ISSN 2176-5480

22nd International Congress of Mechanical Engineering (COBEM 2013)
November 3-7, 2013, Ribeirão Preto, SP, Brazil

MODEL-BASED FRAMEWORK RHEOLOGY FOR THE INTERPRETATION OF LAOS

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Abstract. *The more stablished method employed to generalize the linear viscoelastic oscillatory material functions for the interpretation of Large Amplitude Oscillatory Shear is based on the so-called "Fourier-transform rheology", where the nonlinear response of the material is decomposed into a Fourier series. In this approach, the harmonics associated to the frequencies that are higher than the imposed one are the measurers of the nonlinear response. This methodology has its merits, since it offers an objective rationale for the treatment of complex behavior. However, it has received a lot criticism due to lack of physical interpretation of the role played by the different higher harmonics. This drawback is founded on the very soul of these methodologies: the necessity of a basis of infinite functions in order to provide the full description. Towards the task of joining understanding and predictability of complex material behavior we propose a different philosophy for the interpretation of LAOS results. The methodology consists on choosing a constitutive model whose parameters are clearly and physically interpreted and using it as a framework to understand material behavior. We call this methodology Model-Based Framework Rheology (MBFR). A model can be roughly seen as a combination of basis functions and coefficients or parameters. The philosophy consists on taking the advantage of a our experience and knowledge with respect to a certain model parameter and generalize its concept to a more complex situation by relaxing the usual restriction this parameter has in the model where it was conceived and defined. The resulting analysis is born with a physical interpretation and is ready to be implemented in a different problem. The difficulty, and the strength, of this philosophy comes from finding a model framework with a reasonable degree of complexity. If the basis functions form a too simple set, then the parameters will carry all the complexity of the material. In this case it seems that is not reasonable to expect that the model will perform adequately in different conditions. On the other hand, if one defines an enormous number of functions, there are lots of coefficients to be determined and it is hard to attribute a physical interpretation to these coefficients, what is not desirable also. However, an appropriate choice of the model framework provides a rich interpretation of the results and a reasonable predictiveness of the material behavior in other conditions are obtained. We show that the usual approaches of SAOStrain and LAOStrain have a clear interpretation from the Kelvin-Voigt framework while the usual approaches employed in SAOStress and LAOStress are better interpreted from a Maxwell perspective. A more robust model, where elasticity, viscous response, plasticity and thixotropy are present, is offered as a framework for the analysis of the LAOS response of complex materials.*

Keywords: *keyword 1, keyword 2, keyword 3... (up to 5 keywords)*

1. INTRODUCTION

1.1 General aspects of LAOS

After a long tradition of usage of oscillatory motion in the linear viscoelastic regime, where the material rheological functions G' and G'' are the acclaimed measurable quantities, nowadays, LAOS is considered the most promising methodology to understand the behavior of complex material. LAOS experiments combine two important features: it probes the material in the nonlinear viscoelastic regime and it uses the advantages of the oscillatory motion. The former is a practical need, since many industrial processes subject complex material to complex behavior and because of that, understanding how this material behaves in the nonlinear regime is fundamental for optimization and design purposes. The latter concerns the strength that is attributed to oscillatory motions, namely its capacity of tuning amplitude and frequency independently (Pipkin, 1972). Since we can construct independent Weissenberg and Deborah dimensionless numbers from amplitude and frequency (Giacomin *et al.*, 2011), a sweep of these two entities provides a large spectra of material behavior.

One important and largely employed methodology to understand the complex behavior of these materials is to rep-

ISSN 2176-5480

resent its response in the so-called Lissajous-Bowditch curves. The elastic form is obtained from the trajectory of the response in the stress-strain plane while in the viscous form the response is represented in the stress-strain rate plane. Besides the obvious results expected from a Newtonian and a Hookean materials, the linear response is also predictable in a Lissajous-Bowditch representation, where an elliptical orbit is the projected curve in each plane. Hence, the degree of nonlinearity can be inferred by a "degree of non-ellipticity" of the curve form. This way of interpreting the data can give useful insights and for sure increases the comprehension of material behavior. However, mathematically defined and physically soundable quantities are *sine qua non* conditions for a description of the material behavior. Therefore, the challenge faced by the rheology community is to present measurable and meaningful rheological quantities that can be consider the nonlinear counterparts of G' and G''. Until now, there is no consensual rationale for such generalization.

The first and more stablished method employed to generalize the linear viscoelastic oscillatory material functions 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 to the frequencies that are higher than the imposed one are the measurers of the nonlinear response. An alternative representation form is to use a different-from-sinusoidal set of orthogonal basis. The most representative approach of this form is the Chebyshev polynomials of the first kind (Ewoldt *et al.*, 2008). These two methodologies have their merits, since they offer an objective rationale for the treatment of complex behavior. However, they have received a lot criticism (Cho *et al.*, 2005; Rogers and Lettinga, 2012; Rogers, 2012) due to lack of physical interpretation of the role played by the different higher harmonics. This drawback is founded on the very soul of these methodologies, i.e. on the necessity of a basis of infinite functions in order to provide the full description.

