Non-integer asymptotic scaling of a thixotropic-viscoelastic model in large-amplitude oscillatory shear

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Abstract

We demonstrate that a simple thixotropic-viscoelastic constitutive model has a unique rheological fingerprint that fits data that no other model is known to fit. The key rheological signature is the non-integer power law scaling in asymptotically-nonlinear large-amplitude oscillatory shear (LAOS), sometimes called medium-amplitude oscillatory shear (MAOS). We begin with a minimalist constitutive model that contains only five material parameters, which we show to be the minimum required to capture all fundamental thixotropic and viscoelastic phenomena. We demonstrate that the low amplitude power-law scaling of the asymptotically nonlinear first and third harmonic stresses (scaling as input amplitude squared) is different than that observed in all other known constitutive model predictions (which predict nonlinearities to scale as input amplitude cubed). We then explore the effects of a sixth model parameter n (the most common addition to thixotropic models in the literature), introduced to govern the order of the kinetic rate equation. We show that this parameter gives further variability to this unique signature (with nonlinearities scaling as $\sigma \sim \gamma^{n+1}$). Finally, we compare these model signatures to the experimental signature of a real thixotropic material, demonstrating that models with non-integer amplitude scaling are required to match experimental observations.

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I. Introduction

Thixotropic fluids are commonly modeled by coupling a tensorial rheological constitutive equation to a scalar variable to track the ‘structure’ of the fluid, with the structure evolving by a kinetic rate equation. A precursor to this type of constitutive model was introduced in 1938 [1], while the earliest example to take the currently common form was proposed by Moore in 1959 [2]. Since then a multitude of unique constitutive models have been written and much study has been devoted to understanding thixotropy, connecting microstructural behavior to macro level properties, and accurately modeling rheological phenomena on a continuum level [3]. A general form of the structural kinetic equation, using ξ as the structure parameter that can simplify to other forms seen in the literature is (assuming one-dimensional homogeneous simple shear) [4]

$$\frac{d\xi}{dt} = -k_1 \dot{\gamma}^a \xi^b + k_2 \dot{\gamma}^c (1 - \xi)^d. \quad (1)$$

Table 2 of [4] details which subsets of parameters are employed in various models. The minimalist kinetic equation sets $a = b = d = 1$ and $c = 0$, resulting in the two parameter kinetic equation

$$\dot{\xi} = \kappa_A (1 - \xi) - \kappa_D \xi |\dot{\gamma}|, \quad (2)$$

where $\dot{\xi} = d\xi/dt$. This form was the first to appear in the literature, and bounds ξ between 0 and 1 [2].

Eq. (2) is frequently chosen because conceptually framing the structure kinetics by an aggregation parameter (κ_A) and a destruction parameter (κ_D) is simple and intuitive. As the equation is expanded and simple common variations on this basic form are considered, it will be helpful to rewrite Eq. (2). Rather than an aggregation parameter and a destruction parameter, a mathematically equivalent equation can be written that instead employs a rate parameter and a

critical driving parameter (either a critical stress or a critical strain rate). This can be convenient when considering stress-driven kinetics and strain-driven kinetics, as it provides a single equation that describes both models. This change also makes the breakdown driving parameter dimensionless, which is advantageous when considering the addition of an exponent to that term. The expression [5]

$$\dot{\xi} = k[1 - \xi(1 + \Gamma)] \quad (3)$$

is equivalent to Eq. (2) using the correspondence

$$\kappa_A = k; \kappa_D = \frac{k}{\dot{\gamma}_c} \text{ or } \kappa_D = \frac{k}{\sigma_c} \quad (4)$$

where $\dot{\gamma}_c$ and σ_c a Γ is the forcing parameter defined as

$$\Gamma = \frac{|\dot{\gamma}|}{\dot{\gamma}_c} \text{ or } \Gamma = \frac{|\sigma|}{\sigma_c}. \quad (5)$$

This reframing also carries simple interpretations, as the parameters can be connected to physical properties. The rate constant k can be connected to a material timescale (frequently a Brownian timescale), while the critical stress or strain rate can be connected to the microstructural energy required to break down structure (e.g. the DLVO potential of a colloidal system) [4].

This form is also advantageous when changing the order of reaction of the equation, as the driving parameter Γ is dimensionless, which avoids strange dimensionalities of model parameters when raising the driving term to an exponent, leading to easier physical interpretations. Many models that introduce an exponent simply raise the strain rate to a power n , which means that the units of $[\kappa_D] \doteq s^{n-1}$ where n is not necessarily an integer. Raising the dimensionless parameter Γ to the n achieves the same phenomenological effect on the model, but without the dimensions of a model parameter being dependent upon the value of another

parameter. Therefore, Eq. (3) can be further generalized, incorporating an extra parameter to govern the order of reaction n , given as [5]

$$\frac{d\xi}{dt} = k \left[1 - \xi \left(1 + \Gamma^n \right) \right]. \quad (6)$$

In this form, the definition of the Weissenberg number is

$$\text{Wi} = \Gamma, \quad (7)$$

hence either

$$\text{Wi} = \frac{\dot{\gamma}}{\dot{\gamma}_c} \quad \text{or} \quad \text{Wi} = \frac{\sigma}{\sigma_c}, \quad (8)$$

depending on the parameter that drives destruction. In either framework, it is possible to write a model such that breakdown of structure is driven by stress (which we will call ‘stress-kinetic’) or by strain rate (‘strain-kinetic’). Strain-kinetic is more prevalent in the literature [4,6], but stress-kinetic has also been explored [5,7].

