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ABSTRACT

In a recent paper, we derived expressions for determining the rate-dependent response spectra directly from parallel superposition rheometry data for the case of a certain Lodge-type integral constitutive model. It was shown that, within the confines of linear Yamamoto perturbation theory, the corresponding parallel superposition moduli satisfy the classical Kramers-Kronig relations. Special bases were presented to convert parallel superposition moduli to orthogonal superposition moduli. In the current paper, we obtain similar results for the integral models of Wagner I and, more generally, K-BKZ. These results facilitate the physical interpretation of parallel superposition moduli and direct model-based comparison of parallel and orthogonal superposition moduli in the study of weak nonlinear response.

I. INTRODUCTION

Superposition rheometry is a technique for exploring the nonlinear rheological properties of complex fluids,[1,2] which involves superposition of a small amplitude oscillatory perturbation, of amplitude γ_0 and angular frequency ω, upon a unidirectional flow with a constant strain-rate $\dot{\gamma}$. Two kinds of perturbations may be applied: the first in parallel with the bulk flow and termed parallel superposition rheometry (PSR) and the second orthogonal to the bulk flow and termed orthogonal superposition rheometry (OSR). Following Yamamoto,[3] we express the kinematics of the two techniques as follows:

$$\begin{aligned} x_1(t) &= x_1(t') + [\dot{\gamma}(t-t') + a(e^{i\omega t} - e^{i\omega t'})]x_2(t'), \\ x_2(t) &= x_2(t'), \\ x_3(t) &= x_3(t') + b(e^{i\omega t} - e^{i\omega t'})x_2(t'), \end{aligned} \tag{1}$$

where $a = \gamma_0$ and $b = 0$ for PSR, while for OSR $a = 0$ and $b = \gamma_0$. The oscillatory parts of the stress and strain waveforms generated by the kinematics may be used to define a *superposition complex modulus* $G^*_{\parallel}(\omega, \dot{\gamma})$ or $G^*_{\perp}(\omega, \dot{\gamma})$ (in PSR and OSR, respectively). The subscripts $\parallel$ and $\perp$ serve to distinguish the superposition moduli from each other and the linear complex modulus $G^*(\omega)$.[4]

In linear viscoelasticity, the complex modulus may be written in terms of a memory kernel, $m(s)$, where $s = t - t'$ denotes the time lapse, or in terms of a relaxation spectrum, $H(\tau)$, where τ denotes the relaxation time. Thus,

$$G^*(\omega) = \int_0^\infty m(s)(1 - e^{-i\omega s})ds \tag{2}$$

or

$$G^*(\omega) = \int_0^\infty \frac{i\omega\tau}{1 + i\omega\tau} H(\tau)\frac{d\tau}{\tau}, \tag{3}$$

where $G^*(\omega) = G'(\omega) + iG''(\omega)$. The relaxation spectrum, $H(\tau)$, is the inverse Laplace transform of the memory kernel, with the convention that the forward Laplace transform is taken with respect to the reciprocal relaxation time τ^{-1}, i.e.,

$$H(\tau) = \mathcal{L}^{-1}[m(s)](\tau), \quad m(s) = -\int_0^\infty H(\tau)e^{-s\tau^{-1}}d(\tau^{-1}). \tag{4}$$

Bernstein's theorem[5] tells us that the spectrum $H(\tau)$ is non-negative if and only if the memory kernel is completely monotonic, i.e., as

we go back in time (s increasing), $m(s)$ is monotonically decreasing, its first derivative $\dot{m}(s)$ is monotonically increasing, its second derivative $\ddot{m}(s)$ is monotonically decreasing, and so on, in alternating mode, for all higher derivatives. The linear moduli $G'(\omega)$ and $G''(\omega)$ are non-negative, with $G'(\omega)$ being a monotonically increasing function of frequency. The two moduli are not independent and are related via the Kramers-Kronig relations.[6,7]

In this paper, we shall be concerned with the *response spectra* in both OSR and PSR. For the incompressible K-BKZ constitutive model,[8,9] these spectra are analogous to the linear relaxation spectrum in Eq. (4) in a weakly nonlinear setting. In OSR, there is a well-defined memory kernel which takes on a functional dependence on shear-rates $\dot{\gamma}$, as well as time. This functional dependence is expressed in terms of invariants of the motion. When an appropriate linear perturbation is performed, an associated response spectrum $H_\perp(\tau, \dot{\gamma})$ can be defined as the inverse Laplace transform of a rate-dependent kernel $m(\dot{\gamma}s, s)$, in exactly the same way as in Eq. (4),

$$H_\perp(\tau, \dot{\gamma}) = \mathcal{L}^{-1}[m(\dot{\gamma}s, s)](\tau). \tag{5}$$