There are few options available in the literature that can be used as alternatives to the Fourier-Chebyshev approach. Two of them are worthy of 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 (2012). Although the two of them have different rationales, they offer approaches to analyze the nonlinear material response by considering two "material" functions (instead of infinite functions of Fourier and Chebyshev analysis) that can be interpreted as generalized dynamic moduli. The two approaches present alternative rheological functions that recover the linear viscoelastic moduli in the limit of the linear regime. The SD approach is based on a decomposition of the stress response, of a LAOStrain input of the form $\gamma = \gamma_o \sin \mathrm{wt}$, into two additive parts: σ' and σ''. Where σ' is a function of the strain, γ, and σ'' is a function of the strain rate, $\dot{\gamma} = \omega\gamma$. By symmetry arguments, requiring that σ' is an odd function of γ and an even function of $\dot{\gamma}$ and that σ'' is an even function of γ and an odd function of $\dot{\gamma}$, they come to this unique decomposition and stated that σ' is the elastic part of the stress and σ'' is the viscous part of the stress. Writing $\sigma' = \Gamma'\gamma$ and $\sigma'' = \Gamma''\dot{\gamma}$, they called Γ' and Γ'' the generalized dynamic moduli. The SPP approach was developed in Rogers *et al.* (2011) and Rogers and Lettinga (2012), where the sequence of physical processes was identified in trajectory through the 3D space defined by stress-strain-strain rate. A quantitative oriented form of SPP was presented by Rogers (2012). In this approach, the projection of the binomial vector on the strain-strain rate plane is assumed to be the generalized complex modulus. The projection of this vector into strain and strain rate directions, R' and R''/ω, are considered the generalized dynamic moduli. Although $\Gamma' \neq R'$ and $\Gamma'' \neq R''/\omega$, in the linear viscoelastic regime, both tend to G' and η'.

It is important to notice that G' and G'' moduli are considered **the** representatives of elastic and viscous behavior, respectively, in the linear viscoelastic regime *irrespectively* of the constitutive model of the material. Hence, discovering which are the "true" representatives counterparts of elastic and viscous behavior seems to be the natural path to follow as far as the nonlinear regime is considered. Therefore, the Fourier-Chebyshev analyses generalize G' and G'' by a series of coefficients, G'_n and G''_n in the case of the Fourier series, and e_n and v_n in the case of the Chebyshev functions. In these cases, the first coefficient reduces to linear viscoelastic counterpart and the coefficients associated to functions of higher order vanish in the linear viscoelastic regime. On the other hand the SD-SPP analyses generalize each modulus as a single generic version, and hence, there are two new entities, Γ' and Γ'' in the case of SD, and R' and R'' in the case of SPP, that reduce to their linear viscoelastic counterparts. While having only two rheological functions, instead of an infinity, seems to be an interesting approach it has the intrinsic disadvantage of coupling amplitude, frequency, and time while the Fourier-Chebyshev approach decouple amplitude and frquency from time, being its coefficients not dependent on time. This fact can lead to a necessity on developing further steps on the analysis, as was done by (Cho *et al.*, 2005). On the other hand, authors who apply the Fourier-Chebyshev expansions often use single quantities which are defined independently from the methodology conducted. These quantities are usually defined in a specific experiment: LAOStrain or LAOStress. The main ones are the minimum-strain modulus, G'_M, the large-strain modulus G'_L, the minimum-shear-rate viscosity, η'_M, and the large-shear-rate viscosity, η'_L usually defined in a LAOStrain experiment as (Ewoldt *et al.*, 2008)

$$G'_M \equiv \left.\frac{d\sigma}{d\gamma}\right|_{\gamma=0}; \; G'_L \equiv \left.\frac{\sigma}{\gamma}\right|_{\gamma=\pm\gamma_o}, \tag{1}$$

$$\eta'_M \equiv \left.\frac{d\sigma}{d\dot{\gamma}}\right|_{\dot{\gamma}=0}; \; \eta'_L \equiv \left.\frac{\sigma}{\dot{\gamma}}\right|_{\dot{\gamma}=\pm\dot{\gamma}_o}, \tag{2}$$

ISSN 2176-5480

and the minimum-stress elastic compliance, J'_M, the large-stress elastic compliance, J'_L, the minimum-stress fluidity, ϕ'_M, and large-stress fluidity, ϕ'_L usually defined in a LAOStress experiment as (Dimitriou *et al.*, 2013)

$$J'_M \equiv \left.\frac{d\gamma}{d\sigma}\right|_{\sigma=0};\ J'_L \equiv \left.\frac{\gamma}{\sigma}\right|_{\sigma=\pm\sigma_o}, \tag{3}$$

$$\phi'_M \equiv \left.\frac{d\dot{\gamma}}{d\sigma}\right|_{\sigma=0};\ \phi'_L \equiv \left.\frac{\dot{\gamma}}{\sigma}\right|_{\sigma=\pm\sigma_o}, \tag{4}$$

1.2 New philosophy

The question we raise at this point is: what is wanted from LAOS experiments? Or, what are the true benefits to have generalizations of the linear viscoelastic moduli G' and G''? In a first stage, we can consider that what is aimed is a better *comprehension* of the complex material we are dealing with by splitting the material response into an elastic and a viscous parts. However, a second and very important stage is to aim *predictability*, i.e. the capacity of producing a model that is able to translate the material response obtained in certain controlled circumstances and predict the material response when the material is subjected to different inputs.

Towards the task of joining understanding and predictability of complex material behavior we propose a different philosophy for the interpretation of LAOS results. The methodology consists on choosing a constitutive model whose parameters are clearly and physically interpreted and using it as a framework to understand material behavior. We call this methodology Model-Based Framework Rheology (MBFR). A model can be roughly seen as a combination of basis functions and coefficients or parameters. The philosophy consists on taking the advantage of a our experience and knowledge with respect to a certain model parameter and generalize its concept to a more complex situation by relaxing the usual restriction this parameter has in the model where it was conceived and defined. The resulting analysis is born with a physical interpretation and is ready to be implemented in a different problem. The difficulty, and the strength, of this philosophy comes from finding a model framework with a reasonable degree of complexity. If the basis functions form a too simple set, then the parameters will carry all the complexity of the material. In this case it seems that is not reasonable to expect that the model will perform adequately in different conditions. On the other side of the problem, if one defines an enormous number of functions, there are lots of coefficients to be determined and it is hard to attribute a physical interpretation to these coefficients, what is not desirable also. However, an appropriate choice of the model framework provides a rich interpretation of the results and a reasonable predictiveness of the material behavior in other conditions are obtained. We propose this approach as a complement, rather than a substitution, of the previous methodologies employed in the literature. In fact we will find, whenever it is possible, how to connect one approach from the other.

