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NOVEL LAOS FLOW DATA ANALYSIS FOR AN ELASTO-VISCOPLASTIC MATERIAL

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Abstract. *We performed a thorough rheological characterization of a commercially available hair gel (a Carbopol-based solution), to illustrate a novel analysis of large-amplitude oscillatory shear (LAOS) flow test data. The results indicated that the gel under study was an elasto-viscoplastic material, quite elastic below the yield stress and with a low degree of thixotropy. We present results of the large-amplitude oscillatory shear (LAOS) flow experiments by means of viscous (stress versus shear rate) Bowditch-Lissajous figures. These figures were obtained for different levels of the stress amplitude, encompassing ranges both below and above the material yield stress. We show that the LAOS rheology of structured materials, that possess transition from solid-like to liquid-like behavior, can be captured by the use of a Jeffreys framework, whose parameters (relaxation and retardation times) are allowed to vary with the stress level, combined with yield-stress and thixotropic features. The four stages of this transition, namely 1-pure elastic solid; 2-viscoelastic solid, 3-viscoelastic liquid, 4-viscous liquid are obtained as the structure level of the material decreases. Stress amplitude and frequency are tuned so that one can explore two branches: structure-changing processes, when stress amplitude is above the yield stress and frequency is below the reciprocal of the thixotropic characteristic time; and constant-structure processes, when stress amplitude is below the yield stress or frequency is above the reciprocal of the thixotropic characteristic time. The LAOS measurement results were employed to determine the relaxation and retardation times as functions of the stress amplitude. These functions give all the information needed to understand in detail the physics of the material behavior in shear.*

Keywords: *rheology, viscoelasticity, LAOS*

1. INTRODUCTION

The Large Amplitude Oscillatory Shear (LAOS) flow is nowadays considered one of the most promising methodologies for assessing the mechanical behavior of complex materials. LAOS experiments combine two important features: it probes the material under large stresses, deformations and rates of deformation, while exploring the features of the oscillatory motion. Since most industrial processes involve large stresses and deformations, understanding how complex materials behave under such conditions is fundamental for optimization and design purposes. The referred to attributes of the oscillatory motions stem from its capacity of controlling amplitude and frequency independently. Since we can construct independent Weissenberg and Deborah dimensionless numbers from amplitude and frequency (Giacomin *et al.* (2011)), a sweep of these two entities allows probing these materials throughout a large spectrum of conditions.

The first and presently the most established method employed to extend the classic linear viscoelastic oscillatory material functions to the nonlinear regime is based on the so-called “Fourier-transform rheology" (Wilhelm (2002)), where the nonlinear response of the material is decomposed into a Fourier series. In this approach, the harmonics associated with the frequencies that are higher than the imposed one are the indicators of the nonlinear response.

It is possible to use other sets of orthogonal basis functions, like the Chebyshev polynomials of the first kind (Ewoldt *et al.* (2008)). These infinite series methodologies have their merits, since they offer an objective rationale for the treatment of complex behavior. However, they have received criticism (Cho *et al.* (2005); Rogers and Lettinga (2012); Rogers (2013)) due to a lack of physical interpretation for the different higher harmonics. This drawback stems from the very soul of these methodologies, namely, the necessity of an infinite number of basis functions to obtain the full description of the response wave.

There are rather few options available in the literature that can be used instead of the Fourier-Chebyshev approach. Two of them are worthy mentioning here. The first one is the Stress Decomposition (SD) of Cho *et al.* (2005) and the

second is the Sequence of Physical Processes (SPP) of Rogers (2013). Although they have different rationales, they offer approaches to analyze the nonlinear material response by considering two "material" functions (instead of coefficients of the infinite series analyses) that can be interpreted as generalized dynamic moduli in the sense that they reduce to the classic storage and loss moduli in the limit of the linear viscoelastic regime. The SD approach is based on a decomposition of the stress response to a LAOStrain input of the form $\gamma = \gamma_o \sin \omega t$ into two additive parts: σ' and σ''. σ' is a function of the strain γ, and σ'' is a function of the strain rate $\dot{\gamma} = \omega\gamma$. The SPP approach was developed in Rogers *et al.* (2011) and Rogers and Lettinga (2012). The sequence of physical processes was identified along a trajectory in the 3D space defined by stress, strain, and strain rate. A quantitative form of SPP was proposed in Rogers (2013). In this approach, the binomial vector is assumed to be the generalized complex modulus, and its projections into the strain and strain rate directions, R' and R''/ω, are taken as the generalized dynamic moduli.

