A report on "LAOS Rheology Day," held Friday the 13th at the Colburn Laboratory, University of Delaware

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Participants in the *LAOS* (large amplitude oscillatory shear) *Rheology Day* gathered in Colburn Laboratory at the University of Delaware from around the U.S. to discuss recent advances in the use of large amplitude oscillatory shear to interrogate material properties. The participants included many industrial scientists from DOW, DuPont, ExxonMobil and TA Instruments as well as students and faculty from four institutions. Talks focused on three broad classes of materials — shear thickening colloidal dispersions, shear ordering and melting of block copolymer micelles, and shear banding wormlike micelles — as well as new advances in LAOS rheometry, including: large amplitude microrheology, time resolved SANS (small angle neutron scattering) measurements of microstructure during LAOS, flow velocimetry during LAOS, and stress- versus strain-controlled LAOS measurements. New theoretical predictions for shear banding wormlike micelles, yield stress fluids, and active microrheology of colloidal dispersions were also presented and discussed. The talks were followed by lively discussion, and the following summarizes some of the key outcomes of these discussions that may be of value to the community. Support for this activity from the Department of Chemical and

Figure 1a. Speakers (S) and Organizers (O). From left to right: Jim Swan (S, UD), Gareth McKinley (O, MIT), Chris Dimitriou (S, MIT), Carlos López-Barrón (S, ExxonMobil), Randy Ewoldt (S, UIUC), Kate Gurnon (S, UD), Thomas Ober (S, MIT), Lin Zhou (S, CUNY), Pam Cook (O, UD), Norm Wagner (O, UD).

Figure 1b. A composite view of the participates in the seminar room.

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Summary of Presentations

Three speakers from the University of Delaware: James Swan, Kate Gurnon and Carlos López-Barrón, presented work focused on the development of unsteady, non-equilibrium microstructure in materials deformed under LAOS. Swan described a micro-mechanical model solution of the Smoluchowski equation for a dilute colloidal dispersion deformed by an oscillating micro-rheological probe. The key result of the modeling is that, in contrast to entangled polymer solutions and melts, for colloidal dispersions the hydrodynamic interactions play an important role in determining both the suspension microstructure and the stress response of the dispersion during LAOS. Gurnon and López-Barrón presented results of time resolved oscillatory rheology and small angle neutron scattering (*tOrSANS*) experiments conducted on concentrated colloidal dispersions and solutions of worm-like micelles, respectively. This new technique and a versatile apparatus available for use are explained briefly in the sidebar (p17, top). In Gurnon's case, the resulting flow curves were compared to an analytical solution of the Giesekus model for the stress response of a non-linear viscoelastic material. From this comparison, she concluded that stress resulting from the hydrodynamic interactions among the particles (neglected in the Giesekus model) play a crucial role in the LAOS response. Shear thickening was also evident in the LAOS stress response and in the corresponding microstructure. Thus, both theory and experiment elucidate an important and fundamental difference between the LAOS response of viscoelastic solutions and colloidal dispersions, a topic to be further discussed at the ICR in August. Continuing this theme, López-Barrón observed the intra-cycle organization and melting of structures in block copolymer micellar solutions in ionic liquids. This is evident in the neutron scattering spectra, which enable the creation of "Structure-Lissajous plots" showing the degree of order as a function of the applied strain and strain rate (see second side bar, p17 bottom). When fluidized by shearing well beyond the yield strain, the complex viscosity of the solutions matched that measured in steady shear, confirming the so-called *Delaware-Rutgers* rule [López-Barrón *et al.*, *2012*]. For the case of worm-like micellar solutions, López-Barrón observed cyclic alignment and disordering of the micelles within a cycle of oscillation. The maximum alignment occurs at the peak in strain rate.

Advances in constitutive equation modeling of shear-banding fluids under steady shear and LAOS were presented by Lin Zhou from the New York City College of Technology, CUNY working with Pam Cook of the University of Delaware. In particular, she compared several modern microstructurally-motivated constitutive models for entangled, worm-like micellar solutions (VCM, PEC, PEC+M, *etc*.) and their sensitivity to various flow conditions in the Couette geometry. Zhou observed the formation of two and three shear bands depending on the constitutive model as well as pronounced elastic recoil in many cases.