Below we interpret SAOS and LAOS results from the perspective of the two basis of the viscoelastic concept: the Kelvin-Voigt and Maxwell frameworks. We show that the usual approaches of SAOStrain and LAOStrain have a clear interpretation from the Kelvin-Voigt framework while SAOStress and LAOStress are better interpreted from a Maxwell perspective. A more robust model (de Souza Mendes, 2011; de Souza Mendes and Thompson, 2013) where elasticity, viscous response, plasticity and thixotropy are present is offered as a framework for the analysis of the LAOS response of complex materials.

2. KELVIN-VOIGT AND MAXWELL MODEL-BASED FRAMEWORK TO INTERPRET LAOS DATA

Our primitive understanding of what is an elastic behavior and what is a viscous behavior is deeply connected to Hookean and Newtonian materials, respectively. Here we can notice that the defined rheological functions (Dealy, 1995): shear viscosity, $\eta = \sigma/\dot{\gamma}$ and the elastic modulus, $G = \sigma/\gamma$ can already be interpreted in the light of the proposed philosophy. From the point of view of MBFR, one could call shear viscosity as the *Newtonian viscosity of the material*, η_{NW}, and the shear modulus as the *Hookean modulus of the material*, G_{HK}. Since viscosity and shear modulus are physically soundable entities of purely viscous and purely elastic materials, this rheological functions have a natural interpretation when we deal with more general cases. In this sense, we can say, for example, that the Newtonian viscosity of a Newtonian material is constant while the Newtonian viscosity of a power-law material is a function of the shear rate. The Generalized Newtonian Fluid can be seen, therefore, as imposing to a complex fluid a Newtonian framework, where we had to *generalize* the viscosity concept in a clear way. The same approach was consider by White and Metzner (19XX) when they used a viscosity that is a function of the shear rate in the Maxwell framework. These examples show that the present approach is already being employed, but not in the systematic way we are presenting here. In a first step, the Newtonian viscosity of the material and the Hookean elastic modulus of the material are interesting frameworks for interpreting the results. However, it is intuitive that we need more to understand and predict complex behavior. For example, when the fluid achieves a complexity of such an order that the viscosity of the GNF needs to become a tensor that is a complex function of the kinematics, we see that a more complex framework is necessary. However, this fact does not invalidate the use of these entities for interpreting results data.

ISSN 2176-5480

The next step towards the comprehension of a viscoelastic material comes from one of the two ways of coupling a Hookean mechanism with a Newtonian mechanism: the Kelvin-Voigt model and the Maxwell model. It is not difficult to infer how these two models have shaped our understanding and interpretation of what are the elastic and viscous parts of the material response. It is generally accepted that a Kelvin-Voigt material is the primitive representative of a viscoelastic solid, while a Maxwell material is the primitive representative of a viscoelastic fluid. This is so because the Kelvin-Voigt model, given by

$$\sigma = G_{KV}\gamma + \eta_{KV}\dot{\gamma}, \tag{5}$$

can be subjected to a constant shear stress with no continuous deformation as a fluid requires. In a Maxwell model, given by

$$\sigma + \frac{\eta_{MW}}{G_{MW}}\dot{\sigma} = \eta_{MW}\dot{\gamma}, \tag{6}$$

on the other side, any imposed stress makes the material to deform continuously.

As the title indicates, the work of Ewoldt (2013) defines nonlinear rheological material functions for oscillatory shear. In other words, Ewoldt (2013) establishes the nonlinear rheological functions obtained in a LAOStrain and LAOStress experiment. Since the rheological functions that arise from a sine input are different from a cosine one, a convention must be adopted. Ewoldt (2013) proposes that a sine input of the form $\gamma = \gamma_o \sin \omega \mathrm{t}$ should be adopted in a SAOStrain and LAOStrain and an input of form $\sigma = \sigma_o \cos \omega \mathrm{t}$ should be adopted in SAOStrain and LAOStrain. We are following the same convention for the cases analyzed in the present work.

2.1 SAOStrain

The G' and G'' curves obtained from subjecting a Kelvin-Voigt and a Maxwell viscoelastic models to a SAOS input of $\gamma = \gamma_o \sin \mathrm{wt}$ are

$$G'(\omega) = G_{KV}; \; G''(\omega) = \omega\eta_{KV}, \tag{7}$$

for a Kelvin-Voigt material and

$$G'(\omega) = \frac{\eta_{MW}^2\omega^2}{G_{MW}^2 + \eta_{MW}^2\omega^2}G_{MW}; \; G''(\omega) = \frac{G_{MW}^2}{G_{MW}^2 + \eta_{MW}^2\omega^2}\omega\eta_{MW}, \tag{8}$$

for a Maxwell material. Since G_{KV} and η_{KV} are constants in the Kelvin-Voigt material, the only way that Eq. (7) can be true is if $G'(\omega)$ and $G''(\omega)$ are independent of the frequency, ω. Here we can exemplify how the MBFR approach can be applied. Let us suppose we submit a certain material into the same SAOS input $\gamma = \gamma_o \sin \omega \mathrm{t}$ and we obtain the two curves of $G'(\omega)$ and $G''(\omega)$ as functions of the frequency. From a Kelvin-Voigt framework perspective, we can identify

$$G_{KV} = G'(\omega), \tag{9}$$

as the *Kelvin-Voigt elastic modulus of the material* and

$$\eta_{KV} = \eta'(\omega) = G''(\omega)/\omega \tag{10}$$

as the *Kelvin-Voigt viscosity of the material*. Analogously,

$$G_{MW} = \frac{G^{*2}(\omega)}{G'(\omega)}, \tag{11}$$

and

$$\eta_{MW} = \frac{1}{\omega}\frac{G^{*2}(\omega)}{G''(\omega)} \tag{12}$$

are the *Maxwell elastic modulus, G_{MW}, and Maxwell viscosity, η_{MW}, of the material*, where the complex dynamic modulus, G^*, is defined as $G^* = \sqrt{G'^2 + G''^2}$. What is worthy to note is that this approach gives new interpretations for $G'(\omega)$ and $G''(\omega)$ results from the perspective of the parameters of the chosen model framework. In the case of SAOStrain, the Kelvin-Voigt framework is completely aligned with the dynamic moduli, $G'(\omega)$ is the Kelvin-Voigt elastic modulus of the material and $\eta'(\omega)$ is the Kelvin-Voigt viscosity. In other words, it seems that the Kelvin-Voigt framework was conceived to interpret SAOStrain. Besides interpretation, the results obtained in this SAOS experiment, $G'(\omega)$ and $G''(\omega)$, can be used as inputs of the considered model. Hence, this information can be applied to different conditions (in a Couette flow, for example) using a Kelvin-Voigt framework, but relaxing the parameters G_{KV} and η_{KV} in Eq. (5) to be functions of the shear rate.