2. THE LLAOS METHODOLOGY

The performance of a new model for elasto-viscoplastic thixotropic materials de Souza Mendes (2009, 2011); de Souza Mendes and Thompson (2013); de Souza Mendes *et al.* (2013) was tested by de Souza Mendes and Thompson (2013) in a numerical LAOS experiment. The advantages of this model are discussed in de Souza Mendes and Thompson (2012). One important feature is its ability to describe materials that experience transition from solid-like behavior to liquid-like behavior as a response to a stress input, like gels. The model proposed in de Souza Mendes (2011); de Souza Mendes and Thompson (2013) is based on a Jeffreys mechanical analog, see Fig. 1. The Jeffreys framework was endowed with yield stress and thixotropic features, i.e. the viscosity diverges at stresses below the yield stress, and the model parameters are functions of the current structuring level of the microstructure. Therefore, from a purely elastic solid up to a purely viscous liquid, the different types of behaviors—corresponding to the different structuring levels—can be predicted.

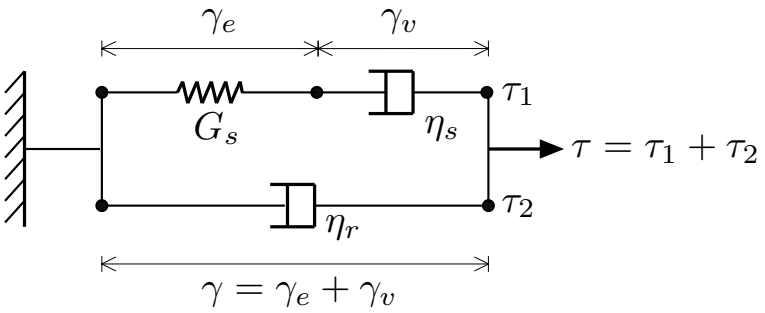


Figure 1. The Jeffreys mechanical analog.

The methodology proposed here consists of using the structuring-level-dependent Jeffreys model as a framework to interpret LAOS results, by exploring its ability of describing such a wide spectrum of mechanical behavior. Since the parameters of the Jeffreys model are well known and easily interpretable quantities, we can take advantage of the familiarity with these parameters and interpret LAOS results in a straightforward manner. To this end, we define the following rheological quantities (Fig. 1): the *structuring-level-dependent relaxation viscosity* η_s, the *structuring-level-dependent retardation viscosity* η_r, and the *structuring-level-dependent elastic modulus* G_s. The *structuring-level-dependent viscosity* is $\eta_v = \eta_s + \eta_r$.

As it will become clear, the methodology proposed here is highly benefited from the ability of the oscillatory test to control independently the stress amplitude and the frequency. The stress level is responsible for breaking up the material microstructure, and hence it dictates the equilibrium structuring level. On the other hand, the frequency determines the cycle period of the experiment, a characteristic time that can be compared with the thixotropic characteristic time of the material. When the frequency is high enough, there are no changes in the material structure, because the time scale of the experiment is much lower then the thixotropic characteristic time of the material.

3. EXPERIMENTAL

In the experiments our goal was to impose a constant stress amplitude while varying the frequency. To eliminate inertia-related artifacts, however, we had to employ the ARES-G2 rheometer (*TA Instruments*), whose torque sensor is installed in its motionless axis. However, this rheometer is a controlled-rate rheometer, and hence a stress amplitude is not directly imposable. Consequently, for each frequency we had to perform preliminary strain amplitude sweep tests to determine the strain amplitude that corresponded to the sought-for stress amplitude.

The cross-hatched parallel-plate geometry was employed throughout. The Weissenberg-Rabinovich (W-R) correction was applied on the steady-state data. This correction is not suitable to oscillatory flows, and for this reason we developed and applied a novel correction for the stress amplitude. This correction is analogous to the W-R correction, but is applicable to the stress amplitude only (not to the instantaneous stress along the cycle), and only for constant-structure motions

(sinusoidal responses). The just mentioned correction is described in detail in a forthcoming publication.