The situation in PSR is more complicated. In particular, the interpretation of $G^*_\parallel$ must allow for coupling of the unidirectional and oscillatory components. As $\dot{\gamma}$ increases away from zero, negative values of $G'_\parallel$ are often reported in the literature (e.g., Refs. 1, 2, and 10–13), thus preventing the conventional interpretation of $G'_\parallel$ and $G''_\parallel$ in terms of intracycle energy storage and dissipation, as per their quiescent counterparts. It is also commonly stated that the real and imaginary parts of $G^*_\parallel$ do not satisfy the Kramers-Kronig relations, even for small amplitude oscillations.

In OSR, the components of $G^*_\perp$ appear to retain the same physical meaning as those of G^* for small perturbation amplitudes.[14,15] Consequently, despite the ease of implementing PSR experiments on commercial rheometers, OSR has (for the past 20 years) been the preferred methodology. However, such experiments require specific hardware, e.g., the TA Instruments Orthogonal Superposition accessory, which employs the rheometer's normal force transducer to generate the oscillatory component,[16] and the availability of relatively large quantities of materials (approximately 50 ml). Furthermore, a recent study of flow induced anisotropy in colloidal gels employed the ratio of G' measured in orthogonal directions as a measure of anisotropy.[15] In that study, in order to avoid "the problems associated with parallel superposition experiments," materials for which microstructural recovery was relatively slow were studied such that small amplitude oscillatory shear experiments probing the anisotropic rheology could be performed following cessation of the unidirectional flow.[15] There is hence clearly a need for further study of superposition moduli to (i) allow for physical interpretation of $G^*_\parallel$ and (ii) facilitate the development of a quantitative interpretation of flow induced anisotropy probed by superposition rheometry.[17]

In Ref. 18, it was shown that, for certain Lodge-type constitutive models, under the constraint of oscillatory perturbations of small amplitude, (i) the real and imaginary parts of $G^*_\perp$ and $G^*_\parallel$ satisfy the Kramers-Kronig relations and (ii) the relationships between the superposition moduli can be derived that may be used as a basis for a quantitative comparison of PSR and OSR data. In the current paper, we show that the same is true for incompressible K-BKZ integral constitutive models. The Wagner I model,[19] studied by Vermant *et al.*,[14] merits a separate study as a special case of K-BKZ, and we begin with this model.

II. THE WAGNER I MODEL

Consider an integral constitutive model for which the stress tensor takes the form

$$\sigma = \int_{-\infty}^{t} m(t-t')h(I_1, I_2)\mathbf{C}^{-1}(t, t')dt', \tag{6}$$

where m is the zero shear-rate memory function, $\mathbf{C}^{-1}(t, t')$ is the relative Finger strain tensor, and h is a damping function depending on the first and second invariants, I_1 and I_2, of $\mathbf{C}^{-1}(t, t')$. In the Wagner I model, h is a single exponential function of the form

$$h(I_1, I_2) = e^{-n\sqrt{I-3}}, \quad I = \alpha I_1 + (1-\alpha)I_2, \tag{7}$$

where $n > 0$ and α are constants. In both OSR and PSR, the first and second invariants are equal. In particular, expanding about $\gamma_0 = 0$, one finds

$$I = I_1 = I_2 = 3 + \dot{\gamma}^2(t-t')^2 + 2a[\gamma_0\dot{\gamma}(t-t')(e^{i\omega t} - e^{i\omega t'})] + O(\gamma_0^2), \tag{8}$$

where $a = 0$ in the case of OSR, with $a = 1$ for PSR (cf. Bernstein[20]).

In this section, we show that there exist orthogonal and parallel response spectra for the Wagner I model, which can be written explicitly in terms of the linear relaxation spectrum $H(\tau)$. To this end, we use expressions for the orthogonal superposition modulus, $G^*_\perp(\omega, \dot{\gamma})$, derived by Vermant *et al.*[14] The parallel superposition modulus, $G^*_\parallel(\omega, \dot{\gamma})$, can then be derived from a result in Bernstein.[20] We also show that, for both OSR and PSR, these superposition moduli satisfy the Kramers-Kronig relations.