Shear banding solutions under LAOS deformation have both time and spatially dependent velocity fields, requiring the development of advanced experimental methods for properly determining the deformation field. This was addressed by Thomas Ober and Chris Dimitriou from the McKinley group at the Massachusetts Institute of Technology. Ober presented a new apparatus for performing flow velocimetry studies of non-linear viscoelastic materials. A laser light sheet is directed into the gap of a cone and plate rheometer through a window at its edge. Scattering from tracer particles, which are dispersed in the material, is collected by imaging a thin focal region illuminated by the laser. This enabled study of the development and evolution of the shear bands formed in worm-like micellar fluids deformed by LAOS. Dimitriou presented a rheological study of Carbopol microgel, a model yielding, elasto-viscoplatic material. He determined that imposing large amplitude, oscillatory stress (which may be termed *LAOStress*) rather than the corresponding strain-controlled protocol (*LAOStrain*) provided the most revealing probe of such materials.

Randy Ewoldt from the University of Illinois, Urbana-Champaign, gave the final presentation of the session in which he discussed the differences between stress and strain control in the context of large amplitude oscillatory deformation. He posed a number of intriguing questions. Which is better, stress or strain control, for characterizing particular materials? What measures of non-linearity analogous to those in "New measures for characterizing nonlinear viscoelasticity in large amplitude oscillatory shear," [Ewoldt *et al.*, 2008] might be obtained from a large, imposed oscillatory stress? What additional material properties may be inferred by comparison of stress- and strain-controlled deformation?

Summary of Discussion

The discussions following the presentations were animated. Two significant topics of discussion are summarized here: (1) the definition of the material coefficients in a stress-controlled LAOS experiment, (2) the definition and organization of the rheological space probed by LAOS.

(1) "To stress or to strain?" - that is the question.

During his presentation, Ewoldt raised the issue that the definitions of higher harmonic Fourier coefficients in LAOS are currently ambiguous. Specifically, the signs of the 3rd, 7th, 11th, etc. harmonics change depending on the seemingly arbitrary choice of representing an oscillatory input as either a sine or cosine in the time

domain. While this arbitrary choice does *not* affect the definitions of first-harmonic coefficients, e.g. J_1' and J_1'' (and therefore linear viscoelastic measures are not affected), it does affect the definitions of the third-harmonic measures such as J_3' and J_3''. This current ambiguity therefore obfuscates any attempt to interpret the meaning of the signs of higher-harmonic *Fourier* coefficients. This has consequences for the theoretical underpinnings and definitions of material measures for both strain-control and stress-control LAOS. Work on strain-control LAOS seems to follow a typical convention, representing the shear strain input as a sine wave, $\gamma(t)=\gamma_0 \sin\omega t$. However in stress-controlled LAOS there is not yet a standard convention.

A resolution was proposed, in two parts. First, although the time-domain *Fourier* coefficients are ambiguous, the deformation-domain *Chebyshev* coefficients are clearly defined and immune to this ambiguity. Chebyshev coefficients are based on orthogonal polynomials in the deformation-domain (i.e. the stress is expressed as a direct function of strain and strain-rate) [Ewoldt *et al.*, 2008], and as a consequence, the coefficients are independent of the time-domain representation of the input as sine or cosine. Second, it was proposed that the current convention for strain-controlled LAOS should be maintained as $\gamma(t)=\gamma_0 \sin\omega t$, and for stress-control LAOS the cosine basis should be used, $\sigma(t)=\sigma_0 \cos\omega t$. Although a sine representation for stress may be more natural experimentally (in order to start with zero imposed stress at time $t = 0$), it was noted that this zero-time reference is arbitrary when analyzing steady-state periodic oscillations in LAOS. The main advantage to the cosine representation is to keep the notation clean and more intuitive and to eliminate the need to include several negative signs within the definitions. Immediate discussion ensued with other participants at the symposium, and after thoughtful exchanges, a consensus formed around these suggested conventions. The mathematical details behind the Fourier coefficient ambiguity have important consequences for data processing of LAOS signals, as well as for the fundamental definitions of higher-harmonic material functions in LAOS.