In order to complete the model, the kinetic equation is coupled to a constitutive equation, which relates the stress and rate of strain tensors as a function of the evolving structure parameter ξ . The focus of this study is to examine trends resulting from the characteristics of the kinetic equation, therefore a minimalist form is chosen for the constitutive equation, employing a Thixoelastic Jeffreys model for the shear stress component $\sigma = \sigma_{12}$,

$$\frac{\dot{\sigma}}{G_0} + \frac{\sigma}{\eta_A} = \left(\xi + \frac{\eta_\infty}{\eta_A} \right) \dot{\gamma} + \frac{\eta_\infty}{G_0} \ddot{\gamma} \quad (9)$$

which is the simplest form that captures key phenomena of both thixotropy and viscoelasticity. See [8] for a discussion of the tradeoffs in choosing the number of model parameters to include, as well as the characteristics of reduced models (e.g. simple shear-thinning). There are many

different microstructures that give rise to thixotropy, and the relationship between microstructural physics and model parameters has only been explored in a few specific cases. For a discussion of the microstructural side of this problem, see [4].

To demonstrate the unique features of this model, this study will explore its signature in large amplitude oscillatory shear (LAOS). Of particular interest is the low-amplitude scaling in asymptotically-nonlinear LAOS [9]. Whereas other known models (such as those summarized in [10,11]) have shear stresses that first scale linearly $\mathcal{O}(\gamma_0)$, and then nonlinearly as $\mathcal{O}(\gamma_0^3)$, the model of Eqs. (6) and (9) will be shown to have asymptotic nonlinearities scaling as $\mathcal{O}(\gamma_0^m)$, where $m = 1 + n$. Experimental data has also shown that the viscoelastic prediction of nonlinearities arising initially at $\mathcal{O}(\gamma_0^3)$ is seen in materials such as polycarbonate and polymethyl methacrylate [12], polystyrene [13,14], high density polyethylene [11], wormlike micelle surfactant solution [15], and polyvinyl alcohol borax hydrogel [9].

Section II explores the model signature when strain-rate dependent kinetics are chosen, with a controlled strain input (LAOStrain). Section III demonstrates that the unusual results seen for this case are not dependent upon choices of stress or strain (neither as the controlled input nor the driver of structure breakdown). Section IV then presents experimental data from a thixotropic soft glassy suspension (Carbopol in water) which exhibits the unique signature predicted by this model, demonstrating that models with non-integer scaling are required to match experimental observations.

II. Model in LAOStrain with Strain-kinetics at Varying n

A useful framework for characterizing constitutive models is asymptotically-nonlinear large amplitude oscillatory shear. Linear oscillatory shear provides two descriptive material functions (e.g. $G'(\omega)$ and $G''(\omega)$), and asymptotically-nonlinear oscillation provides four additional material functions (e.g. $[e_1](\omega)$, $[e_3](\omega)$, $[v_1](\omega)$, and $[v_3](\omega)$) [9], describing leading-order nonlinear effects as a function of the timescale $1/\omega$. A nonlinear contribution is always present in a rheological output signal, but when the amplitude of the input signal is sufficiently small ($Wi \ll 1$) nonlinearities become comparatively negligible. As the input amplitude (e.g. strain amplitude or strain-rate amplitude) increases, each of the higher order nonlinear outputs initially scales as a constant times a power of the input amplitude [9]. Outside of very small amplitudes, this power series expansion does not hold, but in the amplitude-intrinsic regime (defined as where the nonlinear coefficients scale as a power-law of the input amplitude) the coefficients in the power series expansion can be computed (or measured), and provide a characterization of a nonlinear response that is a function of frequency, but not of amplitude. These material functions also carry physical interpretations that lend insight into the model or material behavior [9].

It is common practice to express the stress output in LAOStrain as a Fourier series. Due to the orthogonality of strain and strain rate in the input, a Fourier representation can be used. For an input of $\gamma = \gamma_0 \sin(\omega t)$, the stress harmonics can be expressed as [16]

$$\sigma = \sum_{n \text{ odd}}^{\infty} \sigma'_n \sin(n\omega t) + \sigma''_n \cos(n\omega t) . \quad (10)$$

Only odd n appear when the material exhibits shear symmetry, i.e. the material behaves the same in both shear directions, but with opposite signs. Even harmonics may appear when this shear

symmetry is violated [17], e.g. with anisotropic materials, non-steady state oscillations (frequently the result of a start-up transient), or other non-periodic responses including dynamic wall slip [18]. Under standard assumptions, the frequency content will contain only odd harmonics. Similarly, odd powers are historically used for asymptotic expansions of the stress amplitudes with respect to strain amplitude [11,13,15,19,20]. As will be shown here, the Thixoelectric Jeffreys model requires all integer powers, including even powers [8], in an asymptotic strain expansion. This is unique among currently published model predictions.

Beyond Fourier coefficients, which describe time-domain waveforms, it can be beneficial to explore material functions in the deformation domain, which more directly describe Lissajous curves of stress–strain and stress–strain-rate. Similar to Eq. (10), Chebyshev coefficients are defined by the equations [21]

$$\sigma = \gamma_0 \sum_{n \text{ odd}} e_n(\omega, \gamma_0) T_n(x) + \gamma_0 \omega \sum_{n \text{ odd}} v_n(\omega, \gamma_0) T_n(y) \quad (11)$$

$$x = \frac{\gamma(t)}{\gamma_0}, y = \frac{\dot{\gamma}(t)}{\dot{\gamma}_0}, \quad (12)$$

where T_n are the orthogonal Chebyshev basis functions of the first kind. The conversion between these material functions and the stress harmonics defined in Eq. (10) is given by the expressions

$$e_1 = \frac{\sigma'_1}{\gamma_0}, e_3 = \frac{-\sigma'_3}{\gamma_0}, v_1 = \frac{\sigma''_1}{\gamma_0}, v_3 = \frac{\sigma''_3}{\gamma_0} \quad (13)$$

for an input of $\gamma = \gamma_0 \sin(\omega t)$. The signs of the third harmonic Fourier stress components are dependent upon the choice of input signal (sine or cosine) [22].