A. Orthogonal superposition

In OSR, expanding to first order, the damping function is independent of γ_0 and takes the form

$$h(I_1, I_2) = e^{-n\dot{\gamma}(t-t')}. \tag{9}$$

The superposition moduli can be expressed in the form (cf. Vermant *et al.*[14])

$$G'_\perp(\omega, \dot{\gamma}) = \int_0^\infty \frac{\omega^2\tau^2 H(\tau)}{(1+n\dot{\gamma}\tau)[(1+n\dot{\gamma}\tau)^2 + \omega^2\tau^2]}\frac{d\tau}{\tau}, \tag{10}$$

$$G''_\perp(\omega, \dot{\gamma}) = \int_0^\infty \frac{\omega\tau H(\tau)}{[(1+n\dot{\gamma}\tau)^2 + \omega^2\tau^2]}\frac{d\tau}{\tau}. \tag{11}$$

To show that these moduli satisfy the Kramers-Kronig relations, we introduce the *reduced relaxation time*, λ, defined by

$$\lambda = \frac{\tau}{1+n\dot{\gamma}\tau}. \tag{12}$$

This relaxation time enjoys the following properties:

- λ is a monotonically increasing function of the linear relaxation time τ;
- $\lambda \to (n\dot{\gamma})^{-1}$ as $\tau \to \infty$;
- λ decreases monotonically as the shear-rate increases; and
- the linear relaxation time is recovered ($\lambda \to \tau$) as $\dot{\gamma} \to 0$.

Noting that $\tau = \lambda(1 - n\dot{\gamma}\lambda)^{-1}$, we may write $H(\tau)$ as a function of λ. We adopt the notation

$$H(\tau) = H_\perp(\lambda), \quad 0 \le \lambda < (n\dot{\gamma})^{-1} \tag{13}$$

and will show that $H_\perp(\lambda)$ is the rate-dependent response spectrum under OSR. First, it is convenient to extend the function $H_\perp(\lambda)$ to the full interval $0 \le \lambda < \infty$. Define

$$H_\perp(\lambda) = \begin{cases} H(\lambda(1 - n\dot{\gamma}\lambda)^{-1}), & 0 \le \lambda < (n\dot{\gamma})^{-1}, \\ 0, & (n\dot{\gamma})^{-1} \le \lambda < \infty. \end{cases} \tag{14}$$

Since $H(\tau) \to 0$ as $\tau \to \infty$, the function defined by (14) is continuous at the joint $\lambda = (n\dot{\gamma})^{-1}$. The extension also applies to integrals. Let $f(\lambda)$ be any function such that $f(\lambda)H_\perp(\lambda)$ is integrable over the interval $0 \le \lambda < (n\dot{\gamma})^{-1}$. Then, (14) implies

$$\int_0^{(n\dot{\gamma})^{-1}} f(\lambda)H_\perp(\lambda) = \int_0^\infty f(\lambda)H_\perp(\lambda). \tag{15}$$

We continue the argument by differentiating (12). Let $n\dot{\gamma}$ be a fixed parameter. Then,

$$\frac{d\tau}{(1 + n\dot{\gamma}\tau)^2} = d\lambda, \tag{16}$$

and hence,

$$\frac{d\tau}{(1 + n\dot{\gamma}\tau)^2 + \omega^2\tau^2} = \frac{d\lambda}{1 + \omega^2\lambda^2}. \tag{17}$$

Changing the variable from τ to λ in (10) and (11), and making use of (15), we find

$$G'_\perp(\omega, \dot{\gamma}) = \int_0^\infty \frac{\omega^2\lambda^2}{1 + \omega^2\lambda^2} H_\perp(\lambda) \frac{d\lambda}{\lambda}, \tag{18}$$

$$G''_\perp(\omega, \dot{\gamma}) = \int_0^\infty \frac{\omega\lambda}{1 + \omega^2\lambda^2} H_\perp(\lambda) \frac{d\lambda}{\lambda}. \tag{19}$$

Equations (18) and (19) hold for every value of the parameter $n\dot{\gamma} \ge 0$. They may be combined to form the complex modulus

$$G^*_\perp(\omega, \dot{\gamma}) = G'_\perp(\omega, \dot{\gamma}) + iG''_\perp(\omega, \dot{\gamma}) = \int_0^\infty \frac{i\omega\lambda}{1 + i\omega\lambda} H_\perp(\lambda) \frac{d\lambda}{\lambda}. \tag{20}$$

