach.

3.3.3. Run state: Input the vector as [0, 1] to run numerical-differentiation analysis mode for arbitrary time-dependent tests.

3.3.4. Omega (Fourier analysis): Specify the angular frequency of oscillation, with units of rad/s.

3.3.5. M (Fourier analysis): Define number of higher harmonics to be included in the SPP analysis. Adjust this number to include all the higher harmonics above the noise floor.

Note: This number must be a positive odd number and varies with amplitude and material. We include up to the 3rd harmonic in the MAOS regime, and up to the 55th harmonic at the largest amplitude investigated.

3.3.6. p (Fourier analysis): Specify the total number of periods of measuring time in the input data, which has to be a positive integer.

Note: The more periods of data that are collected, the higher the time resolution of the SPP parameters.

3.3.7. k (numerical differentiation): Define the step size for the numerical differentiation, which has to be a positive integer.

3.3.8. num_mode (numerical differentiation): Specify **num_mode** to be either “0” (standard differentiation) or “1” (looped differentiation).

Note: There are two procedures implemented in the numerical differentiation scheme. The “standard differentiation” makes no assumptions about the form of the data. It utilizes a forward difference to calculate the derivative for the first 2,000 points of the data, a backward difference for the final 2,000 points, and a centered difference elsewhere. The “looped differentiation” assumes that the data is taken under steady-state periodic conditions, and includes an integer number of periods. These assumptions allow a centered difference to be calculated everywhere by looping over the ends of the data.

3.3.9. Select the **run** button at the top once all the variables are specified.

Note: The software will compute all SPP metrics associated with the data, and then display figures associated with the current analysis run and output a text file containing all the calculated SPP metrics for further analysis.

3.3.10. Iteratively adjust the number of harmonics to be included in the analysis from the output Fourier spectrum. Include all higher odd harmonics above the noise floor.

4. Interpreting a LAOS Response

4.1. Navigate to the Cole-Cole plot of the instantaneous SPP moduli $G_t'(t)$ and $G_t''(t)$ that is automatically generated by the SPP software.

Note: A curve in the Cole-Cole plot is considered as the trajectory of the viscoelastic material state, and interpretations can be formed within an oscillation, in intra-cycle processes, or between successive periods, in inter-cycle processes.

4.2. Interpret stiffness by the instantaneous elastic modulus, $G_t'(t)$, and an increase/decrease of $G_t'(t)$ that indicates stiffening/softening. See **Figure 3**.

4.3. Interpret a material's viscosity based on the instantaneous viscous modulus, $G_t''(t)$. An increase/decrease in this parameter represents thickening/thinning.

4.4. Transfer the focus to another Cole-Cole plot of the time derivatives of transient moduli $\dot{G}_t'(t)$ and $\dot{G}_t''(t)$, which provide quantitative information about how much a response is stiffening ($\dot{G}_t'(t) > 0$), softening ($\dot{G}_t'(t) < 0$), thickening ($\dot{G}_t''(t) > 0$), thinning (($\dot{G}_t''(t) < 0$)). See **Figure 3**.

Note: With the values of the derivatives, the rate at which materials undergo stiffening/softening or thickening/thinning can be quantitatively determined.

4.5. Read the center of a trajectory (in a time-weighted average sense) in the Cole-Cole plot of $[G_t'(t)\ G_t''(t)]$ as the dynamic moduli, $[G'\ G'']$.

Note: The dynamic moduli are **averaged** parameters over a cycle of deformation, and are insufficient to provide local information under LAOS.

4.6. Track the relative motion of the trajectory across amplitudes to understand the inter-cycle physics.

Note: Focusing on the relative motion of time-weighted average center is equivalent to a traditional strain amplitude sweep of the dynamic moduli. Nonetheless, one can easily analyze the across-amplitude motion of other specific points, for instance, the strain extrema.

4.7. Determine the transient differential viscosity $G_t''(t)/\omega$ and overlay it on top of a steady-shear flow curve. Compare the transient LAOS response with steady-shear conditions.

4.8. Determine the points of maximum G_t' at the large amplitudes in the Cole-Cole plot of $[G_t'(t)\ G_t''(t)]$. See the star labeled in **Figure 4c**.

4.8.1. Record the values of G_t' and G_t'' at those instants.

4.8.2. Plot them on top of the amplitude sweep of the dynamic moduli. See **Figure 4d**.

Note: Pay attention to any correspondence between the maximum transient elastic modulus and the linear viscoelastic G'.

4.9. Locate the instants of maximum ${G_t}'$ in the elastic Lissajous figure and record the corresponding strain values. See the star labeled in **Figure 4a**.

4.10. If ${G_t}'(t) \gg {G_t}''(t)(t)$, then determine the equilibrium strain $\gamma_{eq}(t)$ and the elastic strain $\gamma_{el}(t) = \gamma(t) - \gamma_{eq}(t) = \sigma(t)/{G_t}'(t)$.

Note. With the displacement stress $\sigma^d \equiv \sigma(t) - {G_t}'\gamma(t) - {G_t}''(t)\,\dot{\gamma}(t)/\omega$, when ${G_t}'(t) \gg {G_t}''(t)$ the equilibrium strain can be determined as $\gamma_{eq}(t) = -\sigma^d(t)/{G_t}'(t)$ and the elastic strain can therefore be determined as the difference between strain and equilibrium strain[5,13]. The requirement of ${G_t}'(t) \gg {G_t}''(t)(t)$ is derived and discussed elsewhere[15].

4.11. Plot the elastic strain as a function of the imposed strain amplitude. See **Figure 4e**. If the elastic strain is independent of the strain amplitude, then indicate this critical strain on the amplitude sweep as in **Figure 4d**.

REPRESENTATIVE RESULTS:

Representative results of the SPP analysis from XG and PEO/DMSO solutions under oscillatory shear tests are presented in **Figures 4** and **5**. We first present the raw data as elastic ($\sigma - \gamma$) and viscous ($\sigma - \dot{\gamma}$) Lissajous-Bowditch curves in **Figures 4a**, **4b**, **5a** and **5b**. To fully understand the intra-cycle physics, the time-dependent Cole-Cole plots obtained from the SPP freeware are presented in **Figures 4c** and **5c**. Interpretations of the plots are discussed in the manner laid out by the legend in **Figure 3** and protocol steps 4.2–4.7, where the relative motion of the trace quantitatively indicates whether the material undergoes stiffening/softening or thickening/thinning in an intra-cycle sense. The time-weighted centers of these trajectories, which represent the average elastic and viscous moduli, correspond to the dynamic moduli, $G'$and G'', shown in **Figure 4d** and **5d**. In the case of large deformations, average parameters are insufficient to describe the material response at any particular instant. Forming a bridge between rheological data and microstructural evolutions has proved a difficult task. Microstructural information obtained from either scattering[9,26] or simulation[12] is often time-resolved and requires a rheological study that matches the temporal resolution. A more complete discussion of the linking the macroscopic SPP analysis and microstructural details can be found in a recent study of soft glassy materials[8].

Using the SPP scheme, we are also able to determine the elastic recoverable strain at moments when the material response is predominantly elastic. In particular, the gel-like structure of XG responds in ways that are reminiscent of soft glassy materials, where the responses go through instants of linear-regime viscoelasticity across the large amplitudes as shown in **Figure 4d**.

Indeed, we identify the instantaneous SPP elastic modulus at large amplitudes in the XG solution that is more than three orders of magnitude larger than the traditional storage modulus, showing the clear benefit of the local measures. Similar results have been observed in studies of soft colloidal glasses[16,21-24], where the points of linear-like elasticity also take place at positions near the strain extrema. This indicates that the material equilibrium is well separated from the place where the experiment started, at zero strain. With the SPP analysis, it is shown in **Figure 4e** that the elastic recoverable strain at the point of maximum elasticity remains nearly constant at 16%, even when the applied strain is as large as 4000%. This constant recoverable strain of approximately 16% corresponds to the critical strain amplitude, γ_c, above which nonlinear behavior is observed in the strain amplitude sweep of **Figure 4d**.

In the case of the PEO solution, the maximum transient elastic modulus across different amplitudes is shown in **Figure 5d**. We identify, using the SPP approach, an increasing stiffness as the amplitude increases, while the storage modulus shows only softening. At the largest amplitudes probed, we identify an instantaneous modulus that is more than an order of magnitude larger than the traditionally-defined storage modulus. The magnitudes of the transient elastic and viscous moduli are comparable at the instants of largest elasticity, meaning that the condition for the SPP to correctly identify the elastic strain is not met.