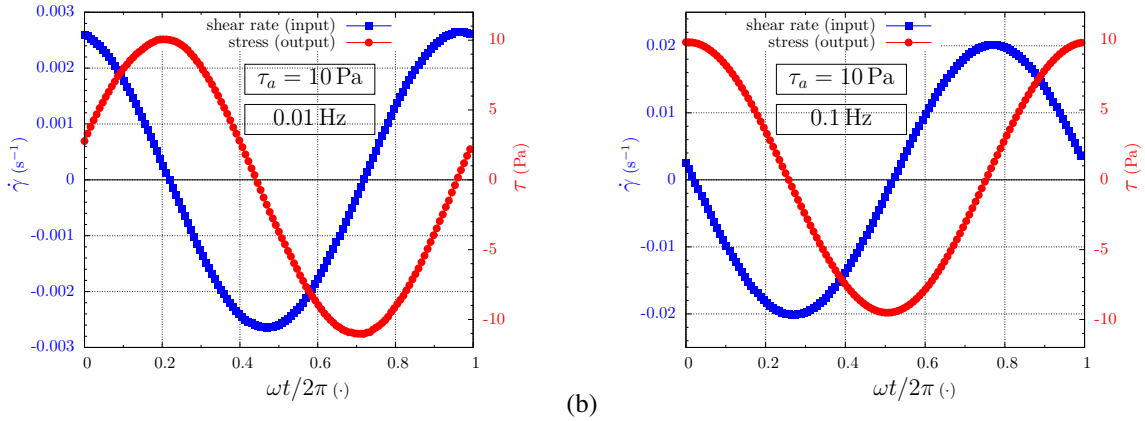
4. RESULTS

To illustrate the main features of the proposed methodology, we performed experiments with a commercial hair gel, as previously mentioned. Before proceeding to the oscillatory experiments, we obtained the flow curve of the material. For the gel employed, it turned out that the Herschel-Bulkley equation fits well the flow-curve data, with a yield stress of $\tau_y = 62.5\,\text{Pa}$, a consistency index of $K = 82\,\text{Pa.s}^n$, and a power-law index of $n = 0.38$.

We then performed oscillatory tests with the parallel plate geometry for two values of the stress amplitude, namely $\tau_a = 10\,\text{Pa} < \tau_y$ and $\tau_a = 125\,\text{Pa} > \tau_y$. These values are corrected for the error introduced by flow inhomogeneity (such a correction is possible for the amplitude only, not for all stress values throughout the cycle). For each stress amplitude, a wide range of frequencies was investigated. These results give an estimate of the thixotropic time scale of the material, say t_c. The region in the $\tau_a \times \omega$ Pipkin plane where structural changes can occur is bounded by the conditions $\tau_a > \tau_y$ and $\omega < 1/t_c$.

Figures 2 shows the raw (i.e. without correction) stress wave response to a sinusoidal shear rate input whose amplitude is chosen to correspond to a (corrected) stress amplitude of $\tau_a = 10\,\text{Pa}$, at frequencies of $0.01\,\text{Hz}$ and $0.1\,\text{Hz}$. We note that even at such a low frequency the stress wave is also sinusoidal, because this case pertains to the linear viscoelastic regime. In these cases of $\tau_a < \tau_y$, it is clear that the structuring level of the microstructure remains unchanged and at its maximum, and the material behaves as a viscoelastic solid (linear viscoelastic regime).

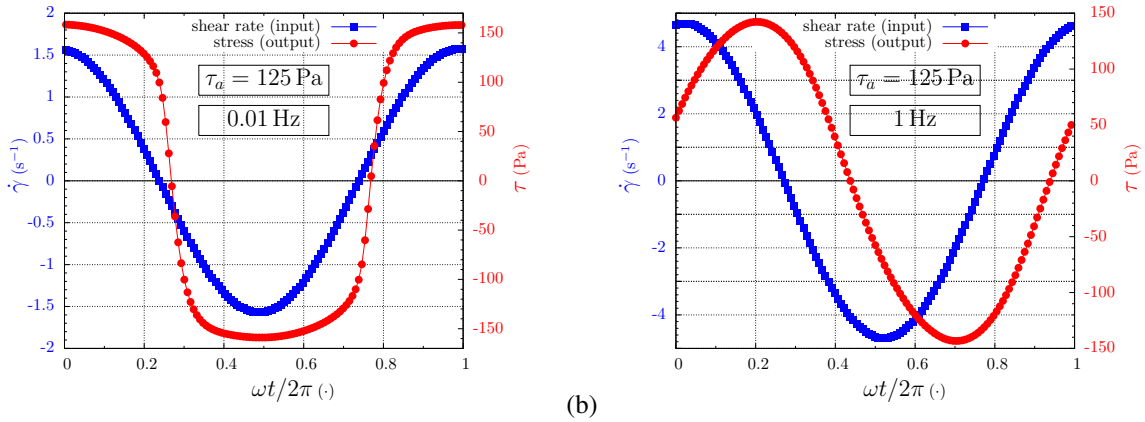
Figure 2. Viscous Lissajous-Bowditch curves, $\tau_a = 10\,\text{Pa} < \tau_y$. The plotted stress is raw (not corrected).