The real and imaginary parts of $G^*_\perp$ satisfy the Kramers-Kronig relations since $G^*_\perp$ is analytic in the open right-hand half of the complex frequency plane, $Re\ \omega > 0$. A sufficient condition for the analyticity is that $\int_0^\infty \lambda^{-1}H_\perp(\lambda)d\lambda < \infty$. This is equivalent to demanding that the plateau modulus $G'_\perp(\infty, \dot{\gamma})$ has a finite value. That this is the case follows from (10) since

$$\begin{aligned} G'_\perp(\infty, \dot{\gamma}) &= \lim_{\omega\to\infty} G'_\perp(\omega, \dot{\gamma}) \\ &= \int_0^\infty \frac{H(\tau)}{1 + n\dot{\gamma}\tau} \frac{d\tau}{\tau} \le \int_0^\infty H(\tau) \frac{d\tau}{\tau} = G'(\infty). \end{aligned} \tag{21}$$

Vermant *et al.*[14] have shown that, for the Wagner I model, the shear viscosity is given by

$$\eta(\dot{\gamma}) = \int_0^\infty \frac{H(\tau)d\tau}{(1 + n\dot{\gamma}\tau)^2}. \tag{22}$$

This may be rewritten as

$$\eta(\dot{\gamma}) = \int_0^\infty H_\perp(\lambda)d\lambda. \tag{23}$$

Equations (18), (19), and (23) establish the function $H_\perp(\lambda)$ as a rate-dependent response spectrum for OSR. Thus, we may write $H_\perp(\lambda) = H_\perp(\tau, \dot{\gamma})$, where

$$H_\perp(\tau, \dot{\gamma}) = \begin{cases} H(\tau(1 - n\dot{\gamma}\tau)^{-1}), & 0 \le \tau < (n\dot{\gamma})^{-1}, \\ 0, & (n\dot{\gamma})^{-1} \le \tau < \infty. \end{cases} \tag{24}$$

For the Wagner I model, we have therefore obtained the following:

Result II.1. There exists an orthogonal response spectrum which is a simple recalibration of the linear relaxation spectrum given by (24).

Result II.2. The orthogonal spectrum has no relaxation time greater than $(n\dot{\gamma})^{-1}$.

Result II.3. The orthogonal superposition moduli derived by Vermant *et al.*[14] satisfy the Kramers-Kronig relations.

B. Parallel superposition

Bernstein[20] derives a relation between the parallel and orthogonal complex moduli, $G^*_\parallel(\omega, \dot{\gamma})$ and $G^*_\perp(\omega, \dot{\gamma})$, for a general K-BKZ model. Since the Wagner I model is a special case of the K-BKZ model, Bernstein's result may be used to derive $G^*_\parallel(\omega, \dot{\gamma})$ for the Wagner I model. The expression so obtained for the modulus $G''_\parallel(\omega, \dot{\gamma})$ agrees exactly with the expression obtained by Vermant *et al.* [Ref. 14, Eq. (35)], but the expression obtained from Bernstein's formula for the modulus $G'_\parallel(\omega, \dot{\gamma})$ does not agree with the expression obtained by Vermant *et al.* [Ref. 14, Eq. (34)]. The moduli obtained by Vermant *et al.* do not satisfy the Kramers-Kronig relations, but we shall show that the moduli obtained from Bernstein's formula do satisfy these relations.

Bernstein's formula may be stated as

$$G^*_\parallel(\omega, \dot{\gamma}) = G^*_\perp(\omega, \dot{\gamma}) + \dot{\gamma}\frac{\partial}{\partial\dot{\gamma}} G^*_\perp(\omega, \dot{\gamma}) \tag{25}$$

and is valid when the memory function and its invariants are expanded to first order in γ_0. Bernstein shows that the result does not necessarily hold outside the K-BKZ class of models. More recently, in Ref. 18, we have shown that a different differential relationship holds for certain Lodge-type models. In theory, the solution of the differential equation (25) gives a formula for converting $G^*_\parallel(\omega, \dot{\gamma})$ to $G^*_\perp(\omega, \dot{\gamma})$ for any K-BKZ model,

$$G^*_\perp(\omega, \dot{\gamma}) = \dot{\gamma}^{-1} \int_0^{\dot{\gamma}} G^*_\parallel(\omega, x)dx. \tag{26}$$

This formula is best implemented by means of a spectral representation for $G^*_\parallel$ (see Sec. III B).

