


Structure-Property Relationships via Recovery Rheology in Viscoelastic Materials

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The recoverable strain is shown to correlate to the temporal evolution of microstructure via time-resolved small-angle neutron scattering and dynamic shear rheology. Investigating two distinct polymeric materials of wormlike micelles and fibrin network, we demonstrate that, in addition to the nonlinear structure-property relationships, the shear and normal stress evolution is dictated by the recoverable strain. A distinct sequence of physical processes under large amplitude oscillatory shear (LAOS) is identified that clearly contains information regarding both the steady-state flow curve and the linear-regime frequency sweep, contrary to most interpretations that LAOS responses are either distinct from or somehow intermediate between the two cases. This work provides a physically motivated and straightforward path to further explore the structure-property relationships of viscoelastic materials under dynamic flow conditions.

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A long-standing challenge in understanding the out-of-equilibrium behavior of soft matter is to link microstructural rearrangements and the macroscopic flow properties. We show, via time-resolved rheo-small-angle neutron scattering (rheo-SANS), that such a link can be made, forming nonlinear rheological structure-property relations, by considering the evolution of the recoverable component of the strain.

The simultaneous collection of macroscopic rheological information and particle- or molecular-level data has been used to understand the interplay between material constituents that cover a wide range of length scales. Recent examples include the applications of scattering techniques in polymeric materials [1–7], confocal microscopy in colloidal systems [8–18], and simulation methods [19–24]. Despite these efforts, rheological structure-property relations remain incompletely understood. Oscillatory shearing provides a reproducible way to probe viscoelastic behaviors and has been used to study a wide array of soft materials [25–31]. Many processing conditions and practical applications of soft materials can be approximated by large amplitude oscillatory shear (LAOS) because it offers independent control of the length scales and timescales of structural rearrangements. As such, LAOS has been widely adopted as a model transient flow protocol capable of eliciting nonlinear responses [2,19,24,32–40].

Typical mathematically based descriptions of experimental responses to LAOS are based on Fourier transformation (FT), which represents the complex sequence of processes exhibited by soft materials in the time domain as a sum of harmonic contributions in the frequency domain [41], performing an averaging of sorts. Physical processes that take place sequentially over intervals of time shorter than a period of oscillation are therefore not easily

discerned via such analysis methods. The lack of a generic understanding of the higher harmonics [42] has limited the widespread adoption of these methods in time-resolved molecular-level studies [2,5,6,34,43,44].

In this Letter, we show that the recoverable strain, an often overlooked rheological metric that was first proposed by Weissenberg [45] and Reiner [46], provides an ideal basis for understanding the complex evolution of the microstructure and the shear and normal stresses of an industrially relevant entangled solution of wormlike micelles (WLMs) and a biopolymer network of fibrin (see Supplemental Material for material preparation [47]). In discussing the experimental reality of recovery tests, Lodge noted that typical experiments are constrained in one dimension. Constrained recovery was incorporated into his transient network theory of polymers, which makes a prediction about the relationship between recoverable strain and the first normal stress difference [48]. Several studies [48–54] have adopted this concept to study polymeric and nanocomposite systems, mostly under steady shear or creep flow. The central variable in these studies [45,46,48–52] is the amount of deformation recovered after the removal of shear stress. Reiner [46] elevated the importance of the recoverable deformation, calling it “the strain,” a definition that has not stuck. Despite significant early efforts, measurements of constrained recovery remain limited, and have not, until now, been applied to the study of structure-property relationships under oscillatory shearing.

The two polymeric materials we study have very different behaviors, which allows us to more clearly illustrate the benefits of our new approach. Wormlike micelles undergo many breakage and reformation events on the timescale of reptation, leading to a Poisson distribution of length scales at equilibrium, and a single relaxation time [55]. They have

therefore been used to study nonlinear flow behaviors of entangled linear and branched polymers [1,56–60]. Fibrin networks are known to possess flow properties that are distinct from common synthetic polymers [35,61–63] because they are primarily elastic and stiffen when strained, protecting tissue from large deformations.