The major advantage of the quantitative SPP scheme is that elastic and viscous properties can be clearly determined at each point in the cycle. In the previous section, it was established that at instants close to the strain extrema, the XG solution responds as if it is in its linear viscoelastic limit while the PEO solution displays a modulus that is marginally larger than that exhibited in the linear regime. We now turn our attention to the next major component in the sequence of physical processes exhibited by both polymer solutions, the flow condition.

The transient differential viscosity, defined as the transient viscous modulus divided by the frequency, $G_t''(t)/\omega$, is displayed in **Figure 6** on top of the steady-shear flow viscosity, determined from independent steady-shear tests. A similar response is observed from both materials, where the transient differential viscosities initially remain constant at low shear rates, followed by an overshoot, before decreasing rapidly. The transient differential viscosities of both solutions change with shear rate approximately the same as the steady-shear flow viscosity, albeit with transient differential viscosities that are slightly below the steady-state conditions. The steady-shear flow response can be viewed as a LAOS experiment in the limit of zero frequency; nonetheless, with the SPP analysis scheme, the transient flow behaviors at any arbitrary imposed frequency can be quantitatively constructed.

The distinct sequence of physical processes exhibited by XG at a strain amplitude of 4000% is displayed in **Figure 7**, where the symbols split the Lissajous-Bowditch curve into different processes of interest. We begin in the region labelled as region #1, which we identify as being viscoplastic in nature. In this interval of the response, the SPP analysis scheme shows nearly zero elasticity, as determined by $G_t'(t)$, which indicates no strain-dependence to the stress. As the shear rate begins to decrease close to the strain extremum, the XG solution stiffens, indicating that the structure responsible for the linear viscoelastic response begins to reform. We term this

'restructuring'. The elastic recoverable strain at this point, at around 16%, is much smaller than the total deformation, which is consistent with the linear-regime viscoelasticity of these gel-like and other glassy systems. A rapid transition from elastic to viscous behaviors, reminiscent of yielding or destructuring, takes place once sufficient strain is acquired from reversal, and is followed by a stress overshoot, during which there is a sharp change in the transient moduli. During the portion of the overshoot when the stress is decreasing, the instantaneous viscous modulus, $G_t''(t)$ is momentarily negative, reflecting the decreasing stress with increasing shear rate. Portions of negative $G_t''(t)$ are therefore not observed in the PEO solutions because of their lack of any overshoot. Lastly, the system goes back to the viscoplastic deformation regime and experiences the distinct intra-cycle sequence twice over a cycle of oscillation.

FIGURE AND TABLE LEGENDS:

Figure 1. A schematic to illustrate a complete process of performing, analyzing and understanding rheological experiments.

Figure 2. **Detailed procedure of loading materials**. (**a**) Attach the lower (PP50) and upper (CP50-2) geometries followed by setting the zero-gap position. (**b**) Load the material onto the center of the lower plate with a pipette or spatula while avoiding bubbles. (**c**) Command the upper geometry to trim gap. Slight overfilling is expected in this step unless pipetting with precise volume. Underfilling should be prevented. (**d**) Gently trim the overfill at the edge of geometries with a square-ended spatula. (**e**) Continue to the measurement gap only when the loading and trimming are good, such that no underfilling is observed around the perimeter of the geometry, and the edges show no distinct fractures.

Figure 3. **Trajectories in time-dependent Cole-Cole plots can be interpreted through these legends**. (**a**) Cole-Cole plot in $[G_t'(t)\ G_t''(t)]$-space, (**b**) in $[\dot{G}_t'(t)\ \dot{G}_t''(t)]$-space.

Figure 4. **SPP-LAOS analysis from the 4 wt% XG solution at the frequency of 0.316 rad/s**. The raw data are presented as elastic (**a**) and viscous (**b**) Lissajous-Bowditch curves. (**c**) Cole-Cole plot of transient moduli $G_t'(t) - G_t''(t)$, where the dashed lines represent the linear-regime dynamic moduli. (**d**) The transient moduli determined at the point of maximum elasticity as a function of strain amplitudes. (**e**) Elastic recoverable strain at the instant of maximum $G_t'(t)$ as a function of strain amplitude.

Figure 5. **SPP-LAOS analysis from 5 wt% PEO in DMSO solution at the frequency of 1.26 rad/s**. (**a**) Elastic and (**b**) viscous Lissajous-Bowditch curves. (**c**) Cole-Cole plot of transient moduli $G_t'(t) - G_t''(t)$, where the dashed lines represent the linear-regime dynamic moduli. (**d**) The dynamic moduli as a function of strain amplitudes.

Figure 6. The transient differential viscosity plotted on top of the steady-shear flow curve from the XG (a) and PEO/DMSO (b) systems. Lines show transient differential viscosity $G_t''(t)/\omega$ determined from LAOS tests while star symbols represent steady-shear flow viscosity.

Figure 7. **The sequence of physical processes under LAOS from the XG solutions**. The symbols shown on elastic Lissajous-Bowditch curves (**a**) correspond to the ones in the time-dependent Cole-Cole plot of transient moduli (**b**).

DISCUSSION:

We have demonstrated how to correctly perform large amplitude oscillatory shear rheometry tests using a commercial rheometer, and to run the SPP analysis freeware to interpret and understand the nonlinear stress responses of two distinct polymer solutions. The SPP framework, which has previously been shown to correlate with structural changes and facilitate understandings of numerous colloidal systems, can be equally applied to polymer systems. The responses of two concentrated polymeric solutions to LAOS have been investigated using the SPP scheme, in which the rheological responses are shown to exhibit complex sequences of processes. These transient intra-cycle interpretations provide essential information on the nonlinear out-of-equilibrium behaviors of polymeric solutions, and provide guidelines for engineers to improve consumer products with desired properties or to transport systems more efficiently.

The gel-like XG solution and the concentrated entangled PEO solution exhibit distinct physical processes that provide clear distinctions between their respective nonlinear behaviors. While the maximum transient elastic modulus of XG remains essentially unchanged across the imposed amplitudes, reminiscent of soft glassy materials that exhibit caging dynamics, the PEO solution displays a local stiffening characteristic that is better described by finite-extensibility concepts typically applied to polymer systems. As a consequence, processes involving each material would be best approximated using glassy and finitely extensible nonlinear elastic (FENE)-type models. In addition to how the maximum elasticity changes with applied strain amplitude, the transient differential viscosity from the two systems show similar behaviors, with apparent overshoots at high shear rates being identified prior to shear thinning. However, the PEO solution displays a lower transient differential viscosity than the steady-state conditions, while the XG solution exhibits no marked difference between steady and dynamic shearing. We therefore identify different pre-yielded processes, but similar post-yield characteristics in the two polymer systems. In both cases, we identify post-yielded conditions that are nearly indistinguishable from steady shearing, showing that it is not necessary to go to the limit of zero frequency in LAOS to obtain reliable information about the flow properties of soft materials.

We identify the nonlinear rheological sequence as containing information about the linear viscoelasticity, the transient flow curves, and the critical strain that is responsible for nonlinear behaviors. This congruence of information obtained via the SPP approach is not possible with any of the FT-based approaches, which treat oscillatory shearing as a special rheological case, with interpretations that are not applicable to other experimental protocols. In contrast, the SPP approach views all materials responses equivalently, providing a clear mechanism for direct comparisons across a range of different tests, such as those made here. We show that the elastic recoverable strain is approximately constant at the point of maximum elasticity for a xanthan gum solution, and this constant elastic strain is indicative of the critical strain of nonlinear regime. We also demonstrate that the transient flow curves can be constructed from the results of the

SPP analysis. In a single LAOS test on a concentrated polymeric solution using the SPP approach, we can therefore confidently determine the linear viscoelastic response at that frequency, portions of the steady-state flow curve that correspond to the conditions imposed, and the amplitude above which responses become nonlinear. Overall, this work provides a general approach to performing and understanding nonlinear rheological behaviors of soft matter, with a particular emphasis on polymer solutions. The approach outlined in this work provides an easy-to-implement methodology that provides clear correlation between small and large-amplitude deformation bulk rheology, which can be used to assist in the rational design and optimization of materials under flow.

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DISCLOSURES:

The authors have nothing to disclose.