Equation (25) enables a straightforward validation of the Kramers-Kronig relations for the parallel superposition moduli of the Wagner I model. To this end, write (20) in the form

$$G^*_\perp(\omega, \dot{\gamma}) = \int_0^\infty \frac{i\omega\tau}{1 + i\omega\tau} H_\perp(\tau, \dot{\gamma}) \frac{d\tau}{\tau}, \tag{27}$$

where $H_\perp$ is defined in (24). The functional dependence of $G_\perp^*(\omega,\dot\gamma)$ on $\dot\gamma$ is made clearer if (27) is rewritten as

$$G_\perp^*(\omega,\dot\gamma)=\int_0^{(n\dot\gamma)^{-1}}\frac{i\omega\tau}{1+i\omega\tau}H(\rho)\frac{d\tau}{\tau}, \tag{28}$$

where H is the linear relaxation spectrum and

$$\rho=\rho(\tau,\dot\gamma)=\tau(1-n\dot\gamma\tau)^{-1}. \tag{29}$$

Now, $H(\rho)\to 0$ as $\tau\to(n\dot\gamma)^{-1}$. Substituting (28) into (25) and applying Liebniz rule for integrals then give

$$G_\parallel^*(\omega,\dot\gamma)=\int_0^{(n\dot\gamma)^{-1}}\frac{i\omega\tau}{1+i\omega\tau}\left[H(\rho)+\dot\gamma\frac{\partial}{\partial\dot\gamma}H(\rho)\right]\frac{d\tau}{\tau}. \tag{30}$$

It is easily shown that $\frac{\partial\rho}{\partial\dot\gamma}=n\rho^2$. Hence, we conclude that

$$G_\parallel^*(\omega,\dot\gamma)=\int_0^{\infty}\frac{i\omega\tau}{1+i\omega\tau}H_\parallel(\tau,\dot\gamma)\frac{d\tau}{\tau}, \tag{31}$$

where $H_\parallel(\tau,\dot\gamma)$ is the parallel response spectrum for the Wagner I model, given by

$$H_\parallel(\tau,\dot\gamma)=\begin{cases}H(\rho)+n\dot\gamma\rho^2H'(\rho), & 0\le\tau<(n\dot\gamma)^{-1},\\ 0, & (n\dot\gamma)^{-1}\le\tau<\infty.\end{cases} \tag{32}$$

Here, $H'(\rho)$ denotes the derivative with respect to the single variable ρ. We shall refer to Eqs. (27) and (31) as *spectral representations* of the superposition moduli.

From (31), we see that the real and imaginary parts of $G_\parallel^*$ satisfy the Kramers-Kronig relations since $G_\parallel^*$ is analytic in the open right-hand half of the complex frequency plane, exactly in a similar fashion to (20). A sufficient condition for the analyticity is that $\int_0^\infty\tau^{-1}H_\parallel(\tau,\dot\gamma)d\tau<\infty$. This can be deduced from the two standard constraints on the linear spectrum H given by

$$\int_0^\infty\tau^{-1}H(\tau)d\tau<\infty\quad\text{and}\quad\int_0^\infty H(\tau)d\tau<\infty. \tag{33}$$

To summarize, for the Wagner I model, we have established the following:

Result II.4. There exists a parallel response spectrum which may be expressed in terms of the linear relaxation spectrum and its first derivative [Eq. (32)].

Result II.5. Like the orthogonal spectrum, the parallel spectrum has no relaxation time greater than $(n\dot\gamma)^{-1}$.

Result II.6. The real and imaginary parts of the parallel complex modulus derived from Bernstein's formula satisfy the Kramers-Kronig relations.