Many constitutive models predict a linear shear stress response at $\sigma \sim \mathcal{O}(\gamma_0)$, no shear stress contributions at order $\sigma \sim \mathcal{O}(\gamma_0^2)$, and leading order shear nonlinearities occurring at order

$\sigma \sim \mathcal{O}(\gamma_0^3)$, including the very general model known as the memory integral expansion (or Boltzmann superposition expansion) [12]. That is, shear stresses occur at odd orders of strain amplitude (normal stress differences occur at even orders). The model detailed in Eqs. (6) and (9) contradicts this long-standing implicit assumption. Our prior work [8] details the response of this model with $n = 1$, demonstrating that leading order nonlinearities arise at order $\sigma \sim \mathcal{O}(\gamma_0^2)$. An examination of the effect of the parameter n as defined in Eq. (6) will show that the order of reaction n changes the scaling of the asymptotic shear nonlinearities to be $\mathcal{O}(\gamma_0^{n+1})$. While prior results have shown integer scaling, there is no reason in perturbation theory restricting these exponents to integer values [23].

In the model of Eqs. (6) and (9), all nonlinearities arise from variation in structure ξ over time. Thus, a first step to understanding the effect of the power law exponent on the nonlinearities in the model response is to explore the temporal changes to the structure at varying values of n . First, it is important to note that the behavior with changing n is fundamentally dependent on the values of the forcing parameter Γ relative to 1. For a fixed value of strain rate (or stress) the steady-state value of ξ is

$$\xi_{ss} = (1 + \Gamma^n)^{-1}. \quad (14)$$

The differential equation governing the evolution of structure is first order in time, hence at any point during an oscillation ξ is tending toward its steady-state value (based on the instantaneous forcing Γ). Therefore it is the function Γ^n in Eq. (14) that expresses the tendency of ξ to change in response to a dynamic input. Figure 1 shows Γ^n as a function of Γ for three different values of n (0.5, 1, and 2). Note that $n = 1$ represents the commonly used simpler kinetic equation shown in Eq (3).

Figure 1 Plot of Γ^n vs Γ at several values of n (specifically 0.5, 1, and 2), showing that the direction of the trend is dependent upon whether each of n and Γ are less than, equal to, or greater than one. The forcing parameter Γ (as a function of time) can be a function of either stress or strain rate, and that the magnitude of Γ^n dictates the magnitude of nonlinearities.

As a function of n , the strength of forcing (magnitude of Γ) may increase or decrease, depending on the value of Γ . For small forcing $< \Gamma 1$, increasing $n > 1$ decreases the forcing Γ^n , whereas for large forcing $> \Gamma 1$ increasing $n > 1$ increases Γ^n . This observation will inform the trends that will be seen in structure variations at changing n . The majority of this work will focus on small

amplitude deformations where $\Gamma \ll 1$ in this regime smaller n will yield stronger nonlinearities.

Figure 2 shows structure ξ as a function of time in response to oscillatory shear $\gamma(t) = \gamma_0 \sin(\omega t)$. Results are from simulation of Eq. (6) with $k = 1$ and $\dot{\gamma}_c = 1$ at varying values of n . The results shown are for steady-state oscillations (i.e. at long time), neglecting startup transients.

Figure 2 Structure as a function of time (at steady-state) at varying values of n for $k=1$, $\dot{\gamma}_c=1$ (equivalent to $\kappa_A=1$, $\kappa_D=1$), and an input signal of $\dot{\gamma}=\sin(\omega t)$. For these parameters $\Gamma_0=1$, thus $0 \leq |\Gamma| \leq 1$; in this regime decreasing n yields stronger nonlinearities (Figure 1)

In this case, $\Gamma_0=1$, thus $0 < |\Gamma| < 1$. Changing the value of n has a slight effect on the shape of the curve, but a significant effect on the average value of ξ . Here, $\Gamma^n \leq 1$, thus smaller n causes more breakdown of structure for a particular value of Γ (Figure 1). Thus, smaller n produces less structure, and lower average value of ξ in Figure 2. In contrast, increasing n keeps a larger average value of structure, but with larger peak-to-peak variation within the cycle.

Non-constant structure causes the constitutive model nonlinearities (Eq. (9)). This depends on the values of the model parameters, in particular Γ_0 and n , as shown in Figure 3.

Figure 3 Structure as a function of time at varying values of n for a) $k = 0.1$, $\dot{\gamma}_c = 0.01$, b) $k = 10$, $\dot{\gamma}_c = 1$, c) $k = 0.1$, $\dot{\gamma}_c = 1$, d) $k = 10$, $\dot{\gamma}_c = 100$. All data are for an input signal of $\dot{\gamma} = \sin(\omega t)$. For these parameters, a) $\Gamma_0 = 100$, b) $\Gamma_0 = 1$, c) $\Gamma_0 = 1$, d) $\Gamma_0 = 0.01$.

For values of $\dot{\gamma}_c \geq 1$ (and hence $\Gamma = \dot{\gamma}/\dot{\gamma}_c \leq 1$ as $\dot{\gamma}_0 = 1$) as seen in Figure 3 b), c), and d) the same trend of average structure is seen as in Figure 2; a greater value of n allows structure ζ to oscillate about a greater mean value. As expected from the same analysis that predicted this correlation (Eq. (14)), when $\dot{\gamma}_c < 1$, and $\Gamma = |\dot{\gamma}|/\dot{\gamma}_c$ as seen in Figure 3 a), the reverse is true and higher n leads to more structure breakdown and lower average ζ . Figure 3 b) and c), both with $\Gamma_0 = 1$, show the same trend in intracycle variation as Figure 2 (also with $\Gamma_0 = 1$), with larger n resulting in greater peak-to-valley variation, while Figure 3 a) and d) (which have more extreme

forcing $\Gamma_0 = 100$ and $\Gamma_0 = 0.01$, respectively) show the opposite. Similar to the average values of ξ , this is also governed entirely by the trends illustrated in Figure 1 and Eq. (14). Note that Figure 3 d), showing small values of Γ , is representative of the asymptotically nonlinear cases that will be the main focus in this work.