(2) The mountains flowed -- Deborah, Péclet, Weissenberg, *et al.*

LAOS is a unique rheological probe because of the ability to impose a simple shear deformation with two independent time scales derived from the peak rate of strain of the flow, $t_s \sim \dot{\gamma}_0^{-1}$, and the frequency of oscillation, $t_0 \sim \omega^{-1}$ [Dealy, *Rheol. Bull.*, July 2010]. The ratio of the two time scales defines the maximum strain amplitude in a cycle: $\gamma_0 = t_0/t_s$. These time scales, in conjunction with a material's own spectrum of internal relaxation times, define a number of dimensionless groups. What are those numbers, in which limits do they relate to familiar flow regimes, and what insight is gained through their interpretation? This was a topic of a lively discussion that is summarized as follows.

The linear response regime is delineated by the region of phase space (t_s, t_0) in which the rheological properties of a material are insensitive to changes in t_s. The shear stress is linear in the rate of strain, and variation in the flow curves is driven by competition between material relaxation processes and the oscillation of the imposed flow. When, for instance, the stress response can be described as that of a single-mode Maxwell material (a spring of stiffness G in series with a dashpot of viscosity η), the material's internal relaxation mechanism is characterized by the time scale $\lambda=\eta/G$. The ratio of this time scale to the period of oscillation defines the Deborah number,

$$De=\lambda/t_0=\eta\omega/G$$

The period of oscillation takes on the role, "time of observation," which is classically used to define the Deborah number. Fittingly, the transition from principally elastic to principally viscous behavior is given by De approximately equal to 1.

For polymeric materials, the modes of internal relaxation (of which there may be many) may not be known *a priori*. Comparison and fitting of viscoelastic models is typically used to determine the appropriate time scale (or scales), t_i. In colloidal dispersions, stress relaxation is affected by diffusion of the colloids themselves. The characteristic internal relaxation time is taken to be a length scale squared divided by a characteristic colloidal diffusivity: $\lambda=a^2/D$. In this case a dimensionless group is defined:

$$\alpha=\lambda/t_0=a^2\omega/D$$

While homologous to the Deborah number, α depends on the choice of the length scale (particle size, inter-particle spacing, *etc*.) and diffusivity (short-time, long-time, self, collective, *etc*.). A particular choice is appropriate when $\alpha \sim 1$ corresponds to a key feature in frequency response of the suspension. This is the mechanical spectroscopic nature of linear response theory.

The steadily imposed deformation of materials is probed when the period of oscillation exceeds all other time scales $t_0 >> t_s, \lambda$. The flow is at most *slowly* varying in time. Here, flow curves are characterized by the ratio,

$$Wi=Pe=\lambda/t_s$$

The same distinction between polymeric and colloidal materials holds here. This ratio is called the Weissenberg number, Wi, in the polymer rheology community and the Péclet number, Pe, among colloid scientists.

The linear response regime is defined by the limit $Wi, Pe \rightarrow 0$, while the steady flow regime is one in which $De, \alpha \rightarrow 0$. Under LAOS then, there are three characteristic dimensionless groups: the maximum

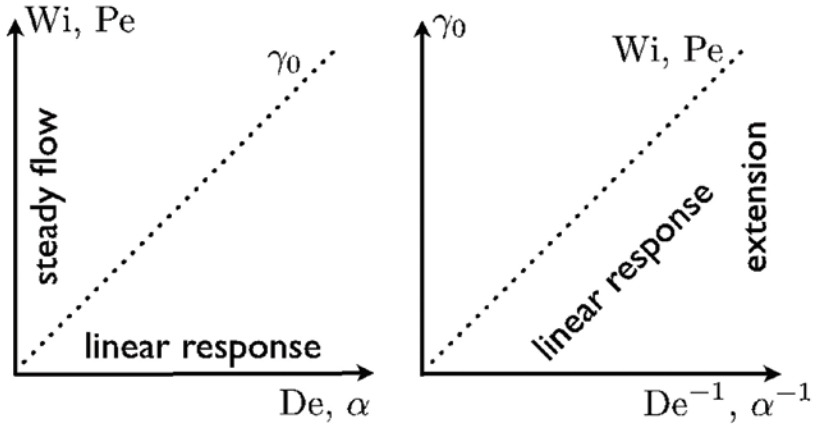

Figure 2: Two projections of the three dependent dimensionless groups: maximum strain amplitude, γ_0; Weissenberg, Wi, or Péclet, Pe numbers; and Deborah number, De, or α. The dotted lines along the diagonals indicate a path along which the denoted dimensionless group is constant. In the first projection, appropriate for viscous materials, regions corresponding to steady flow and linear response run parallel to axes with zero frequency and varying peak rate of strain, or zero peak rate of strain and varying frequency, respectively. In the second, appropriate for elastic materials, the region corresponding to rate-independent extension resides at small frequencies. The region of linear response lies below a diagonal denoting a peak rate of strain well below the characteristic relaxation frequency of the material.