We use *in situ* rheo-SANS to simultaneously monitor the alignment of micellar segments as well as the recovery rheology. Measurements are made in the steady alternating state when all initial transience has decayed. An iterative constrained recovery procedure is employed at 200 distinct evenly spaced instants along an oscillation (see Supplemental Material [47] for detailed experimental protocol, which includes Ref. [64]). The unrecovered part of the strain γ_{un} is the strain the system ultimately recovers to, and the recoverable strain γ_{rec} is the part of the total strain that is elastically recovered. All rheo-SANS measurements are made with an Anton-Paar MCR-501 rheometer with a concentric-cylinder Couette geometry at the NIST Center for Neutron Research (NCNR) on beam line NGB-30. Normal stress differences and additional constrained recovery tests are measured using a DHR-3 rheometer (TA Instruments) with a 4-deg cone and plate geometry.

The alignment of micellar segments is measured in the velocity-gradient (1-2) and velocity-vorticity (1-3) planes using time-resolved rheo-SANS techniques [44,65]. A q range of 0.006 to 0.03 $1/\text{\AA}$ is probed, corresponding to the rodlike scattering of the micelle segments (see Supplemental Material [47]). SANS data are reduced according to NCNR guidelines [66]. A temporal deconvolution protocol [67] is

used to enhance the resolution and accuracy of the measurements.

Oscillatory shearing from WLMs with amplitudes ranging from the linear (Small-amplitude oscillatory shear) to the nonlinear (LAOS) regimes is performed at Deborah numbers ($De = \omega\lambda$, where ω is the angular frequency and λ is the longest relaxation time) of 0.0625 ($\omega = 0.25$ rad/s) and 0.25 ($\omega = 1$ rad/s), where the inertial effects of the stress-controlled procedure are negligible. The traditional elastic and viscous Lissajous curves of the WLMs are displayed in Figs. 1(a) and 1(e) and Figs. 1(c) and 1(g), respectively. The distorted elastic Lissajous curve and the secondary loops of the viscous Lissajous curve indicate that the system undergoes a complex sequence of processes over the course of an oscillation. FT-based analysis schemes quantify the departure from linearity in an average sense, taking the response from an entire period of oscillation as the object to be analyzed. The resulting harmonics therefore have no clear physical relation to the structure at any particular instant. We contrast this with the underlying principle of time-resolved rheo-scattering techniques [44,67], which is that the structure and rheology at any one instant are causally related. A framework that correlates the rheology with real-time structural evolution is needed.

Strain can be decomposed into recoverable and unrecoverable components [45,46]. Recoverable strain is elastic, while viscous properties are dictated by the rate at which strain is acquired unrecoverably. Elastic and viscous Lissajous curves that reflect this view are therefore presentations of stress versus recoverable strain ($\sigma - \gamma_{\text{rec}}$) and