ISSN 2176-5480

2.2 SAOStress

In this subsection and the LAOStress one, we are following the ideas discussed by Ewoldt (2013) and consider a stress input of the form $\sigma = \sigma_o \cos \omega \mathrm{t}$.

The shear storage compliance J', and the shear loss complience J'' obtained from subjecting the Kelvin-Voigt and Maxwell materials to a SAOS input of $\sigma = \sigma_o \cos \mathrm{wt}$ are

$$J'(\omega) = \frac{G_{KV}}{G_{KV}^2 + \eta_{KV}^2 \omega^2};\ J''(\omega) = \frac{\eta_{KV}\omega}{G_{KV}^2 + \eta_{KV}^2\omega^2}, \tag{13}$$

for a Kelvin-Voigt material and

$$J'(\omega) = \frac{1}{G_{MW}};\ J''(\omega) = \frac{1}{\eta_{MW}\omega}, \tag{14}$$

for a Maxwell material. From a Kelvin-Voigt framework perspective, we can identify

$$G_{KV} = \frac{J'(\omega)}{J^{*2}(\omega)};\ \eta_{KV} = \frac{J''(\omega)/\omega}{J^{*2}(\omega)} \tag{15}$$

as the Kelvin-Voigt elastic modulus and Kelvin-Voigt viscosity of the material. And, from a Maxwell framework perspective, we find

$$G_{MW} = \frac{1}{J'(\omega)}; \eta_{MW} = \frac{1}{\omega J''(\omega)} = \frac{1}{\phi'(\omega)} \tag{16}$$

as the Maxwell elastic modulus and Maxwell viscosity of the material. The complex compliance, J^*, is defined as $J^* = \sqrt{J'^2 + J''^2}$ and $\phi'(\omega)$ is the viscous fluidity (tem que ver melhor o termo aqui). Again, the two viscoelastic model frameworks give new interpretations for $J'(\omega)$ and $J''(\omega)$. For a more straightforward interpretation we notice that Eq. (6) can be rewritten as

$$\dot{\gamma} = \phi_{MW}\sigma + J_{MW}\dot{\sigma}, \tag{17}$$

where $J_{MW} = 1/G_{MW}$ is the Maxwell compliance and $\phi_{MW} = 1/\eta_{MW}$ is the Maxwell fluidity. Hence, the Maxwell compliance of the material is the shear storage compliance obtained by the SAOStress experiment while the Maxwell fluidity of the material is the viscous dynamic fluidity obtained in the same experiment.

2.3 Comments on SAOS

When we compare the results obtained from the SAOStrain and SAOStress experiments, we notice that the interpretation of SAOStrain dynamic modulus, G' and G'', provided by the Kelvin-Voigt framework, represented by Eqs. (9) and (10), is simpler and more intuitive than the one provided by the Maxwell framework, represented by Eqs. (11) and (12). This conclusion is not only based on the simpler form of Eqs. (9) and (10), but also on the *terminology* given to G' - *storage* modulus - and G'' - *loss* modulus, since the Hookean-elastic representative parameter, elastic modulus, coincides with the storage modulus and the Newtonian-viscous representative coincides with the dynamic viscosity. On the other hand, the Maxwell framework is more appropriate to interpret SAOStress dynamic storage compliance, J' and dynamic fluidity ϕ', since they are exactly the reciprocal of the Maxwell shear modulus and Maxwell shear viscosity. The importance of this result cannot be overemphasized. The tradition on using oscillatory shear flows in the linear viscoelastic regime and on using Maxwell and Kelvin-Voigt models are, in fact, oscillatory and non-oscillatory versions of the same paradigm, namely *that the response of the material can be decomposed into two additive parts, one that is elastic and the other that is viscous*. As will become clear with the analysis below of LAOStrain and LAOSstress experiments, the interpretations given so far, for the results obtained from subjecting the material large amplitude oscillatory shear, are not free from this paradigm. Since is questionable that the elastic and viscous responses can be split into additive parts, breaking this paradigm has far reaching consequences for richer interpretations of LAOS experiments. When a Maxwell material can be subjected to a SAOStrain experiment and a Kelvin-Voigt material can be subjected to a SAOStress experiment, both results can be seen as somehow odd, the results exposes a strange feeling that *one material fits to one experiment and does not fit to the other, while the other fits the other and does not fit the one*. What we can conclude is that there is no elastic modulus of a material which is non-Hookean, unless a model is used as framework. And there is no viscosity of a material which is non-Newtonian, unless a model is used as framework. However, there are countless examples in the literature of the usage of the term *the elastic modulus of the material*, referring to a complex material with a specific model in mind. In particular, it is common to relate G' with *the elastic modulus* and G'' with a "viscous modulus". In other words, we can find in the literature examples of usage of the Kelvin-Voigt framework to interpret SAOStrain data without being explicit on this point. This happens because of the long tradition on SAOStrain experiments.