C. Wagner I superposition moduli and the response spectra

Unlike the Lodge-type model studied in Ref. 18, the Wagner I model allows for easy interconversion between parallel and orthogonal superposition moduli. Once the damping parameter, n, and the linear relaxation spectrum, H, have been determined, there are explicit expressions available for calculating these moduli. The calculated moduli can then be compared with either PSR or OSR measurements to evaluate the model as a means of predicting the dynamics of the material being studied. The orthogonal superposition moduli are given by (10) and (11), while the parallel moduli are readily calculated by substituting these expressions into Bernstein's formula. Thus, we obtain

$$G_\parallel'=\int_0^\infty H(\tau)\omega^2\tau^2\left[\frac{1}{N(N^2+\omega^2\tau^2)}-\frac{n\dot\gamma\tau}{N^2(N^2+\omega^2\tau^2)}-\frac{2n\dot\gamma\tau}{(N^2+\omega^2\tau^2)^2}\right]\frac{d\tau}{\tau}, \tag{34}$$

$$G_\parallel''=\int_0^\infty H(\tau)\omega\tau\left[\frac{1}{(N^2+\omega^2\tau^2)}-\frac{2n\dot\gamma\tau N}{(N^2+\omega^2\tau^2)^2}\right]\frac{d\tau}{\tau}, \tag{35}$$

where $N=1+n\dot\gamma\tau$.

These two moduli satisfy the Kramers-Kronig relations since, writing $\tau=\lambda(1-n\dot\gamma\lambda)^{-1}$, they may be combined into the complex form

$$G_\parallel^*(\omega,\dot\gamma)=\int_0^\infty\frac{i\omega\lambda}{1+i\omega\lambda}\chi(\lambda)[H(\tau)+n\dot\gamma\tau^2H'(\tau)]\frac{d\lambda}{\lambda},\qquad \chi(\lambda)=\begin{cases}1, & 0\le\lambda<(n\dot\gamma)^{-1},\\ 0, & \lambda\ge(n\dot\gamma)^{-1},\end{cases} \tag{36}$$

with the requisite analyticity properties. As mentioned earlier, Eq. (35) agrees with the expression derived by Vermant *et al.* for $G_\parallel''$. Their expression for $G_\parallel'$, however, differs from (34).

Useful results can also be deduced from the response spectra.

Result II.7. Since the linear spectrum $H(\tau)$ is always non-negative, so is the orthogonal response spectrum $H_\perp(\tau,\dot\gamma)$.

This result follows immediately from (24). The implication is that the orthogonal moduli given by (10) and (11) have the same interpretation in terms of energy storage and loss as do the linear moduli.

Result II.8. Let $H(\tau)$ and $H'(\tau)$ be continuous functions of τ. Provided $\tau^{-2}H(\tau)$ remains finite as $\tau\to 0$, the parallel response spectrum $H_\parallel(\tau,\dot\gamma)$ always has negative parts for sufficiently high shear-rates $\dot\gamma$.

The proof of this result is as follows. From Eq. (32), we infer that

$$H_\parallel(\tau,\dot\gamma)<0\quad\text{when}\quad H'(\rho)<-(n\dot\gamma)^{-1}\rho^{-2}H(\rho). \tag{37}$$

If $\tau^{-2}H(\tau)$ remains finite as $\tau\to 0$, then $\rho^{-2}H(\rho)$ has a supremum, M, say. But $H(\rho)\to 0$ as $\rho\to\infty$. Thus, $H'(\rho)$ has a negative infimum, $-L$, say. The inequality in (37) is satisfied for a range of ρ values, if $L>(n\dot\gamma)^{-1}M$. Since L and M are constants, independent of $\dot\gamma$, the latter inequality will be satisfied for sufficiently large shear-rates.

The implication of Result II.8 is that $G_\parallel'(\omega,\dot\gamma)$ and $G_\parallel''(\omega,\dot\gamma)$ may become negative at higher shear-rates. There are many reports of the negativity of $G_\parallel'(\omega,\dot\gamma)$ in the literature.

III. THE K-BKZ MODEL

The Wagner I model was originally proposed as a special case of the general K-BKZ model with a separable memory kernel. Some of the results derived in Sec. II emerge because of the simple form of the Wagner I memory kernel. For example, the upper limit on relaxation times observed in the response spectra arises from the

exponential damping function and may not arise for other damping functions. Again, the relationship between the response spectra and the linear relaxation spectrum arises from the separability of the memory kernel. However, some of the results on the Wagner I model also hold for the general K-BKZ model. Working to first order in γ_0, it is fairly easy to show that, under weak conditions on the memory kernel, the Kramers-Kronig relations hold in the general case for both OSR and PSR.