(a) (b)

For an imposed shear stress amplitude of $\tau_a = 125\,\text{Pa}$, however, a nonlinear stress wave response is obtained at the same low frequency ($0.01\,\text{Hz}$, Fig. 3a). When the frequency is increased to high enough values, however, the response becomes sinusoidal (Fig. 3b).

Figure 3. Viscous Lissajous-Bowditch curves, $\tau_a = 125\,\text{Pa} > \tau_y$. The plotted stress is raw (not corrected).

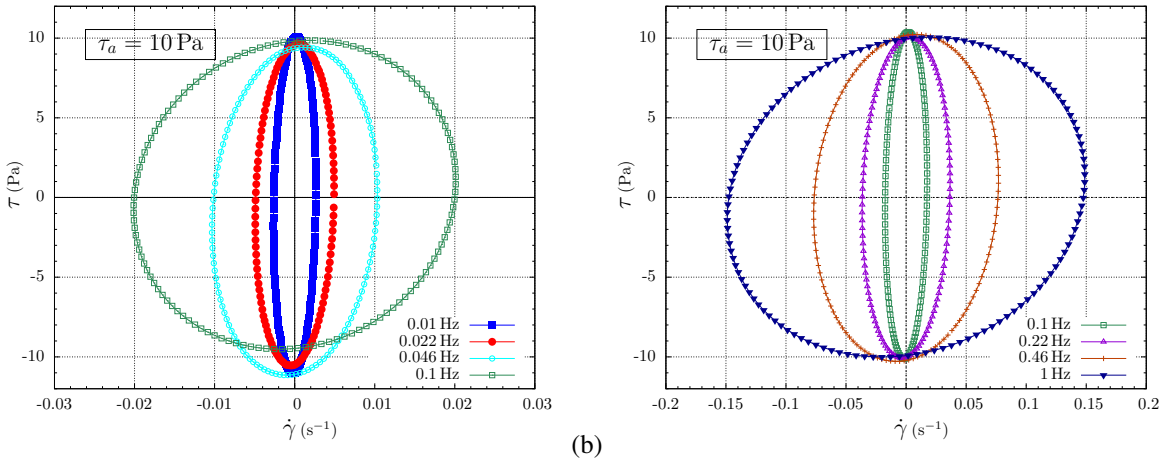


(a) (b)

Viscous Lissajous-Bowditch figures associated with $\tau_a = 10\,\text{Pa}$ are shown in Fig. 4 for a range of frequencies. Since in this case the stress amplitude is below the yield stress, the material remains fully structured throughout the whole cycle, irrespectively of the imposed frequency. Thus, the orbits are always elliptical.

When the imposed stress amplitude is higher than the yield stress, the shape of the orbits depends strongly on the