REFERENCES:

1. Dolz, M., Hernández, M. J., Delegido, J., Alfaro, M. C. & Muñoz, J. Influence of xanthan gum and locust bean gum upon flow and thixotropic behaviour of food emulsions containing modified starch. *Journal of Food Engineering* **81** (1), 179–186, doi:10.1016/j.jfoodeng.2006.10.020 (2007).
2. Gupta, N., Zeltmann, S. E., Shunmugasamy, V. C. & Pinisetty, D. Applications of Polymer Matrix Syntactic Foams. *JOM* **66** (2), 245–254, doi:10.1007/s11837-013-0796-8 (2013).
3. Garcıa-Ochoa, F., Santos, V. E., Casas, J. A. & Gómez, E. Xanthan gum: production, recovery, and properties. *Biotechnology Advances* **18** (7), 549–579, doi:10.1016/S0734-9750(00)00050-1 (2000).
4. Chang, I., Im, J., Prasidhi, A. K. & Cho, G.-C. Effects of Xanthan gum biopolymer on soil strengthening. *Construction and Building Materials* **74**, 65–72, doi:10.1016/j.conbuildmat.2014.10.026 (2015).
5. Rogers, S. A. In search of physical meaning: defining transient parameters for nonlinear viscoelasticity. *Rheologica Acta* **56** (5), 501–525, doi:10.1007/s00397-017-1008-1 (2017).
6. Ferry, J. D. *Viscoelastic properties of polymers*. *John Wiley & Sons* (1980).
7. Bird, R. B., Armstrong, R. C., Hassager, O. *Dynamics of Polymeric Liquids. Volume 1: Fluid Mechanics, John Wiley & Sons: New York (1987)*.
8. Park, J. D. & Rogers, S. A. The transient behavior of soft glassy materials far from equilibrium. *Journal of Rheology* **62** (4), 869–888, doi:10.1122/1.5024701 (2018).
9. Rogers, S., Kohlbrecher, J. & Lettinga, M. P. The molecular origin of stress generation in worm-like micelles, using a rheo-SANS LAOS approach. *Soft Matter* **8** (30), 7831–7839, doi:10.1039/c2sm25569c (2012).
10. Lettinga, M. P., Holmqvist, P., Ballesta, P., Rogers, S., Kleshchanok, D. & Struth, B. Nonlinear Behavior of Nematic Platelet Dispersions in Shear Flow. *Phys Rev Lett* **109** (24), 246001, doi:10.1103/PhysRevLett.109.246001 (2012).

11. Hyun, K., Wilhelm, M., et al. A review of nonlinear oscillatory shear tests: Analysis and application of large amplitude oscillatory shear (LAOS). *Progress in Polymer Science* **36** (12), 1697–1753, doi:10.1016/j.progpolymsci.2011.02.002 (2011).
12. Park, J. D., Ahn, K. H. & Lee, S. J. Structural change and dynamics of colloidal gels under oscillatory shear flow. *Soft Matter* **11** (48), 9262–9272, doi:10.1039/c5sm01651g (2015).
13. Lee, C.-W. & Rogers, S. A. A sequence of physical processes quantified in LAOS by continuous local measures. *Korea-Australia Rheology Journal* **29** (4), 269–279, doi:10.1007/s13367-017-0027-x (2017).
14. Rogers, S. A., Erwin, B. M., Vlassopoulos, D. & Cloitre, M. A sequence of physical processes determined and quantified in LAOS: Application to a yield stress fluid. *Journal of Rheology* **55** (2), 435–458, doi:10.1122/1.3544591 (2011).
15. Wagner, M. H., Rolon-Garrido, V. H., Hyun, K. & Wilhelm, M. Analysis of medium amplitude oscillatory shear data of entangled linear and model comb polymers. *Journal of Rheology* **55** (3), 495–516, doi:10.1122/1.3553031 (2011).
16. Radhakrishnan, R., Fielding, S. Shear banding in large amplitude oscillatory shear (LAOStrain and LAOStress) of soft glassy materials. *Journal of Rheology*. **62** (2), 559–576, doi: 10.1122/1.5023381 (2018)
17. Bharadwaj, N. A. & Ewoldt, R. H. Constitutive model fingerprints in medium-amplitude oscillatory shear. *Journal of Rheology* **59** (2), 557–592, doi:10.1122/1.4903346 (2015).
18. Wilhelm, M. Fourier-Transform Rheology. *Macromolecular Materials and Engineering* **287** (2), 83–105, doi:10.1002/1439-2054(20020201)287:2<83::AID-MAME83>3.0.CO;2-B (2002).
19. Ewoldt, R. H., Hosoi, A. E. & McKinley, G. H. New measures for characterizing nonlinear viscoelasticity in large amplitude oscillatory shear. *Journal of Rheology* **52** (6), 1427–1458, doi:10.1122/1.2970095 (2008).
20. Rogers, S. A. & Lettinga, M. P. A sequence of physical processes determined and quantified in large-amplitude oscillatory shear (LAOS): Application to theoretical nonlinear models. *Journal of Rheology* **56** (1), 1–25, doi:10.1122/1.3662962 (2011).
21. Rogers, S. A. A sequence of physical processes determined and quantified in LAOS: An instantaneous local 2D/3D approach. *Journal of Rheology* **56** (5), 1129–1151, doi:10.1122/1.4726083 (2012).
22. Kim, J., Merger, D., Wilhelm, M. & Helgeson, M. E. Microstructure and nonlinear signatures of yielding in a heterogeneous colloidal gel under large amplitude oscillatory shear. *Journal of Rheology* **58** (5), 1359–1390, doi:10.1122/1.4882019 (2014).
23. van der Vaart, K., Rahmani, Y., Zargar, R., Hu, Z., Bonn, D. & Schall, P. Rheology of concentrated soft and hard-sphere suspensions. *Journal of Rheology* **57** (4), 1195–1209, doi:10.1122/1.4808054 (2013).
24. Poulos, A. S., Stellbrink, J. & Petekidis, G. Flow of concentrated solutions of starlike micelles under large-amplitude oscillatory shear. *Rheologica Acta* **52** (8-9), 785–800, doi:10.1007/s00397-013-0703-9 (2013).
25. Armstrong, M. J., Beris, A. N., Rogers, S. A. & Wagner, N. J. Dynamic shear rheology of a thixotropic suspension: Comparison of an improved structure-based model with large amplitude oscillatory shear experiments. *Journal of Rheology* **60** (3), 433–450, doi:10.1122/1.4943986 (2016).

650 26. Calabrese, M. A., Wagner, N. J. & Rogers, S. A. An optimized protocol for the analysis of
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652 doi:10.1039/C5SM03039K (2016).
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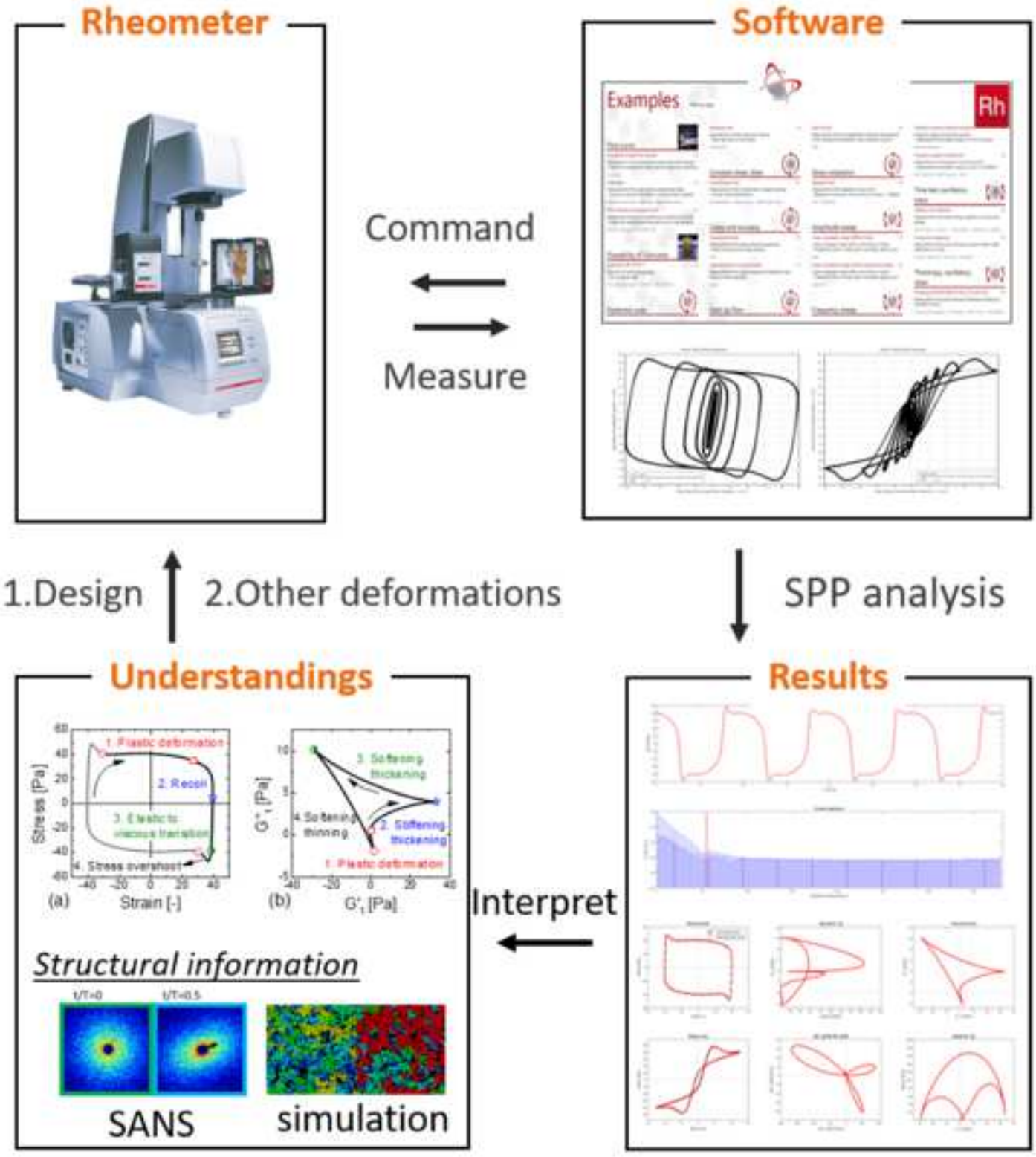