Moving from structure variation to the overall model response in oscillatory shear, we consider the stress harmonics (as defined in Eq. (10)). The low amplitude scaling for the strain-kinetic model ($\Gamma = \dot{\gamma}/\dot{\gamma}_c$ in Eq. (6)) in LAOStrain with $n = 1$ has already been shown in Figure 4 of [8]. To compare with that result, Figure 4 here shows the same measures for $n = 0.5$ and $n = 2$.

Figure 4 Low amplitude stress harmonic scaling for two values of n with Deborah number $De = \frac{\eta_A}{G_0} \omega = 1$, $\lambda k = 1$. Amplitude sweep represents variation in Γ_0 from 0.001 to 10. Open symbols denote negative values. The smaller value of n produces larger nonlinearities at small amplitude (greater magnitudes of σ'_3 and $\sigma'_1 - \sigma'_{LVE}$ for $n = 0.5$), as predicted in the discussion of Figure 1.

For all values of n , the initial scaling of the first harmonics is the expected linear response, $\sigma \sim \gamma_0^1$. The appearance of nonlinearities, however, show a non-standard scaling of $\sigma \sim \gamma_0^{1+n}$ at low amplitude (double-log slope of $1+n$ in Figure 4). As mentioned in Section I, all other

known model solutions predict a slope of 3 [10,24], so the fact that the power law scaling in this model not only deviates from the standard result, but also depends upon the value of a model parameter, is noteworthy. This is the main signature that distinguishes this model from existing predictions.

The stress harmonics can be normalized to define material functions. Figure 5 shows the nonlinear Chebyshev coefficients (as defined in Eq. (11)), which are defined by normalizing stress harmonics by the strain amplitude γ_0 .

Figure 5 Chebyshev coefficients as a function of strain amplitude for varying values of reaction order n as defined in Eq. (6). Smaller values of n produce larger values of nonlinearities at small amplitude, as predicted by Figure 1. A value of $n = 2$ produces the scaling of prior predictions. Data are from simulation with $De = 1$, $\lambda\kappa_A = 1$. Amplitude sweep represents variation in Γ_0 from 10^{-4} to 10. Open symbols denote negative values.

As already established in [8], when $n = 1$ the Chebyshev third harmonics, and the deviations of the first harmonics from their linear values, scale as $\sim \gamma_0^1$ at low strain amplitudes. Figure 5 shows that in the more generalized case, the nonlinear Chebyshev harmonics scale as $\sim \gamma_0^n$. This variable scaling with changing value of a material parameter has not been seen in any existing analysis of any constitutive model. Because of this result the definition of the intrinsic Chebyshev coefficients must be modified to reflect the variable asymptotic scaling. Here we propose the expression

$$\begin{aligned} \sigma(t; \gamma_0, \omega) = & \gamma_0 \{ G'(\omega) \sin \omega t + G''(\omega) \cos \omega t \} + \\ & \gamma_0^m \{ [e_1](\omega) \sin \omega t + \omega [v_1](\omega) \cos \omega t \} + \\ & \gamma_0^m \{ -[e_3](\omega) \sin 3\omega t + \omega [v_3](\omega) \cos 3\omega t \} + \mathcal{O}(\gamma_0^p) \quad \text{where } p > m \end{aligned} \quad (15)$$

(where $m = 1 + n$ for our analysis of this specific model) to account for the new asymptotic scaling $\sigma \sim \gamma_0^{1+n}$, allowing direct comparison of the asymptotic material coefficients across varying order of reaction n . Although here m is directly related to a model parameter, this is not necessary in general, and the value of m in Eq. (15) can be considered a material function that describes the asymptotically-nonlinear response of any material or model.

Figure 6 shows the four amplitude-intrinsic Chebyshev coefficients as a function of frequency for varying values of n . Data are from simulation with $\frac{\eta_A k}{G_0} = 1$. Changing the order of reaction does not change the sign of any of the four material functions for any value of Deborah number.

Figure 6 Intrinsic Chebyshev coefficients as defined in Eq. (15) as a function of frequency for varying values of the order of reaction exponent n . The data for $n = 1$ correspond to the solution presented in [8]. All plots shown are for $\lambda\kappa_A = 1$. Open symbols denote negative values.

Thus n does not affect whether the material response is shear thickening/thinning or strain stiffening/softening, nor whether those trends are driven by large strains or large strain rates (sign interpretations from Fig 7 of [9]). The breakdown order of reaction n does, however, affect the magnitude of all four intrinsic Chebyshev coefficients. Increasing n increases the double-log slope of each material function versus De ; this appears as a slight rotation counter-clockwise of each frequency-dependent curve in Figure 6. Increasing n decreases the magnitude at low De and increases the magnitude at high De . The contour of each material function has one point (near $De = 1$) where the magnitude is the same for all values of n that are shown. The terminal regime

slopes are also changed (decreased at low De and increased at high De) by n —for example the plateaus that are seen at high De in $[v_1]$ and $[v_3]$ when $n = 1$ show a positive terminal slope for the greater values and a negative terminal slope for lesser values, always equal to $n - 1$. This trend comes from the same source as the changing low-amplitude slopes. Increasing ω increases $\dot{\gamma}$, which means an increased Γ (just as increasing γ_0 did). Therefore as described by Figure 1, a larger value of n increases the double-log slope versus ω (Figure 6) as well as γ_0 (Figure 4).