ISSN 2176-5480

2.4 LAOSstrain

In light of what was discussed in the last subsection, we can think of the SD decomposition of Cho *et al.* (2005) presented in detail previously, as a LAOStrain perspective of the paradigm described, i.e. the response of the inputed strain, the stress, is split into two additive parts: σ', the elastic part of the stress, and σ'', the viscous part of the stress. As shown in SAOStrain, the Kelvin-Voigt framework is suitable for interpreting such decomposition because it is founded in the same grounds: elastic and viscous contributions are additive parts of the total stress. Hence, we can use the Kelvin-Voigt MBFR and identify the Kelvin-Voigt elastic modulus, G_{KV}, and viscosity, η_{KV} of the material which was subjected to a LAOStrain experiment with the strain input $\gamma = \gamma_o \sin\omega\mathrm{t}$ and has $\sigma'$and σ'' as stress responses. In this connection, we can equal the elastic contribution of the Kelvin-Voigt model to the elastic contribution of SD, as

$$G_{KV}\gamma = \sigma' \Rightarrow G_{KV} = \frac{\sigma'}{\gamma} = \Gamma', \tag{18}$$

and equal the viscous contribution of the Kelvin-Voigt model to the viscous contribution of SD, as

$$\eta_{KV}\dot{\gamma} = \sigma'' \Rightarrow \eta_{KV} = \frac{\sigma''}{\omega\gamma} = \Gamma'', \tag{19}$$

Here we come to an important conclusion regarding the interpretation of the SD. The SD-generic dynamic moduli are exactly the Kelvin-Voigt elastic and viscous parameters. Hence, the analysis conducted by Cho *et al.* (2005) can be seen, from the perspective of MBFR, as choosing the Kelvin-Voigt model as a framework for interpreting nonlinear viscoelastic data.

Corroborating these ideas, Ewoldt *et al.* (2008) have related the SD method to the FT and CF in a LAOStrain response of the strain input $\gamma = \gamma_o \sin\omega\mathrm{t}$ as

$$\sigma' = \gamma_o \sum_{n\,\mathrm{odd}} G'_n(\omega,\gamma_o)\sin \mathrm{n}\omega\mathrm{t} = \gamma_\mathrm{o} \sum_{\mathrm{n\,odd}} \mathrm{e_n}(\omega,\gamma_\mathrm{o})\,\mathrm{T_n}(\gamma/\gamma_\mathrm{o}), \tag{20}$$

and

$$\sigma'' = \gamma_o \sum_{n\,\mathrm{odd}} G''_n(\omega,\gamma_o)\cos \mathrm{n}\omega\mathrm{t} = \dot{\gamma}_\mathrm{o} \sum_{\mathrm{n\,odd}} \mathrm{v_n}(\omega,\gamma_\mathrm{o})\,\mathrm{T_n}(\dot{\gamma}/\dot{\gamma}_\mathrm{o}). \tag{21}$$

Therefore, they have found what are the Fourier and Chebyshev versions of the same paradigmatic approach, namely to divide the material response into two *additive* parts, elastic and viscous ones. In fact, even before Eqs. (20) and (21) were stated, we could find in the literature the linking between the harmonics $G'_n(\omega,\gamma_o)$ and elasticity while $G''_n(\omega,\gamma_o)$ are frequently linked to viscous effects, the prime and double prime signals associated to the letter G indicate this relation. Aligned with this concept, the letters chosen for the Chebyshev coefficient are e from "elastic" and v from "viscous".

Analogously to what was done with the SD of Cho *et al.* (2005) we can use the Kelvin-Voigt MBFR and identify the relation between Kelvin-Voigt elastic modulus, G_{KV}, and viscosity, η_{KV} with the Fourier harmonics and the Chebyshev coefficients of the material which was subjected to a LAOStrain experiment with the strain input $\gamma = \gamma_o \sin\omega\mathrm{t}$ as the equations below

$$G_{KV}\gamma = \gamma_o \sum_{n\,\mathrm{odd}} G'_n(\omega,\gamma_o)\sin \mathrm{n}\omega\mathrm{t} = \gamma_\mathrm{o} \sum_{\mathrm{n\,odd}} \mathrm{e_n}(\omega,\gamma_\mathrm{o})\,\mathrm{T_n}(\gamma/\gamma_\mathrm{o}) \tag{22}$$

and

$$\eta_{KV}\dot{\gamma} = \gamma_o \sum_{n\,\mathrm{odd}} G''_n(\omega,\gamma_o)\cos \mathrm{n}\omega\mathrm{t} = \dot{\gamma}_\mathrm{o} \sum_{\mathrm{n\,odd}} \mathrm{v_n}(\omega,\gamma_\mathrm{o})\,\mathrm{T_n}(\dot{\gamma}/\dot{\gamma}_\mathrm{o}) \tag{23}$$

Hence, we have a connection between the Kelvin-Voigt elastic modulus of the material and the Fourier or Chebyshev coefficients

$$G_{KV} = \sum_{n\,\mathrm{odd}} G'_n(\omega,\gamma_o)\,\mathrm{cossec}\,\omega\mathrm{t}\sin \mathrm{n}\omega\mathrm{t} = \sum_{\mathrm{n\,odd}} \mathrm{e_n}(\omega,\gamma_\mathrm{o})\,\mathrm{cossec}\,\omega\mathrm{t}\,\mathrm{T_n}(\gamma/\gamma_\mathrm{o}) \tag{24}$$

Analogously, for the Kelvin-Voigt viscosity of the material we arrive at

$$\eta_{KV} = \sum_{n\,\mathrm{odd}} \eta'_n(\omega,\gamma_o)\sec\omega\mathrm{t}\cos \mathrm{n}\omega\mathrm{t} = \sum_{\mathrm{n\,odd}} \mathrm{v_n}(\omega,\gamma_\mathrm{o})\sec\omega\mathrm{t}\,\mathrm{T_n}(\dot{\gamma}/\dot{\gamma}_\mathrm{o}) \tag{25}$$