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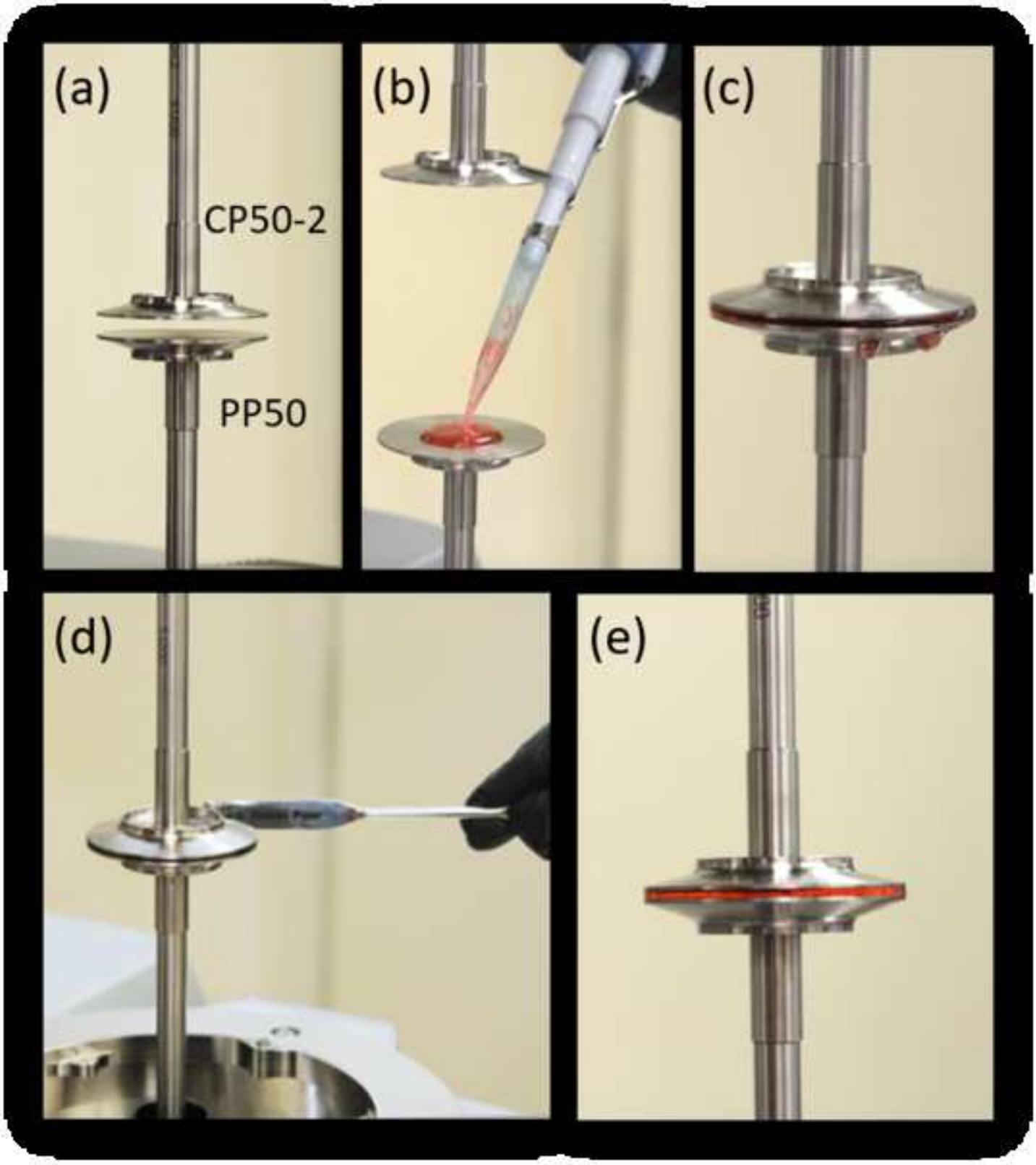

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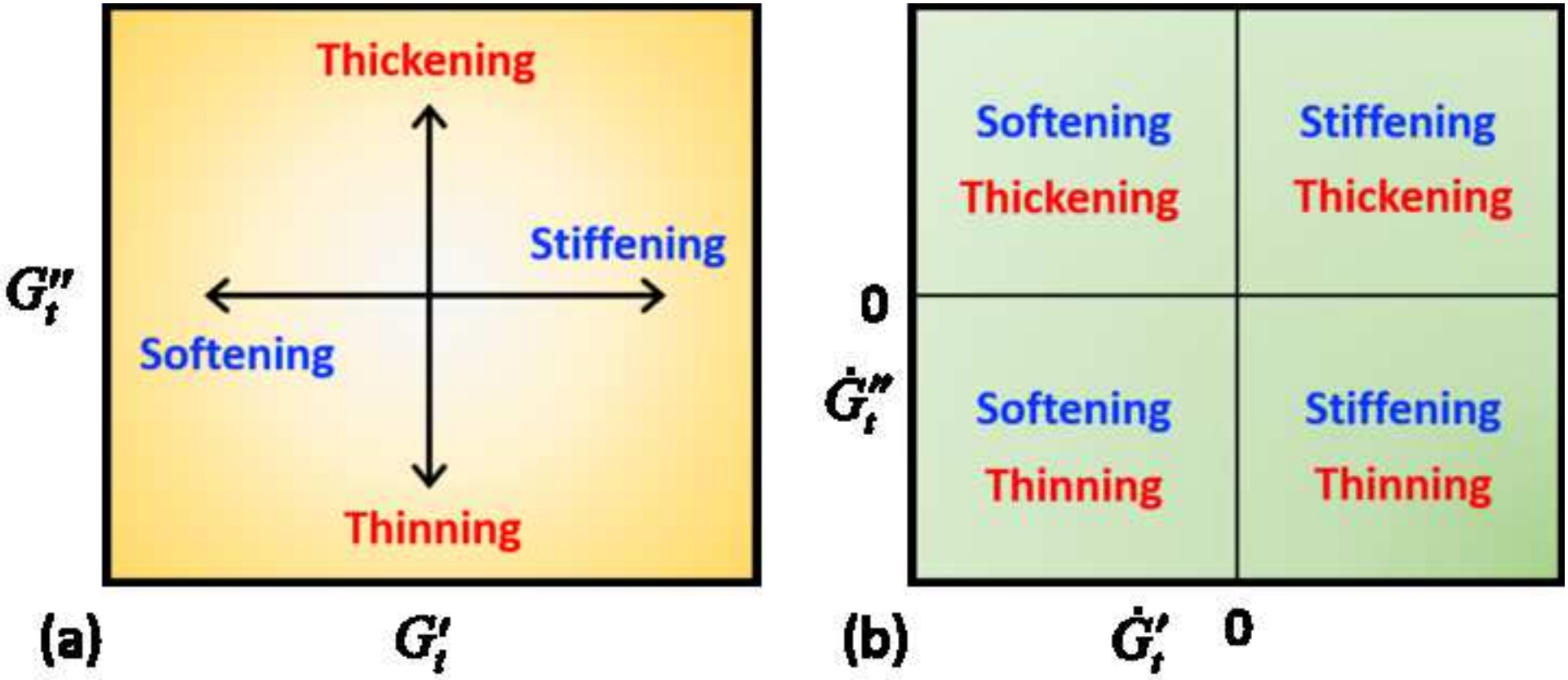