A. Fourier representation of the superposition moduli

The stress tensor for the incompressible K-BKZ model may be written as follows:

$$\sigma = \int_{-\infty}^{t} \left[\frac{\partial U}{\partial I_1} \mathbf{C}^{-1}(t,t') - \frac{\partial U}{\partial I_2} \mathbf{C}(t,t') \right] dt', \tag{38}$$

where U is an elastic energy kernel with time-dependence

$$U = U(I_1(t,t'), I_2(t,t'), t-t')$$

and, as previously, I_1 and I_2 are the first and second invariants of the Finger strain tensor $\mathbf{C}^{-1}(t,t')$.

For OSR, working to first order in γ_0, Tanner and Williams[21] have derived expressions for the superposition moduli, which in complex form may be written as

$$G_\perp^*(\omega,\dot\gamma) = \int_0^\infty \left[\frac{\partial U}{\partial I_1} + \frac{\partial U}{\partial I_2} \right] (1 - e^{-i\omega s}) ds, \tag{39}$$

where $s = t - t'$ denotes the time lapse. Bernstein[20] argues that there exists a function of two variables $w_* = w_*(\gamma, s)$, γ arbitrary, such that in both OSR and PSR,

$$\frac{\partial U}{\partial I_1} + \frac{\partial U}{\partial I_2} = -w_*(\sqrt{I-3}, s), \tag{40}$$

where I is given by (8).

The function $-w_*$ is a non-negative, nonlinear memory function. We will use the more familiar notation

$$m(\gamma, s) = -w_*(\gamma, s) \geq 0. \tag{41}$$

Under constraint (8), we have

$$m(\sqrt{I-3}, s) = \left[\frac{\partial U}{\partial I_1} + \frac{\partial U}{\partial I_2} \right] (I_1, I_2, s). \tag{42}$$

The function m has the property $m(0, s) = m(s)$, where $m(s)$ is the linear memory function.

Working to first order in γ_0, Bernstein[20] derives expressions for the complex superposition moduli in OSR and PSR. In terms of m, these take the form

$$G_\perp^*(\omega,\dot\gamma) = \int_0^\infty m(\dot\gamma s, s)(1 - e^{-i\omega s}) ds, \tag{43}$$

$$G_\parallel^*(\omega,\dot\gamma) = \int_0^\infty \left[m(\dot\gamma s, s) + \dot\gamma \frac{\partial}{\partial \dot\gamma} m(\dot\gamma s, s) \right] (1 - e^{-i\omega s}) ds. \tag{44}$$

Expanding to first order in γ_0, for OSR, we have $m(\sqrt{I-3}, s) = m(\dot\gamma s, s)$, and so Eq. (43) agrees with (39). We shall refer to Eqs. (43) and (44) as *Fourier representations* of the superposition moduli.

It is now a simple matter to establish that the real and imaginary parts of (43) satisfy the Kramers-Kronig relations. The theory of Fourier integrals (see, e.g., Dym and McKean[22]) tells us that, in (43), $G_\perp^*(\omega,\dot\gamma)$ is analytic in the open lower half of the complex frequency plane, $Im\ \omega < 0$, and is the limit of the analytic function as $Im\ \omega \to 0$. This means that $G_\perp^*(\omega,\dot\gamma)$ may be expressed as a Cauchy integral

$$G_\perp^*(\omega,\dot\gamma) = \frac{1}{2\pi i} \int_\Gamma \frac{G_\perp^*(z,\dot\gamma)}{z-\omega} dz, \quad Im\ \omega < 0. \tag{45}$$

Choosing an appropriate indented contour, Γ, taking limits, and then comparing real and imaginary parts lead to the Kramers-Kronig relations. The same argument establishes these relations for $G_\parallel^*(\omega,\dot\gamma)$ in (44), provided that the memory kernel is absolutely integrable. A sufficient condition is $\int_0^\infty |\frac{\partial}{\partial\dot\gamma} m(\dot\gamma s, s)| ds < \infty$.

B. Spectral representation of the superposition moduli

In Sec. II, we saw that the Wagner I model admits spectral representation of its orthogonal and parallel superposition moduli. We begin this section by asking whether the general K-BKZ model also admits such representations. This question may be answered immediately in the same way as it is answered for the linear superposition moduli.