In the limit of the linear viscoelastic behavior where the harmonics higher than the unity are not significant to the response description, the first harmonic tends to the corresponding linear viscoelastic dynamic modulus, the SAOStrain result is recover, i.e. $G_{KV} = G'$ and $\eta_{KV} = \eta'$. In fact we can write Equations (24a) and (25a) as

$$G_{KV} = G'_1(\omega,\gamma_o) + \sum_{n=3,\,\mathrm{odd}} G'_n(\omega,\gamma_o)\frac{\sin \mathrm{n}\omega\mathrm{t}}{\sin\omega\mathrm{t}} \tag{26}$$

$$\eta_{KV} = \eta'_1(\omega,\gamma_o) + \sum_{n=3,\,\mathrm{odd}} \eta'_n(\omega,\gamma_o)\,\frac{\cos \mathrm{n}\omega\mathrm{t}}{\cos\omega\mathrm{t}} \tag{27}$$

Equations (24) and (25) give another interpretation for the harmonics of the Fourier transform and the coefficients of the Chebyshev representations. Equation (24a) can be rewritten to explicit the coefficients of a Fourier series applied to G_{KV} as

$$G_{KV} = \sum_{p\,\mathrm{even}} G_{KV(p)}(\omega,\gamma_o)\cos \mathrm{p}\omega\mathrm{t} \tag{28}$$

where the relation between $G_{KV(p)}$ and G'_n is

$$G_{KV(0)}(\omega,\gamma_o) = \sum_{n\,\mathrm{odd}} G'_n(\omega,\gamma_o) \tag{29}$$

$$G_{KV(p)}(\omega,\gamma_o) = \sum_{n=p+1,n\;odd} 2G'_n(\omega,\gamma_o) \tag{30}$$

while Eq. (25a) can be rewritten to explicit the coefficients of a Fourier series applied to η_{KV} given by

$$\eta_{KV} = \sum_{p\,\mathrm{even}} \eta_{KV(p)}(\omega,\gamma_o)\cos \mathrm{p}\omega\mathrm{t} \tag{31}$$

where the relation between $\eta_{KV(p)}$ and η'_n is

$$\eta_{KV(0)}(\omega,\gamma_o) = \sum_{n\,\mathrm{odd}} (-1)^{\frac{n-1}{2}}\eta'_n(\omega,\gamma_o) \tag{32}$$

$$\eta_{KV(p)}(\omega,\gamma_o) = \sum_{n=p+1,n\;odd} (-1)^{\frac{n-p-1}{2}}2\eta'_n(\omega,\gamma_o) \tag{33}$$

Another interesting result is if we compute the rheological coefficients defined by Eq. (1) from the Kelvin-Voigt MBFR perspective. In this case we have that

$$G'_M \equiv \left.\frac{d\sigma}{d\gamma}\right|_{\gamma=0} = \left.\frac{d\sigma'}{d\gamma}\right|_{\gamma=0} = G_{KV}|_{\gamma=0} + \left[\frac{dG_{KV}}{d\gamma}\gamma\right]_{\gamma=0}$$

$$\Rightarrow G'_M = G_{KV}(0) = \sum_{n\;odd} nG'_n \tag{34}$$

and

$$G'_L \equiv \left.\frac{\sigma}{\gamma}\right|_{\gamma=\pm\gamma_o} = G_{KV}|_{\gamma=\pm\gamma_o} + \eta_{KV}\left.\frac{\dot\gamma}{\gamma}\right|_{\gamma=\pm\gamma_o}. \tag{35}$$

$$\Rightarrow G'_L = G_{KV}(\pm\gamma_o) = \sum_{n\;odd}(-1)^{\frac{n-1}{2}}G'_n \tag{36}$$

Where we have used Eqs.(28)-(30) in order to produce the last equalities of Eqs. (34) and (36)

Therefore, other interpretations for G'_M and G'_L are obtained in this methodology. These known quantities are simply the Kelvin-Voigt elastic modulus of the material evaluated at $\gamma = 0$ and $\gamma = \pm\gamma_o$. So the variable S defined in Ewoldt *et al.* (2008) can be written as

$$S \equiv \frac{G'_L - G'_M}{G'_L} = \frac{G_{KV}(\pm\gamma_o) - G_{KV}(0)}{G_{KV}(\pm\gamma_o)}. \tag{37}$$

Its association with the nonlinearities of the material becomes very clear in this new perspective. As shown in the SAOS-train analysis, the linear viscoelastic regime is well characterized by a Kelvin-Voigt elastic modulus that is independent from the deformation, and therefore, $G_{KV}(\pm\gamma_o) = G_{KV}(0)$.

The same procedure can be applied to η'_M, η'_L, and $T \equiv \frac{\eta'_L-\eta'_M}{\eta'_L}$ (Ewoldt *et al.*, 2008)

$$\eta'_M \equiv \left.\frac{d\sigma}{d\dot\gamma}\right|_{\dot\gamma=0} = \left.\frac{d\sigma''}{d\dot\gamma}\right|_{\dot\gamma=0} = \left.\frac{d\eta_{KV}}{d\dot\gamma}\dot\gamma\right|_{\dot\gamma=0} + \eta_{KV}|_{\dot\gamma=0}$$

ISSN 2176-5480

$$\eta'_M \Rightarrow= \eta_{KV}\left(0\right) = \sum_{n\,odd} (-1)^{\frac{n-1}{2}} n\eta'_n \tag{38}$$

$$\eta'_L \equiv \left.\frac{\sigma}{\dot{\gamma}}\right|_{\dot{\gamma}=\pm\dot{\gamma}_o} = G_{KV}\left.\frac{\gamma}{\dot{\gamma}}\right|_{\dot{\gamma}=\pm\dot{\gamma}_o} + \left.\eta_{KV}\right|_{\dot{\gamma}=\pm\dot{\gamma}_o}, \tag{39}$$

$$\eta'_L \Rightarrow \eta_{KV}\left(\pm\dot{\gamma}_o\right) = \sum_{n\,odd} \eta'_n \tag{40}$$

$$T \equiv \frac{\eta'_L - \eta'_M}{\eta'_L} = \frac{\eta_{KV}\left(\pm\dot{\gamma}_o\right) - \eta_{KV}\left(0\right)}{\eta_{KV}\left(\pm\dot{\gamma}_o\right)} \tag{41}$$