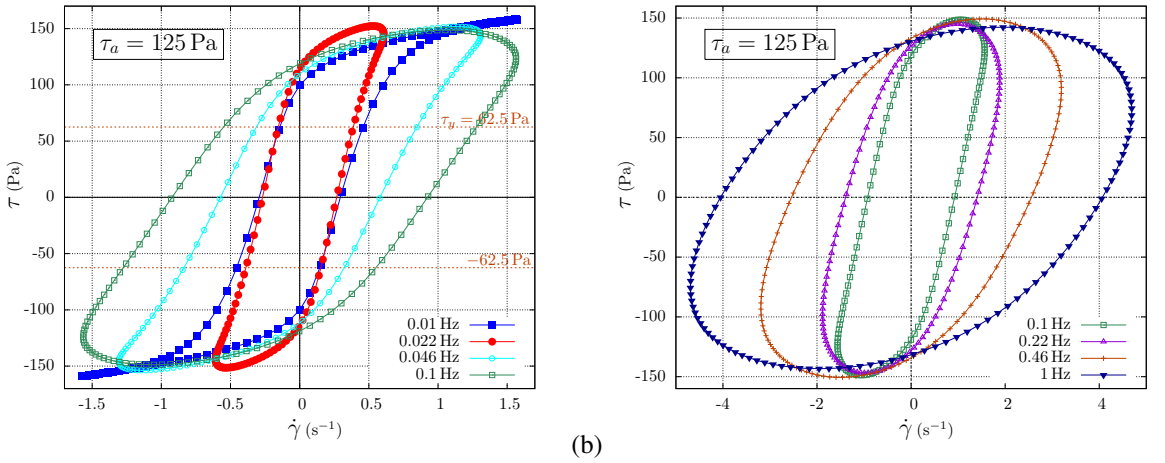
Figure 4. Viscous Lissajous-Bowditch curves, $\tau_a = 10\,\text{Pa} < \tau_y$. The plotted stress is raw (not corrected).



(a) (b)

imposed frequency (Figs. 5. In the low frequency regime (Fig. 5a), non-elliptical orbits are observed, as a result of intra-cycle changes of the structuring level. At higher frequencies (e.g. Fig. 5b), however, the cycle period becomes much smaller than the time scales of the structuring level changes. Hence, the orbits are again elliptical, i.e. a linear viscoelastic regime of a different nature is attained at high enough frequencies, in which the amplitudes are not restricted to small values. However, the structuring level is lower than its maximum, differently from what is observed for the $\tau_a < \tau_y$ cases (the classic linear viscoelastic regime). The higher the imposed stress amplitude, the lower is the structuring level, which is frequency-independent, however.

Figure 5. Viscous Lissajous-Bowditch curves, $\tau_a = 125\,\text{Pa} > \tau_y$. The plotted stress is raw (not corrected).



(a) (b)

The just described experimental fact is also demonstrated theoretically in de Souza Mendes and Thompson (2013). It is worth noting, however, that in general it is not guaranteed that a constant-structure motion is always attainable. There may exist materials whose time scale of microstructure buildup is so small that the structuring level will change significantly along the cycle even at the highest frequencies available. For these materials, LLAOS is not useful. For the hair gel employed here, however, it is clear that constant-structure motions were attained for a wide range of frequencies. It is also observed that the differential equation that originates from the Jeffreys analog admits an analytical solution for oscillatory flows that is valid not only for the classic linear viscoelastic regime, but also for this new linear viscoelastic regime, since in both regimes the Jeffreys material functions remain fixed throughout the cycle. This solution leads to the following form for the ratio of the stress amplitude to the shear rate amplitude $\dot{\gamma}_a$:

$$\frac{\tau_a}{\dot{\gamma}_a} = \sqrt{\frac{(\eta_v/\eta_r)^2 + [(\eta_v - \eta_r)(\omega/G_s)]^{2(1-\alpha)}}{1 + [(\eta_v - \eta_r)(\omega/G_s)]^{2(1-\alpha)}}} \tag{1}$$

where α is an empirical constant.

The ratio $\tau_a/\dot{\gamma}_a$—henceforth referred to as the *LLAOS viscosity*—is reminiscent of the modulus of the complex viscosity that appears in linear viscoelasticity, except that here we always keep τ_a constant while changing the frequency,

whereas the concept of complex viscosity is typically related to tests at constant and small strain amplitudes.

In Figs. 6 and 7 we show fittings of Eq. (1) (blue curve) to the LAOS viscosity data (red circles). The agreement is quite remarkable. The value obtained for α, however, is not equal to unity as predicted by the analytical solution.

Figure 6. The LAOS viscosity for $\tau_a = 10\,\text{Pa} < \tau_y$.