strain amplitude, γ_0; De or α; and Wi or Pe. However, because there are only two independently imposed time scales, one of these dimensionless groups is auxiliary, for example

$$\gamma_0 = \mathrm{Wi}/\mathrm{De} = \mathrm{Pe}/\alpha$$

Therefore, the optimally designed LAOS experiment requires careful consideration of the relevant physics governing the stress response of the material. For instance, should we vary Wi and De independently in a material most sensitive to the maximum strain amplitude? Two revealing projections onto this three parameter domain are depicted in Figure 2. Here equivalent linear variation in the peak rate of strain and oscillation frequency leads to experiments with fixed maximum strain amplitude. Similarly, linear variation in the maximum strain amplitude and inverse oscillation frequency leads to experiments with fixed peak rate of strain. For rheologically-complex materials that are primarily viscous in nature (*e.g.* colloidal dispersions below the glass transition), the former projection may be preferable as the coordinate axes (vertical: $\dot{\gamma}_0$ or Wi or Pe, horizontal: ω or De or α) represent the realms of steady flow and linear response respectively. For materials with a prominent elastic response, the latter projection (vertical: γ_0, horizontal: ω^{-1} or De^{-1} or α^{-1}) represents defined, rate independent, extension on the far right and at low frequencies. Linear response is a region bounded by the diagonal along which the peak rate of strain is faster than the characteristic relaxation time of the material. Note that these phase spaces complement the traditional Pipkin phase space, (γ_0 vs. ω). However, unlike these projections, lines through the origin do not denote simple boundaries in Pipkin space. Figure 2 was developed as a succinct expression of the rheological space probed by LAOS that can aid in designing and interpreting LAOS experiments as well as facilitate comparison to theory.

Attendees enthusiastically supported the LAOS symposium and the lively discussion and debates during and following the presentations and discussions highlighted the excitement surrounding the LAOS technique. The value of bringing together experimentalists and theorists to identify and address the most pressing issues was most apparent, and there will be significant follow-up to this at the International Congress of Rheology in Portugal in August.

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tOrSANS: Measurement of atomic to mesoscopic microstructure simultaneous with rheology under LAOS

Rheologists are constantly challenged to elucidate the microstructural origins of the nonlinearities inherent in viscoelastic materials. Of specific interest here are the time-dependent microstructural changes for materials undergoing large amplitude oscillatory shear (LAOS). During the recent LAOS Symposium at UD, we introduced a novel technique to measure those microstructural changes of a material undergoing LAOS using small angle neutron scattering (SANS). Highlighted in this *Bulletin* are the first measurements using the time-resolved oscillatory rheo-Small Angle Neutron Scattering technique (*tOrSANS*), an instrument constructed for the SANS diffractometer D22 at the Institute Laue-Langevin (Grenoble, France) in conjunction with Lionel Porcar (ILL) and Aaron Eberle (NIST, now ExxonMobil). These geometries are currently available for use at the National Center for Neutron Research at NIST as well as at the Institute Laue Langevin, Grenoble. More information can be found at the Center for Neutron Research at UD (www.cns.che.udel.edu) or the Neutron Scattering Society of America's web site (www.neutronscattering.org).