2.5 LAOStress

The work of Dimitriou *et al.* (2013) shows that, for the material analyzed, namely a carbopol gel, it is more interesting to separate the strain into an elastic contribution and a non-elastic one than to separate the stress into elastic and non-elastic parts. They called the non-elastic part a *plastic* part instead of viscous part. Their first attempt to model the carbopol gel was based on the paradigm here highlighted, but coming from a different input, i.e. the same rationale that make one define the linear viscoelastic compliances J', J'' of SAOStress, was adapted to a LAOStress context. The Fourier Transform of the output of a LAOStress experiment with an input of the form $\sigma = \sigma_o \cos\omega\mathrm{t}$ is given by

$$\gamma = \sigma_o \left[\sum_{n\,\mathrm{odd}} J'_n(\omega,\sigma_o)\cos \mathrm{n}\omega\mathrm{t} + \sum_{\mathrm{n\,odd}} \mathrm{J}''_\mathrm{n}(\omega,\sigma_\mathrm{o})\sin \mathrm{n}\omega\mathrm{t},\right] \tag{42}$$

Dimitriou *et al.* (2013) created a Strain Decomposition, a strain version of the SD made by Cho *et al.* (2005), by dividing the strain output from a LAOStress experiment into two additive parts, γ' and γ'', which were called *apparent elastic strain* and *apparent plastic strain*, respectively. They used the analogous symmetry assumptions, that γ' is a single-valued function of the stress σ and $\dot{\gamma}''$ is a single-valued function of σ. Combining this decomposition with the Fourier and Chebyshev representations of a LAOStress input of $\sigma = \sigma_o \cos\omega\mathrm{t}$ they arrive into

$$\gamma' = \sigma_o \sum_{n\,\mathrm{odd}} J'_n(\omega,\sigma_o)\cos \mathrm{n}\omega\mathrm{t} = \sigma_\mathrm{o} \sum_{\mathrm{n\,odd}} \mathrm{c_n}(\omega,\sigma_\mathrm{o})\,\mathrm{T_n}(\sigma/\sigma_\mathrm{o}), \tag{43}$$

and

$$\dot{\gamma}'' = \sigma_o \sum_{n\,\mathrm{odd}} n\omega J''_n(\omega,\sigma_o)\cos \mathrm{n}\omega\mathrm{t} = \sigma_\mathrm{o} \sum_{\mathrm{n\,odd}} \mathrm{f_n}(\omega,\sigma_\mathrm{o})\,\mathrm{T_n}(\sigma/\sigma_\mathrm{o}), \tag{44}$$

In order to proceed and conduct the LAOStress-Maxwell analysis, which is the counterpart of the LAOStrain analysis conducted in the last subsection, we need to take the time derivatives of σ and γ', which are given by

$$\dot{\sigma} = -\omega\sigma_o \sin\omega\mathrm{t} \tag{45}$$

$$\dot{\gamma}' = -\sigma_o \sum_{n\,\mathrm{odd}} n\omega J'_n(\omega,\sigma_o)\sin \mathrm{n}\omega\mathrm{t} = \sigma_\mathrm{o} \sum_{\mathrm{n\,odd}} \mathrm{f_n}(\omega,\sigma_\mathrm{o})\,\dot{\mathrm{T}}_\mathrm{n}(\sigma/\sigma_\mathrm{o}). \tag{46}$$

From Eq. (17) we have that

$$J_{MW}\dot{\sigma} = \dot{\gamma}';\ \phi_{MW}\sigma = \dot{\gamma}'' \tag{47}$$

Therefore,

$$J_{MW} = \sum_{n\,\mathrm{odd}} nJ'_n(\omega,\sigma_o)\frac{\sin \mathrm{n}\omega\mathrm{t}}{\sin\omega\mathrm{t}} = J'_1(\omega,\sigma_o) + \sum_{n=3\,\mathrm{odd}} nJ'_n(\omega,\sigma_o)\frac{\sin \mathrm{n}\omega\mathrm{t}}{\sin\omega\mathrm{t}}. \tag{48}$$

$$\phi_{MW} = \sum_{n\,\mathrm{odd}} n\omega J''_n(\omega,\sigma_o)\frac{\cos \mathrm{n}\omega\mathrm{t}}{\cos\omega\mathrm{t}} = \phi_1(\omega,\sigma_o) + \sum_{n=3\,\mathrm{odd}} n\phi'_n(\omega,\sigma_o)\frac{\cos \mathrm{n}\omega\mathrm{t}}{\cos\omega\mathrm{t}}. \tag{49}$$

Equation (**??**) can be rewritten so as to explicit its Fourier coefficients as

$$J_{MW} = \sum_{p\,\mathrm{even}} J_{MW(p)}(\omega,\sigma_o)\cos \mathrm{p}\omega\mathrm{t}. \tag{50}$$

ISSN 2176-5480

where $J_{MW(p)}$ is given by

$$J_{MW(0)} = \sum_{n\,\mathrm{odd}} nJ'_n(\omega, \sigma_o), \quad (51)$$

$$J_{MW(p)} = \sum_{n=p+1, n\, odd} 2nJ'_n(\omega, \sigma_o). \quad (52)$$

Analogously, Eq. (**??**) can also be rewritten in a Fourier form as

$$\phi_{MW} = \sum_{p\,\mathrm{even}} \phi_{MW(p)}(\omega, \sigma_o) \cos \mathrm{p}\omega \mathrm{t}. \quad (53)$$

where $\phi_{MW(p)}$ is given by

$$\phi_{MW(0)} = \sum_{n\,\mathrm{odd}} (-1)^{\frac{n-1}{2}} n\phi'_n(\omega, \sigma_o), \quad (54)$$

$$\phi_{MW(p)} = \sum_{n=p+1,\,\mathrm{odd}} (-1)^{\frac{n-p-1}{2}} n\phi'_n(\omega, \sigma_o), \quad (55)$$