In summary, the addition of the sixth model parameter n to govern the order of reaction for breakdown (Eq. (6)) brings about a fundamental change in the model response when the value of $n \neq 1$. The unique power-function scaling of the nonlinear harmonics at small amplitudes is shown to be a function of n , which makes this model quite different in that aspect from any other model that has been analyzed in LAOS. This also requires a flexible definition of the amplitude-intrinsic material functions (Eq. (15)) to accommodate the dependence of this scaling on the value of a model parameter, or in general to accommodate experimental observations of non-standard amplitude scaling. Furthermore, varying the value of n is shown to affect the frequency-dependent asymptotic nonlinear fingerprint of this model. The form of modifying the order of reaction that has been explored here is one of many that exist in the literature; given the broad and fundamental impact of this modification, changing the order of reaction in other manners stands as an interesting subject for further exploration. The next section delves more deeply into one specific category of choices that are made when building and characterizing a thixotropic model; that of (i) breakdown driven by strain rate or stress, and (ii) LAOS with strain or stress as the controlled input.

III. Model generalization to choices of stress or strain

In examining thixotropic constitutive models in LAOS, there are two places where there is a choice of stress versus strain. First, the kinetic equation governing structure evolution can be driven either by stress (stress-kinetic) or by strain rate (strain-kinetic) (Eqs. (5) and (6)).

Mathematically this is very simple to write for either choice when the equation is formulated as in Eqs. (3) and (5). Second, the oscillatory input wave used for characterization can be either stress-controlled (LAOStress) or strain-controlled (LAOStrain). Table 1 outlines the four possible combinations of choices between stress and strain for thixotropic structure models in LAOS. Certain combinations are more amenable to analytical solutions as indicated in Table 1.

Table 1 The four possible combinations of choices between stress and strain for thixotropic structure models in LAOS.

	$\dot{\gamma}$ -kinetic Eq. (6)	σ -kinetic Eq. (6)
LAOStrain $\gamma = \gamma_0 \sin(\omega t)$	$\xi = \xi(\omega t; \gamma_0, k, \dot{\gamma}_c, n)$ <ul style="list-style-type: none"> • Analytical solution attainable for some n • Analytical asymptotic nonlinearities $\sim \gamma_0^{1+n}$ 	$\xi = \xi(\omega t; \gamma_0, k, \sigma_c, n, G_0, \eta_A, \eta_\infty)$ <ul style="list-style-type: none"> • Numerical asymptotic nonlinearities $\sim \gamma_0^{1+n}$
LAOStress $\sigma = \sigma_0 \sin(\omega t)$	$\xi = \xi(\omega t; \sigma_0, k, \dot{\gamma}_c, n, G_0, \eta_A, \eta_\infty)$ <ul style="list-style-type: none"> • Numerical asymptotic nonlinearities $\sim \sigma_0^{1+n}$ 	$\xi = \xi(\omega t; \sigma_0, k, \sigma_c, n)$ <ul style="list-style-type: none"> • Analytical solution attainable for some n • Analytical asymptotic nonlinearities $\sim \sigma_0^{1+n}$

When the constitutive equation is sufficiently simple (as it is in the case of Eq. (9)), it is possible to solve analytically for the asymptotic harmonic coefficients when the same parameter drives structure evolution and is the controlled input wave (diagonal entries of Table 1), and the value of n is set to 1 [8,25]. (Solutions are also achievable—but often more complex—for select

other values of n). As laid out in Table 1, in these ‘matched’ cases the kinetic equation has no dependence on the constitutive equation, and can be solved directly for $\xi(t)$. This expression can then be substituted into the constitutive equation, allowing for a full analytical solution. The analytical solution for this strain-kinetic model in LAOStrain is presented in [8] (see the Supplemental Information in [8] for the full derivation), and the solution for this stress-kinetic model in LAOStress is presented in [25]. In both cases, the solution shows that when $n = 1$, the dependence on input amplitude does not change with the choice of stress or strain ($\sigma \sim \gamma_0^2$ for strain, $\gamma \sim \sigma_0^2$ for stress). Full solution for arbitrary n has not been obtained analytically, we provide an analytical solution for the amplitude scaling, showing that the amplitude to the power $1 + n$ appears for both stress and strain control for the general thixotropic-viscoelastic model of Eqs. (6) and (9) (see Supplemental Information of this paper for analytical solution).

When structure evolution is not driven by the controlled input parameter (off-diagonal entries in Table 1), analytical work is more complex, as the kinetic equation is coupled to the constitutive equation. However, numerical simulation of the models can be used to demonstrate the low-amplitude power law scaling of the stress harmonics. Figure 7 shows the results of such simulation (both for strain-controlled oscillations of the stress-kinetic model and for stress-controlled oscillations of the strain-kinetic model), which again show the power law behavior with exponent $1 + n$ for the asymptotic nonlinear responses. Thus, the low-amplitude scaling shows no dependence on the choices of stress versus strain, either in the kinetic equation or the LAOS input.

Figure 7 Amplitude dependence of stress harmonics for a) LAOStrain of the stress-kinetic model and b) LAOStress of the strain-kinetic model. These plots represent the a) upper right and b) lower left segments of Table 1. The intrinsic nonlinear scaling (limit of small γ_0) depends on the order of reaction parameter n .