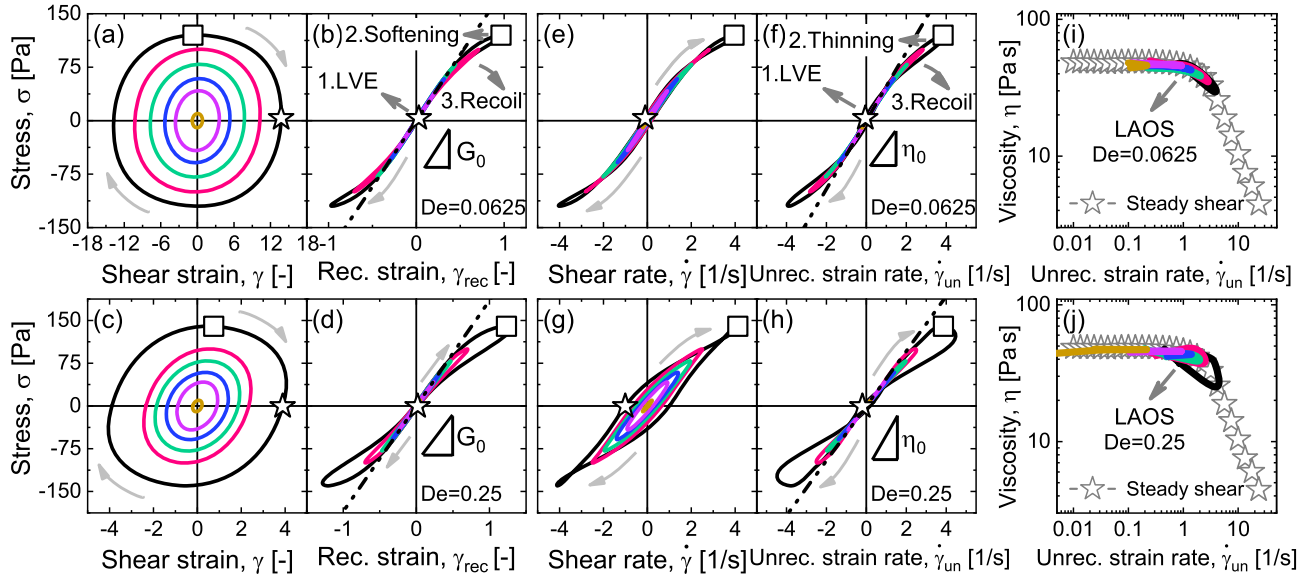


FIG. 1. Lissajous curves in the traditional ($\sigma - \gamma$, $\sigma - \dot{\gamma}$) and proposed ($\sigma - \gamma_{\text{rec}}$, $\sigma - \dot{\gamma}_{\text{un}}$) frames at $De = 0.0625$ (a),(b),(e),(f) and $De = 0.25$ (c),(d),(g),(h) from WLMs. The lines in the proposed elastic and viscous views have slopes equal to the plateau modulus $G_0 = 180\text{Pa}$ and the zero-shear viscosity $\eta_0 = 48\text{ Pa s}$. The stars and squares correspond to zero and maximum recoverable strain at the largest amplitude, respectively. Shear viscosity $\eta = \sigma/\dot{\gamma}_{\text{un}}$ determined from LAOS on top of the steady-shear flow curve at $De = 0.0625$ (i) and $De = 0.25$ (j).

stress versus unrecoverable strain rate ($\sigma - \dot{\gamma}_{\text{un}}$). The slopes of the $\sigma - \dot{\gamma}_{\text{rec}}$ and $\sigma - \dot{\gamma}_{\text{un}}$ curves for Hookean solids and Newtonian fluids retain their clear meaning of being the modulus and viscosity, respectively. Plots of stress versus recoverable strain for a Newtonian fluid will have undefined slopes because purely viscous fluids acquire no strain recoverably. Our proposal therefore removes the current possibility of defining a modulus for a purely Newtonian fluid or a viscosity for a purely Hookean solid.

The proposed elastic Lissajous curves, $\sigma - \gamma_{\text{rec}}$, from WLMs under LAOS are shown in Figs. 1(b) and 1(d). The new presentations show significant differences from the traditional plots that use the total strain. At the instants close to the total strain extremes [stars in Figs. 1(a) and 1(c)], the recoverable strain is nearly zero, indicating that the material is closest to its equilibrium configuration and is therefore undeformed. Similar behavior has been observed in polymeric and colloidal systems [68–72], where a constant linear-regime elasticity exists near the strain extrema under LAOS. At both investigated frequencies, the $\sigma - \gamma_{\text{rec}}$ curves show straight lines of equal slope at $|\gamma_{\text{rec}}| < \sim 0.5$, which indicates an elastic modulus of 180 Pa. This value corresponds to the plateau modulus [indicated by lines in Figs. 1(b) and 1(d)], $G_0 = 180$ Pa, which is typically determined at much higher frequencies ($De \gg 1$), indicating that the elastic modulus of the transient micellar network is constant across a wider range of lower frequencies than previously thought [Fig. S2(a) [47]]. We contrast these observations with the storage modulus, which is frequently taken as a measure of elastic modulus, which has values of $G' (De = 0.0625) = 0.62$ Pa and $G' (De = 0.25) = 10.3$ Pa (Fig. S7 [47]).