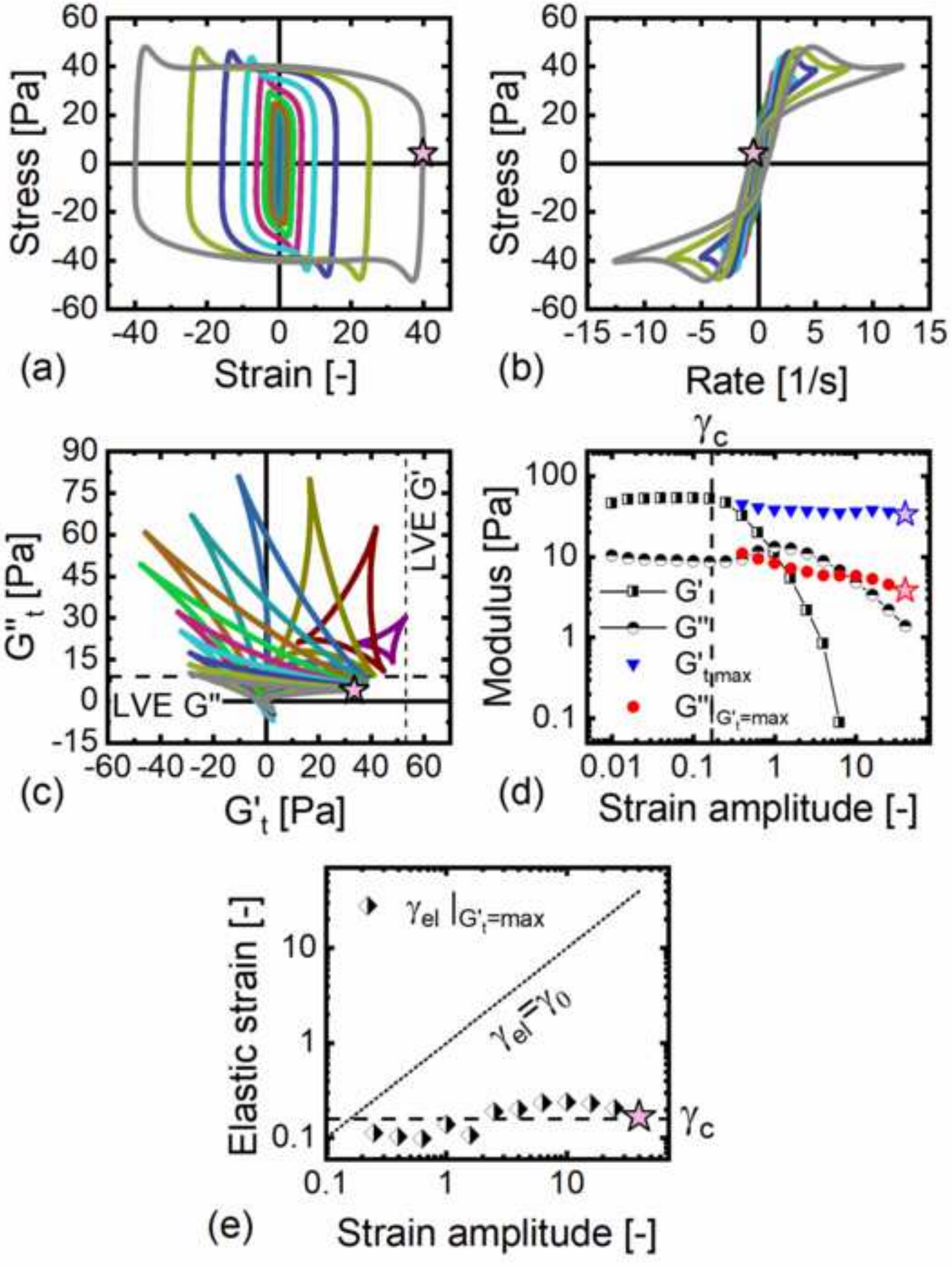

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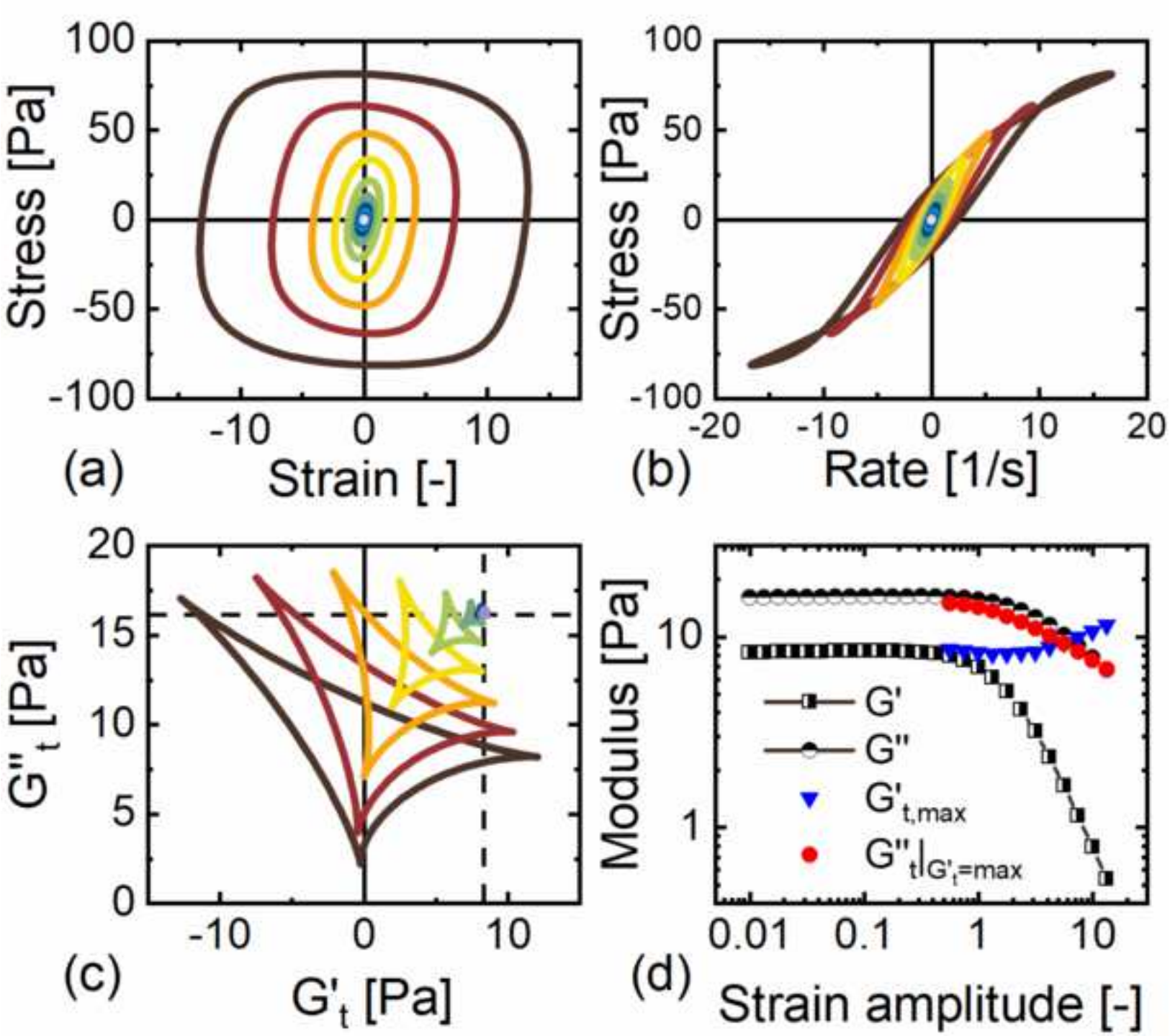