In summary, the leading order at which nonlinearities arise can be expressed by the equations

$$(\sigma_1' - \gamma_0 G') \sim \gamma_0^{1+n} \quad (16)$$

$$(\sigma_1'' - \gamma_0 G'') \sim \gamma_0^{1+n} \quad (17)$$

$$\sigma_3' \sim \gamma_0^{1+n} \quad (18)$$

$$\sigma_3'' \sim \gamma_0^{1+n} \quad (19)$$

in LAOStrain, and the equations

$$(\gamma_1' - \sigma_0 J') \sim \sigma_0^{1+n} \quad (20)$$

$$(\gamma_1'' - \sigma_0 J'') \sim \sigma_0^{1+n} \quad (21)$$

$$\gamma_3' \sim \sigma_0^{1+n} \quad (22)$$

$$\gamma_3'' \sim \sigma_0^{1+n} \quad (23)$$

in LAOStress, where J' and J'' are the linear dynamic compliances. These relations hold both for stress-driven and strain-driven structure breakdown. We will now present experimental data of controlled strain oscillations that show the unique signature of non-integer amplitude scaling.

IV. Experimental data

The unique model prediction for asymptotically-nonlinear amplitude scaling, Eqs. (16)-(23), is not just theoretical. Here, we demonstrate a model material that shows a low-amplitude power law scaling of $1 + n \neq 3$, i.e. different than the standard viscoelastic prediction. Longer thixotropic restructuring times tend to carry greater experimental difficulties, hence a material with a short thixotropic restructuring timescale is chosen: an aqueous solution of Carbopol 940. Carbopol is a polyacrylic acid that is cross-linked on its surface, resulting in sponge-like molecules that swell to create a jammed suspension in solution; for characterization, see [26]. Samples were prepared by mixing powdered Carbopol 940 with distilled water (1.00% by weight), and adding a concentrated solution of NaOH until the mixture reached a pH of 7. All experiments were performed on a TA Instruments ARES-G2 rotational rheometer (separated motor-transducer instrument) using a 50 mm diameter parallel plate geometry with a gap of 500 μ m. Contacting surfaces were covered with adhesive-backed sandpaper to prevent slip. As a parallel disk geometry is used, corrections are needed to attain true stress values [27]. However, as the amplitude scaling is required for calculation and unknown before data processing, we present unprocessed data here. This does not affect the measured value of the low-amplitude scaling, which is our focus here.

A standard test for identifying thixotropy is a transient rate step-down [28]. A material is pre-sheared at a high rate to steady-state, then the shear rate steps down and the transient stress is observed. An undershoot in the stress after the step-down in rate indicates that the material is thixotropic. Figure 8 shows the results of this test on a 1.00 wt% solution of Carbopol.

Figure 8 Thixotropic recovery test of Carbopol 940, 1 wt% in water (pH7). Stepping shear rate down from 10^3 s^{-1} to 10^{-1} s^{-1} , the stress undershoot indicates the presence of a finite thixotropic restructuring time.

Carbopol shows a clear stress undershoot, and hence is a thixotropic material. The timescale for the stress to achieve a constant steady-state value is on the order of seconds, which is shorter than many commonly used model thixotropic materials (e.g. Laponite, which has a restructuring time on the order of tens to hundreds of seconds [6]).

In oscillatory shear, we begin the exploration of asymptotic nonlinearities by looking at the first harmonics. Figure 9 a) shows σ_1' and σ_1'' at a frequency $\omega = 1 \text{ rad/s}$, and amplitude varying from $\gamma_0 = 0.1\% - 100\%$. Figure 9 b) shows the elastic and viscous moduli (the stress harmonics normalized by strain amplitude), which may be more familiar to some readers. Data were collected sweeping both from high to low and from low to high amplitude to verify that time-

dependent experimental effects (such as long transients or evaporation) are not the cause of any peculiar scaling. The fact that $\sigma_1' > \sigma_1''$ suggests a high Deborah number at this frequency, $\omega = 1 \text{ rad/s}$.

Figure 9 Oscillatory strain amplitude sweep of aqueous Carbopol 940 at 25°C, $\omega = 1 \text{ rad/s}$. a) Stress harmonics b) moduli for 1.00 wt% Carbopol 940 (pH 7). Data show the expected linear scaling at sufficiently small strain amplitude. Low torque limit for this geometry is $\sigma_{\min} = 10^{-5} \text{ Pa}$.

The first harmonics show linear scaling ($\sigma_1' \sim \gamma_0$, $\sigma_1'' \sim \gamma_0$) at sufficiently low strain amplitudes.

Nonlinearity (here, deviation from lines $\sim \gamma_0^1$) is visually apparent for $\gamma_0 \approx 1\% - 10\%$.

There are four independent nonlinearities that can be measured to identify amplitude scaling: first harmonics σ_1' and σ_1'' deviating from their linear values, and the appearance of third harmonics σ_3' and σ_3'' [9]. It is experimentally easier to measure the third harmonics rather than the nonlinear first harmonic deviations. At leading order, third harmonic nonlinearities are deviations from zero, whereas first harmonic nonlinearities are deviations from a measured linear value, which carries its own uncertainty, and has a larger magnitude than the sought deviations. All four signals are typically small enough that environmental noise plays a role, and can

preclude accurate measurement; often only a subset of the four can be reliably measured. Figure 10 shows the four leading order nonlinearities for Carbopol.

Figure 10 The four asymptotic deviations from linearity in oscillatory shear at 25°C, $\omega = 1$ rad/s. a) Elastic first, b) viscous first, c) elastic third, and d) viscous third stress harmonics as a function of strain amplitude. Data show power law scaling not equal to the traditionally expected $\sim \gamma_0^3$ dependence. Open symbols denote negative values. Low torque limits shown are empirically determined from the presented data [29]. The 10^{-5} Pa limit corresponds to an instrument torque limit of 3 nN·m.