The new viscous Lissajous curves from WLMs under LAOS, $\sigma - \dot{\gamma}_{\text{un}}$, are shown in Figs. 1(f) and 1(h). Similar to the $\sigma - \gamma_{\text{rec}}$ curves, straight lines with constant slopes are obtained in the small and intermediate amplitudes. This slope is independent of frequency and equal to the zero-shear viscosity η_0 determined from steady shearing (straight lines in Fig. 1). The viscosities determined during LAOS and steady shearing are favorably compared in Figs. 1(i) and 1(j). Over the course of an oscillation at $De = 0.0625$, the two protocols yield similar data. Even at the higher frequency ($De = 0.25$), the viscosity determined from the linear viscoelastic (LVE) and thinning portions in LAOS is consistent with the flow viscosity on the upward sweep.

The determination of a constant elastic modulus and a constant viscosity in the linear regime across a broad range of frequencies requires reconciliation with the frequency dependence of the dynamic moduli, G' and G'' . The storage and loss moduli are known to represent the average amount of energy stored and dissipated per unit volume over a cycle of oscillation [73], while the elastic modulus presented here is the modulus in a force-extension perspective. Having determined the elastic modulus and the viscosity, and the amount of deformation that is recoverable

and unrecoverable at each instant, the instantaneous energy storage and dissipation rate can be quantified at any time: $W_s(t) = \frac{1}{2}G(t)\dot{\gamma}_{\text{rec}}^2(t)$ and $\dot{W}_d(t) = \eta(t)\dot{\gamma}_{\text{un}}^2(t)$. Averaging the instantaneous energy storage and dissipation over an oscillation results in metrics that are related to the dynamic moduli: $W_{s,\text{av}} = (\gamma_0^2/4)G'$ and $\dot{W}_{d,\text{av}} = (\gamma_0^2/2)\omega G''$. We show that following an energetic analysis, one can transform from the elastic modulus and viscosity to the energetic parameters, G' and G'' (Figs. S7 and S8 [47]). The linear-regime dynamic moduli can therefore be obtained within a LAOS response if one focuses exclusively on the response to small recoverable strains (Fig. S7 [47]). We suggest on this basis that LAOS tests, rather than being treated as being fundamentally different from other tests [74–76], sequentially present information regarding the linear-regime relaxation spectrum and the steady-state flow curve, and how the material transitions between the two states.

At instants when the total strain is large (stars in Fig. 1), the recoverable strain and the unrecoverable strain rate are minimal, and the WLMs exhibit linear viscoelasticity characterized by G_0 and η_0 . Measuring the evolution of the recoverable and unrecoverable strains establishes a clear sequence of processes during a period of oscillation: LVE behavior followed by both softening and thinning, and recoil, taking place twice per oscillation.

Unlike the significant differences between the total and recoverable strains in WLMs, the fibrin network shows nearly complete strain recovery (Fig. S3 [47]). The oscillatory shearing response of fibrin at an imposed frequency of 1 rad/s is presented in Fig. 2(a). Across all deformation amplitudes, when $|\gamma_{\text{rec}}| < \sim 0.05$, we observe straight lines with the same slope, indicating a single modulus that is approximately equal to G' . This equivalence is because $\gamma_{\text{rec}} \approx \gamma$, which is not true for elastic liquids, such as the WLMs.

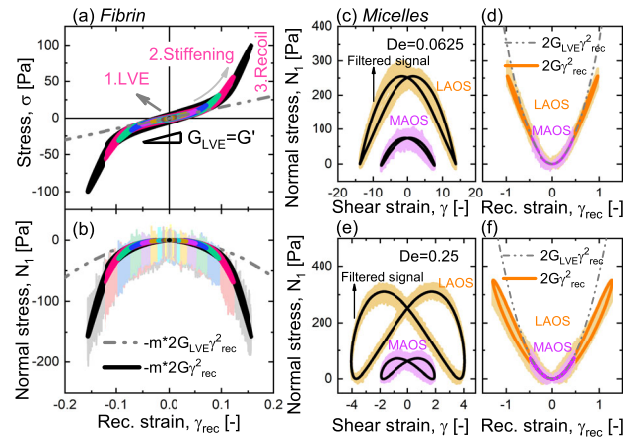


FIG. 2. Shear (a) and normal stress (b) are plotted against the recoverable strain from the fibrin. Normal stress from WLMs with respect to the strain γ and the recoverable strain γ_{rec} at $De = 0.0625$ (c),(d) and $De = 0.25$ (e),(f).