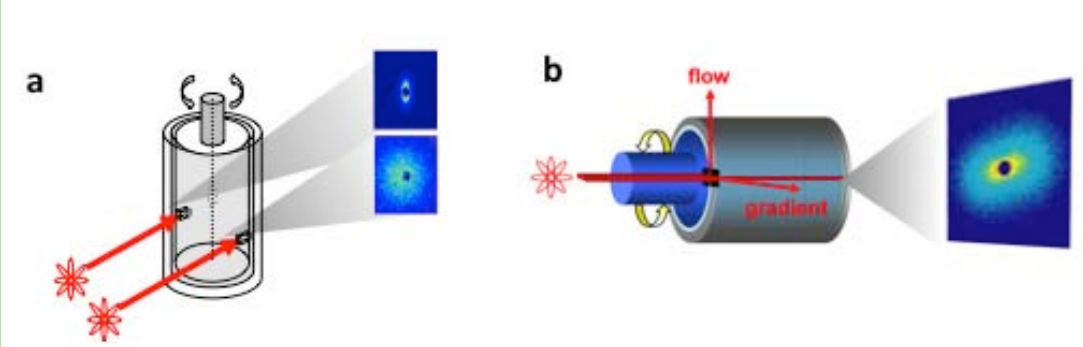

Figure 3. a) Geometry for *tOr-SANS* experiments in the 1,3 and 2,3 planes of flow and b) new geometry that directly probes the shear plane (1,2 plane of flow) (adapted from Helgeson et al. "Neutron transmission measurements of concentration profiles in non-homogeneous shear flows," 2010 Annual Report, NIST Center for Neutron Research, Gaithersburg, MD. p. 38-39, 2010).

The shear rheology is measured via a stress-controlled rheometer (Anton Paar MCR 501) outfitted with a custom-made quartz Couette geometry enabling simultaneous probing by neutrons (quartz is nearly invisible to neutrons) [Anton Paar, 2012]. Two planes of shear may be investigated using the Couette geometry configuration (Figure 3a).

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Viewing rheological data from LAOS experiments

There are thus a number of complementary and inter-connected ways to view the rheological information extracted from a LAOS experiment. These can be summarized graphically as shown in Figure 5. One may represent the sinusoidal input and associated linear (or nonlinear) output as time series (as shown in Figure 5(a). Alternatively by choosing a set of orthogonal basis functions (e.g. such as the Fourier series or Chebyshev polynomials T_n) one can quantify the spectral content of the nonlinear output signal as shown in Figure 5(b). When the output stress is decomposed into elastic and viscous components,

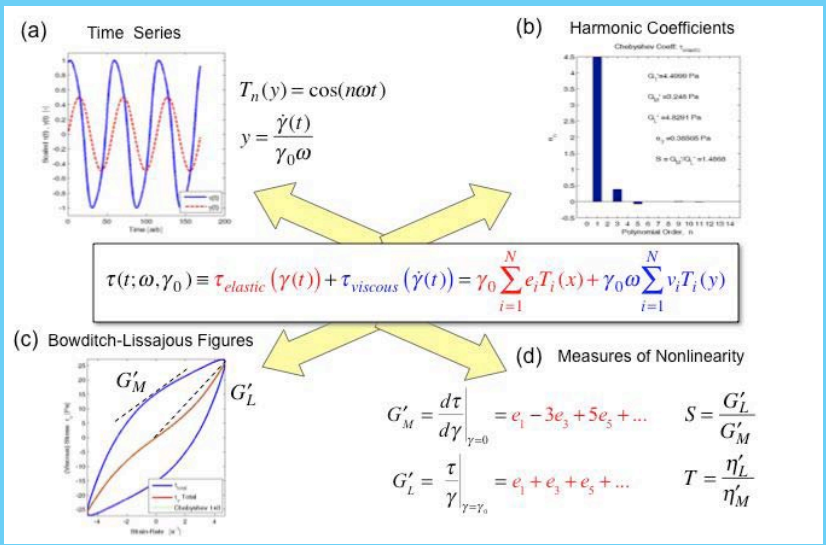

Figure 5. Various methods for plotting LAOS rheometry data.

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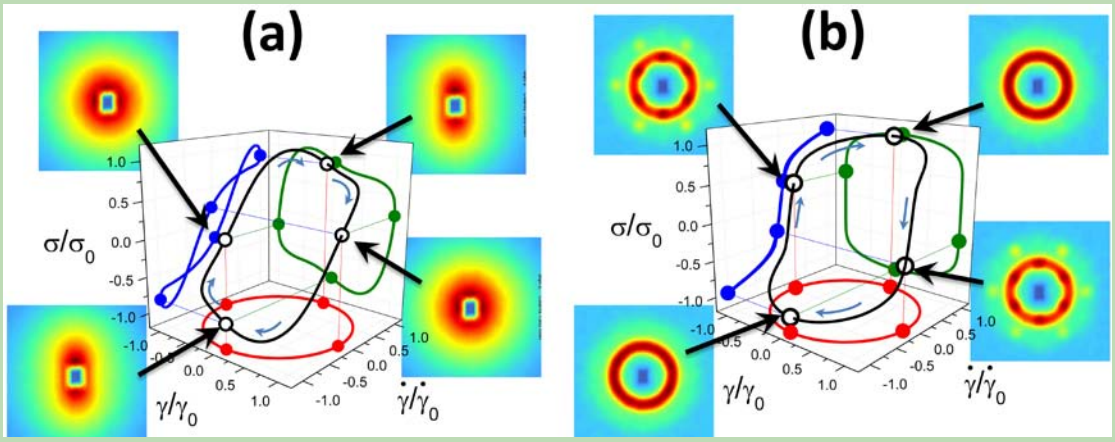