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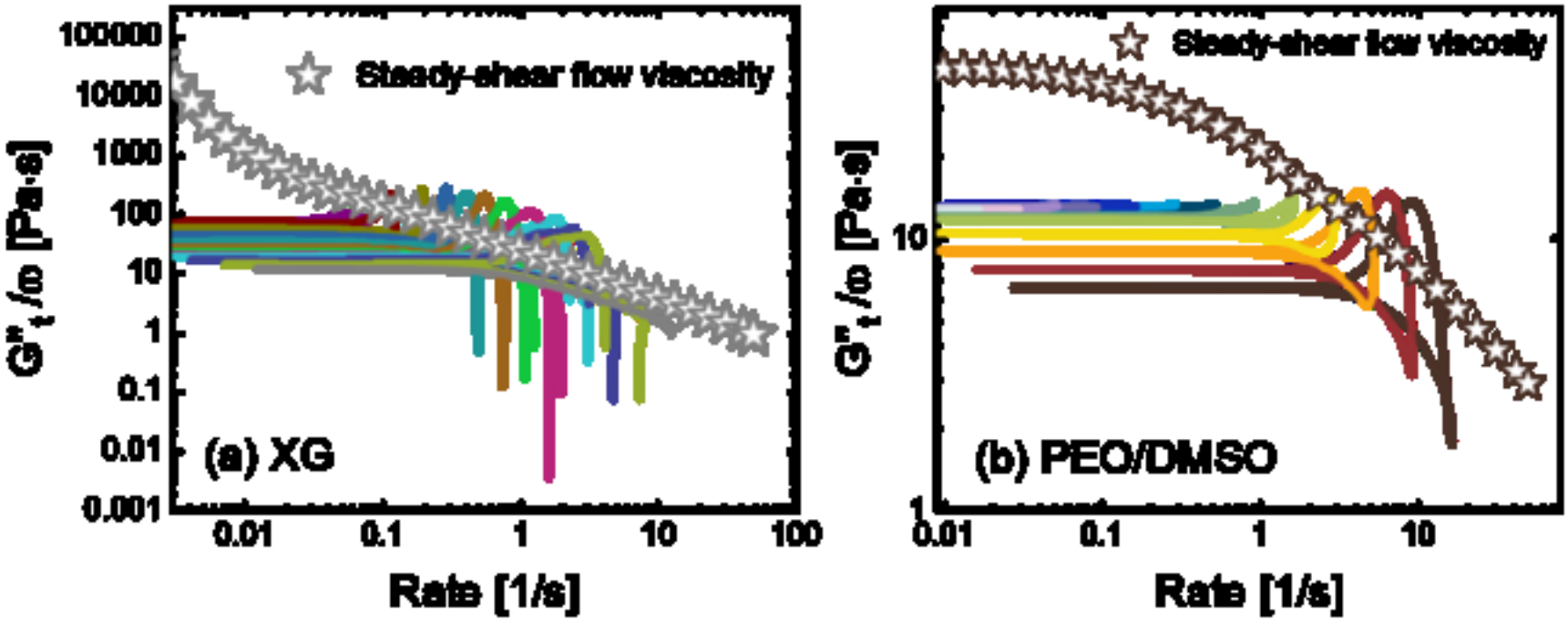

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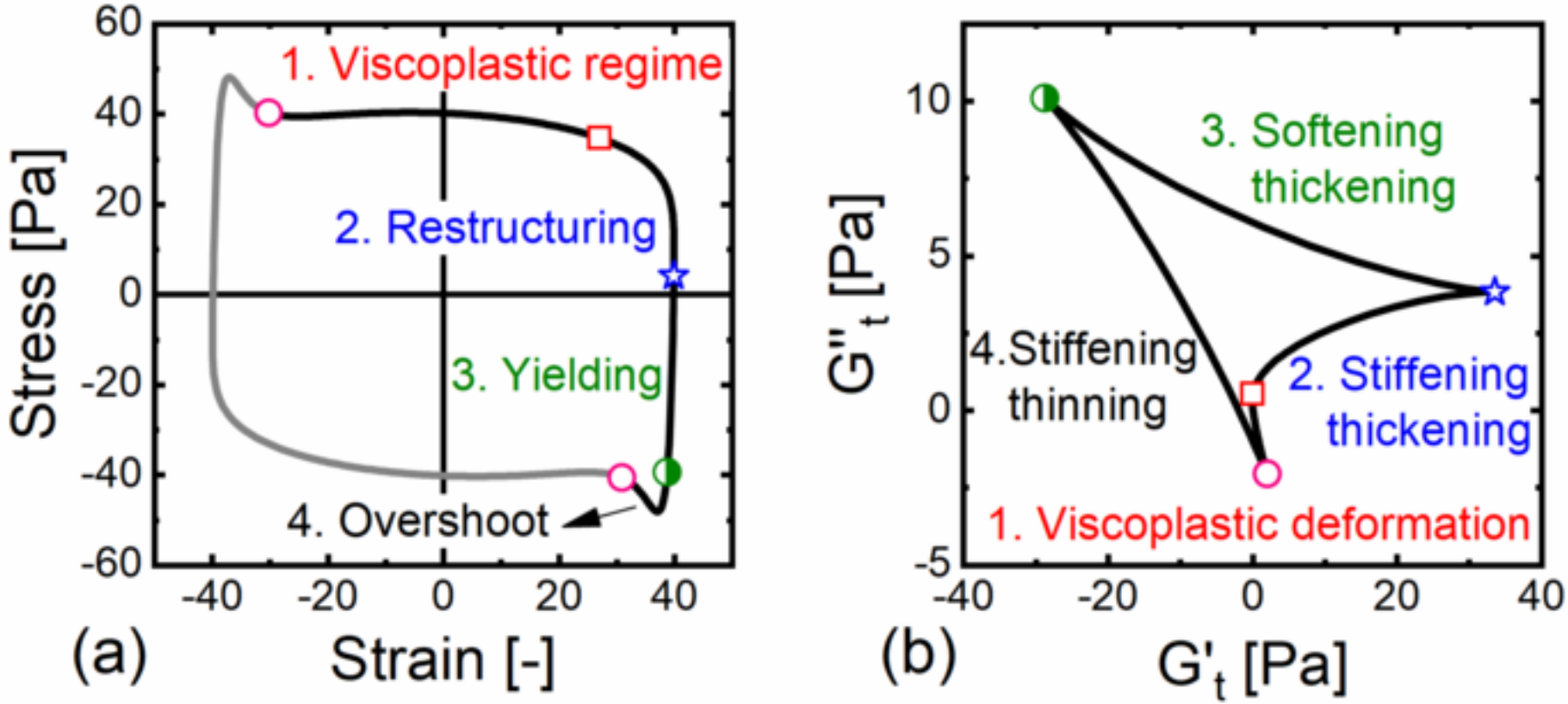

Name of Material/ Equipment	Company	Catalog Number	Comments/Description
SPP analysis software	Simon Rogers Group (UIUC)	SPPplus_v1p1	tached as supplementary files
MATLAB	Mathwork		
Rheometer	Anton Paar	MCR 702 TwinDrive	
50mm 2-degree cone	Anton Paar	CP50-2	Upper measuring system
50mm plate	Anton Paar	PP50	Lower measuring system
Xanthan gum (XG)	Sigma-Aldrich	11138-66-2	
Polyethylene oxide (PEO)	Sigma-Aldrich	25322-68-3	Mv=1,000,000
Dimethyl sulfoxide (DMSO)	Sigma-Aldrich	67-68-5	

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You will find Editorial comments and Peer-Review comments listed below. Please read this entire email before making edits to your manuscript.
NOTE: Please include a line-by-line response to each of the editorial and reviewer comments in the form of a letter along with the resubmission.

Editorial Comments:

• Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammatical errors.
We have proofread the manuscript a couple of times to make sure there are no spelling or grammatical errors.

• Please reduce the number of keywords/phrases to at most 12.
The change has been made.

• Please simplify the title and avoid using the colon in the title if possible.
The title has been simplified to, “Measuring and understanding the large amplitude oscillatory shear response of soft materials”.

• **Introduction:** Please ensure that appropriate references to published literature are provided.
Appropriate references are provided throughout the manuscript.

• **Protocol Language:**The JoVE protocol should be almost entirely composed of numbered short steps (2-3 related actions each) written in the imperative voice/tense (as if you are telling someone how to do the technique, i.e. "Do this", "Measure that" etc.). Any text that cannot be written in the imperative tense may be added as a brief “Note” at the end of the step (please limit notes). Please re-write your ENTIRE protocol section accordingly. Descriptive sections of the protocol (e.g. Lines 143-158) can be moved to Representative Results or Discussion. The JoVE protocol should be a set of instructions rather a report of a study. Any reporting should be moved into the representative results.
We have rewritten the protocol and made the changes required.

• **Protocol Detail:** Please note that your protocol will be used to generate the script for the video, and must contain everything that you would like shown in the video. **Please add more specific details (e.g. button clicks for software actions, numerical values for settings, etc) to your protocol steps.** There should be enough detail in each step to supplement the actions seen in the video so that viewers can easily replicate the protocol.
Details have been added to the protocol steps.

• **Protocol Numbering:** Please adjust the numbering of your protocol section to follow JoVE’s instructions for authors, 1. should be followed by 1.1. and then 1.1.1. if necessary and all steps should be lined up at the left margin with no indentations. There must also be a one-line space between each protocol step.
The changes have been made.