In each plot, the data points at low amplitude exhibit random noise, with random signs and approximately constant maximum amplitude that represents the noise floor of the stress (torque) measurement. These data clearly show that the first harmonic nonlinearities have a significantly higher noise level, as a consequence of the uncertainty in the linear value. This also contributes to obscuring the power-law slope as the signals emerge from the noise. To demonstrate this, Figure 11 shows two calculations of the first harmonic viscous nonlinearity from the same signal

using two different values of the linear loss modulus G'' . The difference between the two linear values used is less than 5% of the linear signal, yet it drastically alters the slope at low amplitude (although in each case, the slope $m = 1.25 - 2.25$ is less than the standard $m = 3$ assumption).

Figure 11 Values of the first harmonic viscous nonlinearity for two different fit values of G'' (data shown are one of the four sweeps shown in Figure 10). The uncertainty in the plateau value G'' (inset) propagates to uncertainty in power-law scaling γ_0^m . This source of uncertainty is not present for third harmonic nonlinearities.

It is important to acknowledge that the lower limit observed in this test is an experimental limit (not a material limit), hence the noise floor may be hiding behavior that is not present in the data that are shown. However, the fact that the magnitudes of the nonlinearities are small compared to the magnitudes of the linear signals supports the idea that the observed slopes are in fact the terminal scalings. Other materials have exhibited terminal regime behavior at comparable ratios of nonlinear-to-linear signals (e.g. [9]).

For our purposes, third harmonics are more reliable for determining the amplitude scaling of the leading order nonlinearities. Each of the third harmonic stresses shown in Figure 10 c)-d) appears to show a power-law scaling closer to γ_0^2 rather than the traditionally expected scaling of γ_0^3 . The viscous third harmonic (Figure 10d) show cleaner data than the elastic third harmonic (Figure 10c), hence we examine the viscous σ_3'' more closely here.

Properly trimming the data set to minimize the effect of noise is critical to accurately fitting the asymptotic slope. At strains that are too small, the data are too noisy, and at strains that are too high, the data become fully nonlinear and no longer exhibit the asymptotic scaling. The numerical value of the experimental noise threshold can be estimated by looking at the power spectrum of the harmonic decomposition, which is shown in Figure 12 for $\omega = 1$ and multiple values of γ_0 .

Figure 12 Stress harmonic power spectrum at varying input strain amplitude for $\omega = 1$ rad/s. Noise floor is consistent with the data shown in Figure 10 c)-d) ($\sigma_{noise} \approx 10^{-5}$ Pa), and shows weak dependence on γ_0 at low amplitudes.

An estimate of the $\sigma_{noise} \approx 10^{-5}$ Pa comes from the stress amplitude at high harmonic number (where the material signal is smaller than the noise), which appears as a plateau on the right side of Figure 12. The noise floor does increase at higher strain amplitudes, but this variation is small, especially around strain amplitude $\gamma_0 = 1\%$, where subsequent measurements of asymptotic scaling take place.

Figure 13 shows power-law fits of the data that exceed the noise floor.

Figure 13 Fit to asymptotically nonlinear data using various numbers of points above the noise floor. a) Fit values of n using variance weighting as a function of points used. All data sets start at the noise floor and count to higher strain as labeled in b). Fit line plotted in b) uses the values attained from simultaneously fitting to all four runs using the first six points above the noise floor. Data shown are same data in Figure 10d). The non-integer value of $m = 2.38$ (from the simultaneous fit using 6 points) indicates a thixotropic model parameter fit value of $n = 1.38$ (Eq. (6)).

As discussed in Section II, all other published model solutions predict $m = 3$ [10,24], while most simple thixotropic models (those with first-order reaction kinetics) predict $m = 2$ [8], and those featuring the more general kinetic equation of Eq. (6) predict $m = n + 1$ (as shown in our work here). Figure 13 shows fits using a varying number of points above the noise floor (all using variance weighting). Fits are shown both for each of the four data sets individually, as well as a simultaneous fit to all four. For fits using 6 or 7 points (where m is not changing strongly with number of points and the uncertainty does not exceed 10%) values of m range from 2.29 to 2.66 (all with an uncertainty of approximately 0.1), with the simultaneous fit yielding a value of $m = 2.38 \pm 0.12$, which is the value that is plotted in Figure 13b). This indicates allowing m to take non-integer values produces a significantly better agreement between data and theory (Eq. (6) with variable n) than if m were assumed to take a value of 3.

V. Conclusions

Prior work had demonstrated that in oscillatory shear, a simple thixotropic constitutive model produced a low-amplitude power law scaling that had previously not been observed, with power-law exponent $m = 2$ rather than $m = 3$ [8]. Here, this result is expanded to show that the scaling can take a value other than the expected viscoelastic value, but also can be non-integer and dependent upon the value of a fit parameter within the model. In a minimalist thixotropic model, a single parameter governing the order of reaction of the kinetic equation can modify the low-amplitude power law dependence (Eq. (6), parameter n), which shows $m = 1 - n$. This phenomenon is not dependent upon the choice of stress or strain rate, either in the kinetic equation or as the input signal for characterization (Eqs. (16)-(23)). Further, experimental data for the amplitude-intrinsic regime of aqueous Carbopol 940 is presented (a thixotropic, soft-glassy material), demonstrating that a real material system exhibits this previously unexpected scaling behavior, contradicting the prediction of all other constitutive models that have been solved in asymptotic LAOS, except for the model described here (Eqs. (6) and (9)). This result is significant in that it can help inform constitutive model selection. While prior predictions were uniform, there is no fundamental reason that a material need exhibit the standard viscoelastic low-amplitude scaling. Other existing theoretical frameworks have allowed for non-integer relationships (for example parallel disk corrections for asymptotic nonlinearities [27]). This signature can therefore be an effective tool in evaluating constitutive model selection and model parameter calibration, as well as distinguishing materials using asymptotically-nonlinear signatures.