Figure 4. Stress response and SANS profiles during LAOS of (a) a 6 wt% aqueous solution of CPCl/NaSal, with molar ratio [NaSal]/[CPCl]= 0.5 at 25 °C ($\omega = 0.56$ rad/s and $\gamma_0 = 10$) and (b) a 24 wt% Pluronic F127/EAN solution at 40 °C ($\omega = 1$ rad/s and $\gamma_0 = 100$). The arrows indicate the direction of oscillation.

The neutron beam may be configured to travel along the velocity-gradient direction, thereby interrogating the flow-vorticity (1-3) plane of shear (this orientation is also known as "normal" or "radial"). Alternatively, the neutron beam is collimated into a thin slit and aligned parallel to the flow direction (also known as "tangential") thereby investigating the gradient-vorticity (2-3) plane. This instrument for examining complex fluids under steady shear has been recently documented by Porcar *et al.* [2011]. The recent review by [Eberle and Porcar, 2012] describes the use of this and related devices for structure-property determination across a broad range of materials and applications. What is new here? The *tOrSANS* technique allows one to interrogate materials while making dynamic oscillatory measurements. It requires the synchronization of the time-resolved mechanical deformation of the oscillation cycle and the time-resolved neutron detection, thus enabling real-time measurements of structure and rheology.

Time-resolved scattering methods rely on time binning the detector output into several memory modules [Butera *et al.*, 1996; Porcar *et al.*, 2004]. For LAOS this binning is done over an oscillation cycle. The technique can track microstructure changes occurring at frequencies ≤ 10Hz with time bins on the order of tens of milliseconds in length. This corresponds to 30-60+ bins per cycle. The measurement is repeated over many oscillation cycles (100-1000+ cycles) to achieve adequate statistics for SANS analysis. A prerequisite for choosing a material to interrogate with this technique is that it behaves the same for each subsequent oscillation cycle — in other words, the oscillatory stress response achieves an *alternance* state [Giacomin *et al.*, 2011]. Successful implementation of this technique to capture the changes in microstructure of a material during LAOS relies on careful synchronization of the oscillation period, binning time length and the number of repeated cycles, all of which depend upon the material under investigation.

Two samples were interrogated in the 1-3 plane using *tOr-SANS*: a wormlike micellar solution (WLM) and a polymeric micellar crystal. Figure 4a shows the three-dimensional representation of the Lissajous curves depicting the stress response during LAOS as a function of strain and strain rate for an aqueous solution of 6% cetylpyridinium chloride (CPCl)/sodium salicylate (NaSal) in 0.5M NaCl/D_2O. This model WLM has been extensively studied during steady shear by [Berret *et al.*, 1997; Rehage and Hoffmann, 1988; Rehage and Hoffmann, 1991] and many others. Also shown at indicated points are the SANS spectra obtained in the 1-3 plane (normal orientation). An isotropic pattern indicates no flow-induced orientation, such as would be observed at rest, whereas a highly oriented pattern indicates strong flow orientation. As observed, the points of highest shear rate correspond to highest orientation during the oscillation cycle, whereas the points of zero shear (and nearly zero stress) correspond to nearly un-oriented WLMs. The degree of orientation can be quantified from the pattern, structure-property relationships created, and this can be used to test constitutive models derived from microstructure.

Of particular interest are the secondary loops in the stress-strain rate projection of the Lissajous curves for WLM during LAOS. Ewoldt and McKinley [2010] attributed these secondary loops to a stress overshoot, a phenomenon commonly observed during the startup of flow of polymer solutions. Using *tOrSANS* in the 1-3 plane of shear, the microstructure is shown to transition from a highly entangled state of micelles (isotropic scattering profile) to an aligned state of the WLM (anisotropic profile). A further adaption of the *tOrSANS* method to flow start up was also performed (not shown here) to further investigate the relationship between these curious secondary loops in the Lissajous stress curve as a result of the transition between the highly

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