• **Protocol Highlight:** Please highlight ~2.5 pages or less of text (which includes headings and spaces) in yellow, to identify which steps should be visualized to tell the most cohesive story of your protocol steps.
1) The highlighting must include all relevant details that are required to perform the step. For example, if step 2.5 is highlighted for filming and the details of how to perform the step are given in steps 2.5.1 and 2.5.2, then the sub-steps where the details are provided must be included in the highlighting.
2) The highlighted steps should form a cohesive narrative, that is, there must be a logical flow from one highlighted step to the next.
3) Please highlight complete sentences (not parts of sentences). Include sub-headings and spaces when calculating the final highlighted length.
4) Notes cannot be filmed and should be excluded from highlighting.
5) Please bear in mind that software steps without a graphical user interface/calculations/ command line scripting (e.g. section 3,4) cannot be filmed.
6) Please ensure that the manuscript title best reflects the filmable content (i.e. the portions you highlight).

A portion of the protocol to be visualized is highlighted.

• **Discussion:** JoVE articles are focused on the methods and the protocol, thus the discussion should be similarly focused. Please ensure that the discussion covers the following in detail and in paragraph form (3-6 paragraphs): 1) modifications and troubleshooting, 2) limitations of the technique, 3) significance with respect to existing methods, 4) future applications and 5) critical steps within the protocol.
The changes are made according to the comments.

• **Figures:** Please remove the embedded figures from the manuscript. Figure legends, however, should remain within the manuscript text, directly below the Representative Results text.
We have removed the figures while the captions are placed below results text.

• **Commercial Language:**JoVE is unable to publish manuscripts containing commercial sounding language, including trademark or registered trademark symbols (TM/R) and the mention of company brand names before an instrument or reagent. Examples of commercial sounding language in your manuscript are TwinDrive, RheoCompassTM, Anton Paar, Origin or Excel, Matlab, etc.
1) Please use MS Word's find function (Ctrl+F), to locate and replace all commercial sounding language in your manuscript with generic names that are not company-specific. All commercial products should be sufficiently referenced in the table of materials/reagents. You may use the generic term followed by "(see table of materials)" to draw the readers' attention to specific commercial names.
The use of commercial names have been removed, with the exception of MATLAB. MATLAB is the key software to implement the theme software in the protocol and the authors think it is important to let users know that it is the platform our software is constructed on. Many articles in JoVE have taken the same approach with a lab-made software, mentioning "MATLAB" by name to inform the readers. (Please see the three examples below) We have greatly reduced the use of the term.

Ibáñez-Ventoso, C., Herrera, C., Chen, E., Motto, D., Driscoll, M. Automated Analysis of *C. elegans* Swim Behavior Using CeleST Software. *J. Vis. Exp.* (118), e54359, doi:10.3791/54359 (2016).
Nikolaus, J., Karatekin, E. SNARE-mediated Fusion of Single Proteoliposomes with Tethered Supported Bilayers in a Microfluidic Flow Cell Monitored by Polarized TIRF Microscopy. *J. Vis. Exp.* (114), e54349, doi:10.3791/54349 (2016).
Rajagopal, V., Bass, G., Ghosh, S., Hunt, H., Walker, C., Hanssen, E., Crampin, E., Soeller, C. Creating a Structurally Realistic Finite Element Geometric Model of a Cardiomyocyte to Study the Role of Cellular Architecture in Cardiomyocyte Systems Biology. *J. Vis. Exp.* (134), e56817, doi:10.3791/56817 (2018).

• Please define all abbreviations at first use.
We have made sure the abbreviations are defined at first use.

• Please use standard abbreviations and symbols for SI Units such as µL, mL, L, etc., and abbreviations for non-SI units such as h, min, s for time units. Please use a single space between the numerical value and unit.
All the changes are made according to the comment.

• If your figures and tables are original and not published previously or you have already obtained figure permissions, please ignore this comment. If you are re-using figures from a previous publication, you must obtain explicit permission to re-use the figure from the previous publisher (this can be in the form of a letter from an editor or a link to the editorial policies that allows you to re-publish the figure). Please upload the text of the re-print permission (may be copied and pasted from an email/website) as a Word document to the Editorial Manager site in the "Supplemental files (as requested by JoVE)" section. Please also cite the figure appropriately in the figure legend, i.e. "This figure has been modified from [citation]."
The results here are all new and have not been reported elsewhere.

Comments from Peer-Reviewers:
We thank all reviewers for their detailed comments and questions. We believe that addressing the comments and questions in the manuscript have strengthened it greatly.

Reviewer #1:
The paper describe a procedure to analyze and interpret the LAOS experiments using a Matlab code, based on the Sequence of Physical Processes (SPP) technique. The shown procedure is useful for

experimentalists, but brings no novelty for the topic. The results and interpretation are more or less classic, but the work is useful for newcomers in the field.

I have two recommendations/observations for the authors:
1. To point very clear if the tests are strain or stress controlled. Ideal should be to perform both and to analyze the differences .... (maybe in a future work!).

The rheometer used in this study can be configured into either a stress-controlled or a strain-controlled instrument. As strain-controlled LAOS is desired in this study, we have configured the rheometer into a typical strain-controlled rheometer, where the upper motor operates solely as a torque transducer and the bottom motor acts as a drive unit. We have made the point stronger by including a note in the instrument setup section that a typical strain-controlled configuration is used in the study.

We have also replicated the same measurements on another strain-controlled rheometer (an ARES-G2 from TA Instruments) to confirm that the responses are consistent.

We agree that it would be interesting to perform some both strain- and stress-controlled experiments in the future and analyze the differences.

2. To show the evolution of the Lissajous Figures with the strain amplitude sweep curve (corresponding between Fig. 4a and Fig. 4b with Fig. 4d, see the paper from Polymer 104 (2016) 215-226).

We thank the reviewer for the comment. The suggested paper in Polymer is interesting and we enjoyed reading it. We also like the style the authors used to correlate the figures. Nonetheless, the figures in the current manuscript, shown as Figs 4a, 4b, and 4d, have a clear correspondence because of the strain amplitudes that are easily read off the abscissa. We have also used different colors across Figs 4a and 4b to more clearly differentiate between separate curves. We therefore do not think that extra information on the amplitude sweep plot is required. We aim to use the amplitude sweep (Fig. 4d) to emphasize the correspondence between maximum $G_t{}'(t)$ across amplitudes and the value of linear regime G'.

I think the format and the work is suitable for this type of publications. Therefore, if the authors take into account my observations, I recommend the paper to be published in Journal of Visualized Experiments.

Reviewer #2:
Manuscript Summary:
This paper tries to give explanation about SPP analysis under LAOS flow for two polymer solution. It is very interesting. Especially, visualization of LAOS test is very meaningful. Therefore, I think publication of this paper should be considered. However, I listed some my questions (a few minor questions).

Major Concerns:
No

Minor Concerns:
Page 3, line 123-124
The authors said "two concentrated polymer suspension".
But, in my opinion, XG solution and PEO solution is not suspension but polymer solution. Suspension can make confusion to general reader.
This appear at other page of manuscript. I suggest to change it.

That is an excellent point and we agree that they are in solution form, not suspension. We did change all the wording in the manuscript accordingly.

Reviewer #3:

Manuscript Summary:

This manuscript reports the use of matlab analysis feature along with experimental measurements on a commercial rheometer. Given that the large deformation behaviour of soft matter is of great interest, several methods have been proposed, and the protocol presented in this work adds to this. However, I have some concerns regarding the manuscript, especially since it is intended to be a "method" report.

Major Concerns:

1. With a new method, it would be helpful to show some idealized response. Generally, we might want to talk about Newtonian fluid, crosslinked rubber, Maxwell fluid (material with a single relaxation time) etc, while introducing viscoelastic response. Are there no such idealized responses which can be shown here? This manuscript reports results with two polymeric solutions, and given their complex response, I am afraid that efficacy of method is not well brought out.

We do not intend for the current manuscript to report a brand new method of analysis. Instead, it aims to instruct readers as of how to correctly measure and understand a LAOS response with a published framework that has already been used in a number of studies. For the exemplary use of the method, please see *Korea-Australia Rheology Journal* **29** (4), 269–279. 2017 and *Journal of Rheology* **62** (4), 869–888. 2018

We agree that some simple examples should be shown when proposing a new analyzing framework. In fact, when the framework was first proposed (*Rheologica Acta* **56** (5), 501–525. 2017), results from several models were shown, including generalized Newtonian fluid (p.510), the elastic Bingham model (p.511), and the corotational Maxwell model (P.512). Experimental results from a Maxwellian material with a single relaxation time are also shown in Figs. 6-8 to inform readers as how these rheologically-simple models/materials behave.

The current manuscript, by contrast, aims to apply the technique to somewhat more complex materials such as the investigated polymer solutions, and guide the readers through the process of understanding the complex response from these materials.