Acknowledgments

This work was supported by the National Science Foundation under Grant No. CBET-1351342.

References

- [1] C. Goodeve, G. Whitfield, The measurement of thixotropy in absolute units, *Transactions of the Faraday Society*. 34 (1938) 511–520.
- [2] F. Moore, The rheology of ceramic slips and bodies, *Transactions of the British Ceramic Society*. 58 (1959) 470–494.
- [3] R.G. Larson, Constitutive equations for thixotropic fluids, *Journal of Rheology*. 59 (2015) 595–611.
- [4] J. Mewis, N.J. Wagner, Thixotropy., *Advances in Colloid and Interface Science*. 147-148 (2009) 214–27.
- [5] D. Quemada, Rheological modelling of complex fluids. I. The concept of effective volume fraction revisited, *The European Physical Journal Applied Physics*. 1 (1998) 119–127.
- [6] H.A. Barnes, Thixotropy - a review, *Journal of Non-Newtonian Fluid Mechanics*. 70 (1997) 1–33.
- [7] P.R. de Souza Mendes, Modeling the thixotropic behavior of structured fluids, *Journal of Non-Newtonian Fluid Mechanics*. 164 (2009) 66–75.
- [8] B.C. Blackwell, R.H. Ewoldt, A simple thixotropic–viscoelastic constitutive model produces unique signatures in large-amplitude oscillatory shear (LAOS), *Journal of Non-Newtonian Fluid Mechanics*. 208-209 (2014) 27–41.
- [9] R.H. Ewoldt, N.A. Bharadwaj, Low-dimensional intrinsic material functions for nonlinear viscoelasticity, *Rheologica Acta*. 52 (2013) 201–219.
- [10] N.A. Bharadwaj, R.H. Ewoldt, Constitutive model fingerprints in medium-amplitude oscillatory shear, *Journal of Rheology*. 59 (2015) 557–592.
- [11] A.J. Giacomin, R.B. Bird, L.M. Johnson, A.W. Mix, Large-amplitude oscillatory shear flow from the corotational Maxwell model, *Journal of Non-Newtonian Fluid Mechanics*. 166 (2011) 1081–1099.

- [12] W.M. Davis, C.W. Macosko, Nonlinear dynamic mechanical moduli for polycarbonate and PMMA, *Journal of Rheology*. 22 (1978) 53.
- [13] D.S. Pearson, W.E. Rochefort, Behavior of concentrated polystyrene solutions in large-amplitude oscillating shear fields, *Journal of Polymer Science: Polymer Physics Edition*. 20 (1982) 83–98.
- [14] M.H. Wagner, V.H. Rolón-Garrido, K. Hyun, M. Wilhelm, Analysis of medium amplitude oscillatory shear data of entangled linear and model comb polymers, *Journal of Rheology*. 55 (2011) 495.
- [15] A.K. Gurnon, N.J. Wagner, Large amplitude oscillatory shear (LAOS) measurements to obtain constitutive equation model parameters: Giesekus model of banding and nonbanding wormlike micelles, *Journal of Rheology*. 56 (2012) 333.
- [16] J.M. Dealy, K.F. Wissbrun, *Melt Rheology and Its Role in Plastics Processing: Theory and Applications*, Van Nostrand Reinhold, New York, 1990.
- [17] K. Hyun, M. Wilhelm, C.O. Klein, K.S. Cho, J.G. Nam, K.H. Ahn, et al., A review of nonlinear oscillatory shear tests: Analysis and application of Large Amplitude Oscillatory Shear (LAOS), *Progress in Polymer Science*. 36 (2011) 1697–1753.
- [18] M.D. Graham, Wall slip and the nonlinear dynamics of large amplitude oscillatory shear flows, *Journal of Rheology*. 39 (1995) 697.
- [19] S. Onogi, Non-Linear Behavior of Viscoelastic Materials. I. Disperse Systems of Polystyrene Solution and Carbon Black, *Journal of Rheology*. 14 (1970) 275.
- [20] X.-J. Fan, R. Byron Bird, A kinetic theory for polymer melts VI. calculation of additional material functions, *Journal of Non-Newtonian Fluid Mechanics*. 15 (1984) 341–373.
- [21] R.H. Ewoldt, A.E. Hosoi, G.H. McKinley, New measures for characterizing nonlinear viscoelasticity in large amplitude oscillatory shear, *Journal of Rheology*. 52 (2008) 1427.
- [22] R.H. Ewoldt, Defining nonlinear rheological material functions for oscillatory shear, *Journal of Rheology*. 57 (2013) 177.
- [23] M. Holmes, *Introduction to Perturbation Methods*, Springer, 1995.
- [24] C. Saengow, A.J. Giacomin, C. Kolitawong, Exact Analytical Solution for Large-Amplitude Oscillatory Shear Flow, *Macromolecular Theory and Simulations*. (2015).
- [25] B.C. Blackwell, *Thixotropic-viscoelastic rheological fingerprints in large amplitude oscillatory shear*, University of Illinois at Urbana-Champaign, 2013.

- [26] J.M. Piau, Carbopol gels: Elastoviscoplastic and slippery glasses made of individual swollen sponges, *Journal of Non-Newtonian Fluid Mechanics*. 144 (2007) 1–29.
- [27] N.A. Bharadwaj, R.H. Ewoldt, Single-point parallel disk correction for asymptotically nonlinear oscillatory shear, *Rheologica Acta*. 54 (2015) 223–233.
- [28] J. Mewis, N.J. Wagner, *Colloidal suspension rheology*, Cambridge University Press, 2012.
- [29] R.H. Ewoldt, M.T. Johnston, L.M. Caretta, Experimental challenges of shear rheology: how to avoid bad data, in: S. Spagnolie (Ed.), *Complex Fluids in Biological Systems*, Springer, 2015.