2.6 Comments on LAOS

The first thing to notice from the analysis above is that there is a tendency of interpreting SAOStrain and LAOStrain experiments from a Kelvin-Voigt framework while SAOStress and LAOStress from a Maxwell framework. From the Fourier-Chebyshev perspective, the major difference between the coefficients $G'_n - G''_n$ and $J'_n - J''_n$, or $e_n - v_n$ and $c_n - f_n$ is that they are defined in different tests, $G'_n - G''_n$ and $e_n - v_n$ in strain input tests and $J'_n - J''_n$ and $c_n - f_n$. It is worth noticing that this tendency is based on the paradigm here stated and repeated, that the viscoelastic response can be decouple into two additive parts one elastic and the other non-elastic. What we want to make clear is that, although this approach has no undesirable consequences in the linear viscoelastic regime, it seems not to be consistent when a complex material is subjected to nonlinear input as is done in LAOS. When we substitute the Kelvin-Voigt parameters, G_{KV} and η_{KV} obtained from a SAOStrain experiment, Eqs. (9) and (10), into the Kelvin-Voigt model, represented by Eq. (5) we have the same stress response that is obtained if we substitute the Maxwell parameters, Eqs. (11) and (12), into Eq. (6). The same reasoning applies to SAOStress. Hence, the linear viscoelastic regime is not capable of discriminating the two materials.

The results reported by Dimitriou *et al.* (2013) show an interesting connection between viscous and plastic effects. This fact is represented by calling the non-elastic response of the material, usually termed viscous term, they used the terminology *plastic*, using a solid-mechanics oriented choice, since in solid mechanics, the phenomenon associated to dissipation is linked to plasticity. In other words, the found that, for the carbopol gel investigated, which presents a yield stress character, viscous and plastic features are coupled in the non-elastic term. As deeply discussed by de Souza Mendes and Thompson (2012), this finding is in clear opposition to some models that merge elastic and yield stress features in the same term (called Type I models), and is in clear accordance to other models that use the same coupling (called Type II models).

3. The lack of physical significance of the total strain, γ

Maxwell

$$\tau + \frac{\eta}{G}\dot{\tau} = \eta\dot{\gamma} \quad (56)$$

$t < 0, \tau = \dot{\tau} = \gamma = \dot{\gamma} = 0$

$t = 0^+, \gamma = \gamma_A$

$$\Rightarrow \tau(t) = G\gamma_A \exp\left(-\frac{\mathrm{G}}{\eta}\mathrm{t}\right) \quad (57)$$

From the mechanical analog, $\gamma_e = \gamma_A \exp\left(-\frac{\mathrm{G}}{\eta}\mathrm{t}\right)$. After a time $t = t_1$

$$\Rightarrow \tau(t_1) = G\gamma_A \exp\left(-\frac{\mathrm{G}}{\eta}\mathrm{t}_1\right) \quad (58)$$

At this point, the material has “forgotten" its original configuration. The unrecoverable strain is given by

$$\gamma_p = \gamma_A \left[1 - \exp\left(-\frac{\mathrm{G}}{\eta}\mathrm{t}_1\right)\right] \quad (59)$$

This deformation is the one that remains when the stress is removed, i.e. is the preferred configuration of the material. Let us suppose, at time t_1^+ we impose that the material goes from $\gamma = \gamma_A$ to $\gamma = \gamma_A + \gamma_B$, $\gamma_B \neq \gamma_A$. This implies that

$$\tau(t) = \left[G\gamma_A \exp\left(-\frac{\mathrm{G}}{\eta}\mathrm{t}_1\right) + \mathrm{G}\gamma_\mathrm{B}\right] \exp\left[-\frac{\mathrm{G}}{\eta}(\mathrm{t} - \mathrm{t}_1)\right] \tag{60}$$

and

$$\gamma_e = \left[\gamma_A \exp\left(-\frac{\mathrm{G}}{\eta}\mathrm{t}_1\right) + \gamma_\mathrm{B}\right] \exp\left[-\frac{\mathrm{G}}{\eta}(\mathrm{t} - \mathrm{t}_1)\right] \tag{61}$$

and

$$\gamma_p = \gamma_A + \gamma_B - \left\{\left[\gamma_A \exp\left(-\frac{\mathrm{G}}{\eta}\mathrm{t}_1\right) + \gamma_\mathrm{B}\right] \exp\left[-\frac{\mathrm{G}}{\eta}(\mathrm{t} - \mathrm{t}_1)\right]\right\} \tag{62}$$

Hence, the level of stress is dependent on time t_1, the amount of time that we keep the material at a constant deformation, while the total deformation is $\gamma = \gamma_A + \gamma_B$.

4. BEYOND MAXWELL AND KELVIN-VOIGT MBFR

4.1 The Jeffreys framework

As the analysis above has shown, Maxwell and Kelvin-Voigt models were indirectly used to interpret LAOS data. The main quantities used in the literature have a clear interpretation when we apply the Maxwell-MBFR to a stress input response and a Kelvin-Voigt-MBFR to a strain input.

There are some ways of combining springs and dashpots in order to produce a one step further framework, departing from the Maxwell or Kelvin-Voigt models in such a way that it can reduce to one or the other, depending on the chosen limiting values for the modulus and/or viscosities. One interesting one that was shown to provide an excellent performance in some cases was the one proposed by de Souza Mendes et al. (2013). It is an example of application of the present ideas.

5. REFERENCES

The list of references must be introduced as a new section, located at the end of the paper. The first line of each reference must be aligned at left. All the other lines must be indented by 0.5 cm from the left margin. All references included in the reference list must have been mentioned in the text.

References must be listed in alphabetical order, according to the last name of the first author. See the following examples:

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