2. Figures 3 and 4(c)/5(c) are backbones for the discussion of analysis based on the proposed protocol. However, 4(c)/5(c) have not been given adequate attention during discussion. For example, the manuscript states that "To fully understand the intra-cycle physics, the time-dependent Cole-Cole plots obtained from the SPP freeware are presented in Figures 4(c) and 5(c). Interpretations of the plots are discussed in the manner laid out by the legend in Figure 3." However, I did not notice the interpretations as claimed in this sentence.

We have addressed this and made the point stronger. Please see the following revised sentences.
“To fully understand the intra-cycle physics, the time-dependent Cole-Cole plots obtained from the SPP freeware are presented in Figures 4(c) and 5(c). Interpretations of the plots are discussed in the manner laid out by the legend in Figure 3, where the relative motion of trace quantitatively indicates whether the materials undergo stiffening/softening or thickening/thinning in an intra-cycle sense.”

Also, a more detailed interpretation is specifically provided in Fig. 7, where we break a single oscillation into four distinct processes, to guide readers to better understand the physical processes in an oscillation.

3. As a method reporting, would it not be useful to report other measures (mentioned in the manuscript) and demonstrate how the current protocol is "better" or "complementary"?

Other commonly-used methods include Fourier-transform rheology and the Chebyshev description, which have been shown to be trivially related. Fourier transform-based frameworks analyze the nonlinearity of stress response and report corresponding parameters, including I_3/I_1, Q and Q_0 etc. These parameters are useful in terms of mathematically quantifying the distortion of stress, but clear physical interpretations that might allow an experimentalist to connect them to the physical process a material undergoes is still missing from the literature. This lack of physical meaning somewhat restricts experimentalists from further applying these methods and making correlations with structural parameters. For instance, the structural information obtained from either simulation or scattering techniques are typically time-resolved, yet FT-based frameworks all average the stress response over a complete cycle of deformation.

One of the advantages of the SPP framework is that the local information regarding elastic and viscous components can be universally defined, and the physical meanings of these parameters are clear. This local information is useful and valuable to scientists interested in the correlation between bulk rheology and microstructure evolution. Please see J. Rheol. 62. 2018 p.869-888.

We have pointed out the limitations of these other methods in the introduction and provided specifics regarding how SPP provides a better understanding than the other techniques.

Minor Concerns:
Definitions of transient, differential, steady viscosity - please check the consistency/correctness in y-axes labels / caption in Figure 6 and the adjoining discussion in lines 388-391.

We have made changes in the manuscript accordingly. The viscosity determined from $G_t''(t)/\omega$ is now referred as “transient differential viscosity”, and the one determined from a steady-shear test is called “steady-shear flow viscosity.” The wordings are used consistently throughout the manuscript.

Reviewer #4:
Manuscript Summary:
A useful method for analyzing LAOS data within the SPP method is presented and illustrated for two typical polymeric fluids. The presentation is concise and informative and the method should be fairly easy to follow (although I do not have access to the software to determine if indeed it functions as suggested). The manuscript is well written and the major concerns can probably be easily handled in revision.

Major Concerns:
* As the method is software based, and although it is listed as available upon request, should it not be part of the JOVE publication?

This is a really good suggestion, and we appreciate the reviewer’s point. We have now attached the software package to the article so that it is available for readers to download as a supplementary file.

* Two polymer solutions are tested and presented- but not clearly compared and contrasted. The strength of the method lies in part in being able to distinguish between classes of material behavior. It is strongly

suggested to add one paragraph comparing and contrasting the results of the method for the two polymers. In short, what can we learn?
Excellent point. A paragraph comparing the results from the gel-like XG and the concentrated entangled PEO solutions has been added to address the comment. Please see lines #450-465.

* Temperature control is very, very important in rheology and it was not clear how this was achieved and to what level of accuracy?
The method to control temperature is added in the protocol part.
In the current study the temperature is controlled at 25±0.1 °C and 35±0.1 °C for XG and PEO solutions, respectively, which is included in a note in the protocol section. (line #184-186)

* Slip is always a problem when going into a nonlinear measurement. in the FT method of Wilhelm, slip can be detected - can this be detected in the SPP method?

We would argue slip is not necessarily always a problem in nonlinear measurements. There are soft materials that have been confirmed not to slip under shear with direct-imaging techniques. Please see as an example *Phys Rev Lett*, 98(19), p.8357, 2007. Other studies have also shown that with roughened geometries slip can be prevented.

We have performed the same flow conditions with a roughened geometry to make sure that slip is not an issue in the investigated materials. Good agreement is seen with different geometries and a no-slip assumption is therefore supported. A number of studies investigating the same materials did not report slip issues with smooth geometries as well. As an example, please see *J. Non-Newtonian Fluid Mech.* 107 (2002) p.51-65 or *Fibers and Polymers.* 7. (2) 2006 p.129-138 for the study of xanthan gum solutions, and please see *Polymer* 104. 2016 p.171-178 and *Rheol Acta* 52. 2013 p.841-857 for the study of PEO solutions.

A few studies reported that FT-rheology is capable of interpreting slip. For instance, one work (*Macromolecules* 40. 2007 p.4250-4259) proposed to use a sinusoidal, a rectangular, a triangular, and a saw tooth wave as a basis and the time domain signal is described by these characteristic functions to interpret linear behavior, softening, stiffening, and slip or shear bands. Because these four characteristic waves are not orthogonal to each other, the interpretation from the idea of this superposition cannot be generally applied. That is, the results that one obtains from the fitting will be determined by the order in which one fits each characteristic function. Slip, in this case, is therefore not clearly interpreted.

Another common approach in FT-rheology to interpret slip from the presence of even harmonics. However, even harmonics represent an asymmetric stress response and slip is only one of many possible causes of the observable even harmonics. A transient unsteady-state response, shear banding, or a thixotropic behavior could also give rise to even harmonics. Further, if slip happens in a symmetric manner, then even harmonics would also fail to capture the behavior, and the slip would be conflated with the odd harmonic response. We think the information from Fourier transform rheology is useful, but cannot "detect" slip without complementary imaging techniques for the above reasons.

The SPP technique does not contain any information that is not contained in the FT-based approaches. The argument that has been made in favor of the SPP approach is one of presentation: the SPP approach has been shown to present the data contained in LAOS experiments in such a way as to clearly relate back to the physics of the materials or models under deformation.

Minor Concerns:
* The abstract needs to concisely explain the value of the contribution. It can also have less of "we..." - who else?

The reviewer's point is well made. We have rewritten the abstract to strengthen the value of the contribution, with several major points of the study added. The sentences starting with "we…" have been revised as well.

* P3 LAOS may not be that representative of the nonlinear flows typical in processing because these seldom involve flow reversals such as observed in LAOS. The comments about this should be qualified.

Excellent point. The following sentence is included in the manuscript to make the distinction that we use LAOS to approximate the practical conditions that may not necessarily involve flow reversal.
"Although these practical conditions may not necessarily involve flow reversal as in oscillatory shear, the flow field can be easily approximated and tuned with the independent control of applied amplitude and imposed frequency in an oscillatory test. Furthermore, the SPP scheme can be used as described here to understand a broad range of flow types, including those that do not include flow reversals such as the recently-proposed UD-LAOS[22], in which large amplitude oscillations are applied in one direction only (leading to the moniker "uni-directional LAOS"). For simplicity, and for illustrative purposes, we restrict the current study to traditional LAOS, which does include periodic flow reversal."

* P7 A stress controlled rheometer is used to do strain controlled LAOS. Some proof of the accuracy of this must be shown.

The rheometer used in this study can be configured as either a stress-controlled or a strain-controlled instrument. As strain-controlled LAOS is desired in this study, we have configured the rheometer as a typical strain-controlled rheometer, where the upper motor operates solely as a torque transducer and the bottom motor acts as a drive unit. We have made the point stronger by including a note in the instrument setup section that a traditional strain-controlled rheometer is used in the study.

"Note: The MCR-702 rheometer can be configured in either a CMT (combined motor-transducer) or SMT (separate motor transducer) modes. With only a single motor integrated in the rheometer head, it acts as a traditional CMT stress-controlled rheometer and the data obtained require inertia corrections. With two motors incorporated in a SMT mode, the upper motor operates solely as a torque transducer and the bottom motor acts as a drive unit thus converting the rheometer into a strain-controlled rheometer."

We have also replicated the same measurements on another strain-controlled rheometer (an ARES-G2 from TA Instruments) to confirm that the responses are consistent.

Suppl 1_Primary running software

Suppl 2_function_print

Suppl 3_function_numerical

Suppl 4_function_read

Suppl 5_function_fourier

Suppl 6_function_figures

Suppl 7_Sample data 1

Suppl 8_Sample data 2

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Supplemental Coding Files

0100.txt

Suppl 9_Sample data 3