With increasing recoverable strain, the fibrin stiffens [35]. Immediately after the recoverable strain reversal, the fibrin recoils to its LVE configuration. Our sequencing of the fibrin responses under oscillatory shearing is in resonance with other studies that account for the unique mechanical properties as a sequence of structural hierarchy with respect to the (recoverable) strain [63,77,78].

While many studies have focused exclusively on the shear stress response to LAOS, normal stress differences have received little attention [79–81]. A full exposition of the extra stress tensor necessarily involves both normal and shear components. Janmey *et al.* [80] studied fibrin networks and saw negative normal stresses under shear. A micromechanical model has been proposed and used to study normal stress differences of soft glasses [81]. Despite these works, a clear link between normal stress differences and other components of the extra stress tensor under LAOS remains incompletely understood. In their study of silicone polymers, Benbow and Howells concluded that “the observation of recoverable elastic strain may be taken as a necessary and sufficient condition for observable normal stress” [50]. Their conclusion, however, was drawn from steady, unidirectional shearing, and has not been examined under transient shear, nor linked to any structural measure.

The first normal stress difference N_1 from WLMs is shown in Figs. 2(c) and 2(e), where the raw response was filtered to remove noise (black lines). When plotted against the total strain, typical bow-tie shapes are observed. The normal stress trajectory also depends strongly on the imposed amplitude, as the weakly nonlinear response obtained from medium amplitude (MAOS) and the fully nonlinear response (LAOS) clearly differ. When the normal stress differences are plotted in the recoverable strain domain, $N_1 - \gamma_{\text{rec}}$, there is collapse onto the same parabolic master curve, showing that the MAOS and LAOS cases undergo similar sequences within a cycle of oscillation. We therefore observe a quadratic dependence of the normal stress difference on the recoverable strain.

To form a more quantitative understanding of the normal stress difference, we apply an expression derived by Lodge, from his transient network theory of polymers [48]. Lodge showed that the ratio of the first normal stress difference to the shear stress under constrained recovery is $N_1/\sigma = 2\gamma_{\text{rec}}$. We exploit this relationship to provide a description of the first normal stress difference with respect to the recoverable strain, $N_1(t) = 2G(t)\gamma_{\text{rec}}^2(t)$, where $G(t)$ is the recoverable strain-dependent elastic modulus determined from the $\sigma - \gamma_{\text{rec}}$ plots. The calculated N_1 values are shown in Figs. 2(d) and 2(f) in comparison with the experimental WLM results at the two frequencies. In both cases there is exceptional agreement. Additionally, we show the theoretical prediction from the linear regime, $N_1(t) = 2G_{\text{LVE}}\gamma_{\text{rec}}^2(t)$ as dashed lines, and note the departure from LVE behavior at $\gamma_{\text{rec}} \approx 0.5$, in agreement with the shear stress rheology.

The fibrin normal stress is shown in Fig. 2(b) as a function of the recoverable strain. The negative normal stress indicates that the fibrin contracts under shearing [80]. Despite having fundamentally distinct structure and properties from WLMs, the magnitude of the normal stress still increases quadratically with the recoverable strain. While it is known that biopolymers do not follow classical rubbery elasticity [61], we empirically observe that the normal stress is well described by $N_1(t) = -2mG(t)\gamma_{\text{rec}}^2(t)$, where m is found to be 5. Having $m > 1$ agrees with the finding that these biopolymers tend to show larger normal stresses than synthetic polymers [78,80]. With the results from the two distinct systems, we conclude that the recoverable strain dictates not only the shear stress but also the complex normal stress.