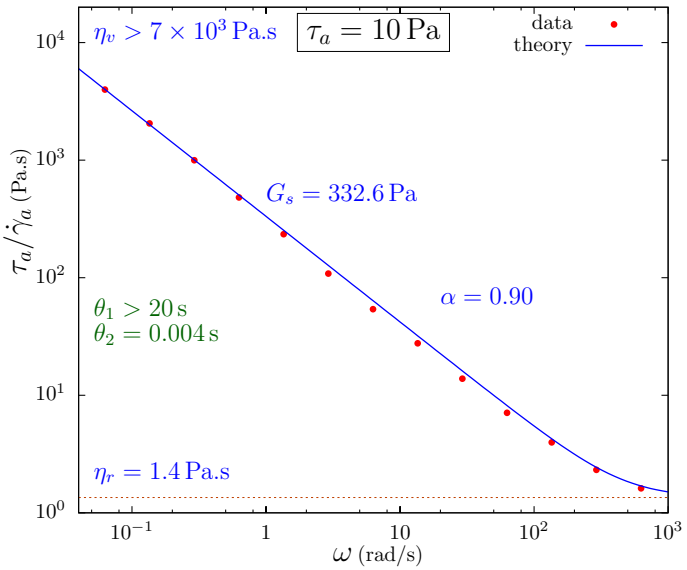
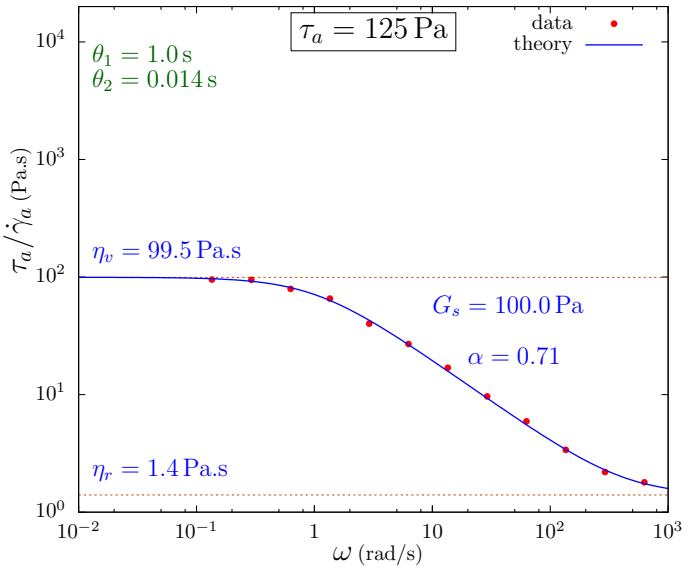


Figure 7. The LAOS viscosity for $\tau_a = 125\,\text{Pa} > \tau_y$.



The parameter η_v is the asymptotic value of the LLAOS viscosity $\tau_a/\dot{\gamma}_a$ as the frequency becomes very small. At intermediate frequencies $\tau_a/\dot{\gamma}_a$ is roughly equal to $\eta_s^{\alpha}(G_s/\omega)^{(1-\alpha)}$, i.e. the geometric mean between η_s and G_s/ω weighted by α. The retardation viscosity η_r is the asymptotic value of $\tau_a/\dot{\gamma}_a$ as the frequency becomes very large. The values obtained for α, however, are not equal to zero as predicted by the analytical solution, which means that the Jeffreys framework does not represent exactly the mechanical behavior of the present gel. Thus α indicates the departure from the Jeffreys-like behavior. It is worth noting that for α = 0 (Jeffreys behavior) the value of $\tau_a/\dot{\gamma}_a$ at intermediate frequencies, namely $\tau_a/\dot{\gamma}_a \approx G_s/\omega$, involves the elastic modulus G_s only, meaning that in this frequency range the response as predicted by the Jeffreys framework is purely elastic. On the other hand, the fact that the data for the gel indicates non-zero α values implies a viscoelastic mechanical response of the gel at intermediate frequencies. At the two extremes of the frequency spectrum, however, the mechanical response predicted by the Jeffreys framework is purely viscous, thus in accordance with the observed behavior of the gel.

5. CONCLUSIONS

With such fittings it is possible to obtain the material functions as functions of the stress amplitude (or microstructural state). In the case of the present gel it is seen that, as the structuring level is decreased, η_v decreases dramatically, η_r remains constant, G_s decreases very mildly, and α increases also mildly. Differently from other LAOS analyses, the physical meanings of these material functions are quite evident. Moreover, if we elect η_v as a measure of the structuring level, as done in the newer thixotropy models (de Souza Mendes, 2009, 2011; de Souza Mendes and Thompson, 2013), we can readily determine quantitatively G_s, η_r and α as functions of the structuring level.

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