The experimentally determined physical processes observed in the macroscopic rheological responses are mirrored in the microstructural evolution of the WLMs as shown in Fig. 3 for the $De = 0.25$ case for a total strain amplitude of $\gamma_0 = 4$. Shown in Fig. 3(a) is the $\sigma - \gamma_{\text{rec}}$

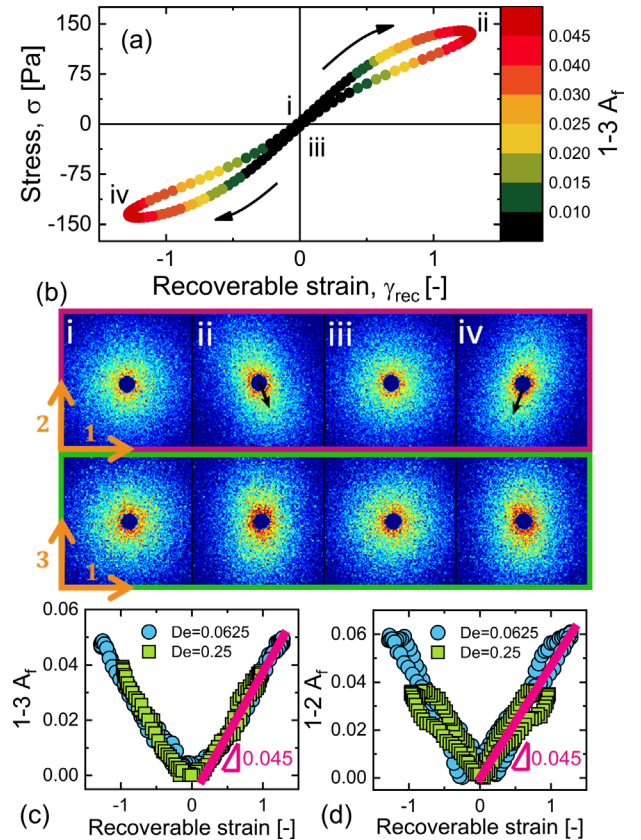


FIG. 3. Correlation between macroscopic rheology and microscopic structure. (a) Proposed elastic Lissajous figure ($\sigma - \gamma_{\text{rec}}$) coupled with 1-3 alignment factor A_f denoted by the color scale. (b) 2D SANS patterns at zero (i and iii) and maximum (ii and iv) recoverable strain in both velocity-gradient and velocity-vorticity planes. Alignment factors in the 1-3 (c) and 1-2 (d) planes are plotted as functions of the recoverable strain, showing the same proportionality constant of 0.045.

figure, with a color scale that reflects the degree of alignment observed in the 2D SANS patterns shown in Fig. 3(b). We quantify the alignment of the micellar segments by defining an alignment factor (A_f) as $A_f = \int_0^{2\pi} I_c(q^*, \phi) \cos[2(\phi - \phi_0)] d\phi / \int_0^{2\pi} I_c(q^*) d\phi$, where $I_c(q^*, \phi)$ is the azimuthal intensity over q^* and ϕ is the azimuthal angle with the segmental q range $q^* = 0.006$ to 0.03 $1/\text{\AA}$. ϕ_0 represents an orientation angle. The alignment factors in the 1-2 and 1-3 planes are presented as functions of the recoverable strain in Figs. 3(c) and 3(d).

Contrary to the established view that shear-induced alignment correlates with shear rate at low frequency and strain at high frequency [6], we observe that the alignment of micellar segments is linearly proportional to the magnitude of the recoverable strain regardless of the imposed frequency. Further, the same proportionality coefficient is determined in both the 1-2 and 1-3 planes: $A_f = 0.045|\gamma_{\text{rec}}|$. We therefore build a remarkably consistent physical picture: when the recoverable strain is small, linear viscoelastic responses are elicited, even under LAOS, and the scattering patterns are identical to equilibrium conditions with no alignment of the micellar segments. As the magnitude of the recoverable strain increases, so too do the alignment factor and shear and normal stresses. Even when the modulus begins to drop at large $|\gamma_{\text{rec}}|$ [points ii and iv in Fig. 3(a)], the alignment is still linearly dependent on $|\gamma_{\text{rec}}|$.

Biopolymers such as fibrin are known to align and stretch with strain [82], exhibiting unique force-extension relationships [62,80]. We have shown that almost all strain is acquired recoverably by fibrin networks. Our results from both the shear-thinning linear entangled micelles and the strain-stiffening fibrin networks therefore show that it is the recoverable strain that provides the basis of accurate nonlinear structure-property relations of soft polymeric materials.

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