Result III.1. A sufficient condition for the existence of the orthogonal and parallel response spectra is that the nonlinear memory function $m(\dot\gamma s, s)$ is completely monotonic. We may then write

$$G_\perp^*(\omega,\dot\gamma) = \int_0^\infty \frac{i\omega\tau}{1+i\omega\tau} H_\perp(\tau,\dot\gamma) \frac{d\tau}{\tau}, \tag{46}$$

$$G_\parallel^*(\omega,\dot\gamma) = \int_0^\infty \frac{i\omega\tau}{1+i\omega\tau} H_\parallel(\tau,\dot\gamma) \frac{d\tau}{\tau}, \tag{47}$$

where

$$H_\parallel(\tau,\dot\gamma) = H_\perp(\tau,\dot\gamma) + \dot\gamma \frac{\partial}{\partial\dot\gamma} H_\perp(\tau,\dot\gamma), \tag{48}$$

which may be inverted to give

$$H_\perp(\tau,\dot\gamma) = \dot\gamma^{-1} \int_0^{\dot\gamma} H_\parallel(\tau,x) dx. \tag{49}$$

Result III.1 follows from Bernstein's theorem. Since $m(\dot\gamma s, s)$ is completely monotonic, there is a non-negative function $H_\perp(\tau,\dot\gamma)$ such that m may be written in the form

$$m(\dot\gamma s, s) = \int_0^\infty \frac{1}{\tau} H_\perp(\tau,\dot\gamma) \exp\left(-\frac{s}{\tau}\right) \frac{d\tau}{\tau}. \tag{50}$$

Substituting (50) into (43) and (44) gives the required spectral representations.

It is instructive to examine the relationship between spectral and Fourier representations more fully. Having found two representations for $G_\perp^*(\omega,\dot\gamma)$, it is natural to write

$$\int_0^\infty \frac{i\omega\tau}{1+i\omega\tau} H_\perp(\tau,\dot\gamma) \frac{d\tau}{\tau} = \int_0^\infty m(\dot\gamma s, s)(1 - e^{-i\omega s}) ds. \tag{51}$$

This equation must be treated with care. It is valid for all real values of the frequency ω, but it is not valid everywhere in the complex frequency plane. The spectral representation on the left is analytic in the open right-hand half plane, while the Fourier representation

on the right is analytic in the open lower half plane. The equation is therefore valid in the lower right quadrant of the complex frequency plane. However, since the domain of analyticity of the two analytic functions intersects, we have the elegant result that the integral on the left of Eq. (51) is the analytic continuation of the Fourier representation into the upper right quadrant, while the integral on the right is the analytic continuation of the spectral representation into the lower left quadrant. The same is true for the representations of $G_{\parallel}^{*}(\omega,\dot{\gamma})$.

The above result illustrates the fact that there is usually more than one way of establishing the Kramers-Kronig relations. More details may be found in the book by King (Ref. 23, Chap. 19).

IV. RESPONSE SPECTRA AND INTERCONVERSION

For the Wagner I model, interconversion between parallel and orthogonal superposition moduli is a straightforward exercise because of the explicit forms derivable for each modulus. For the general K-BKZ model, interconversion is not so straightforward unless the functional dependence of $G_{\parallel}^{*}(\omega,\dot{\gamma})$ on $\dot{\gamma}$ is known. In this section, we propose one approach to introducing a functional dependence on $\dot{\gamma}$, which was also studied in Ref. 18 The functional dependence is introduced via the response spectra.

A. Locally exact solutions

We shall find local solutions of Eq. (48) for $H_{\perp}$ in terms of $H_{\parallel}$ by restricting attention to a local range of shear-rates $0 < \dot{\gamma}_a < \dot{\gamma} < \dot{\gamma}_b < \infty$, which we denote by $\Gamma_{ab} = (\dot{\gamma}_a, \dot{\gamma}_b)$. We anticipate that Γ_{ab} covers part of the measurable range of shear-rates in PSR. Without loss of generality, we may write

$$H_{\parallel}(\tau,\dot{\gamma}) = \lambda H(\tau) + \bar{H}_{\parallel}(\tau,\dot{\gamma}), \tag{52}$$

$$H_{\perp}(\tau,\dot{\gamma}) = \lambda H(\tau) + \bar{H}_{\perp}(\tau,\dot{\gamma}), \tag{53}$$

where $H(\tau)$ denotes the linear relaxation spectrum and λ is a constant. In (52) and (53), it is to be assumed that H and $\int_0^{\tau} H_{\perp}$ are non-negative, but no such assumption is made regarding $H_{\parallel}$, $\bar{H}_{\perp}$ or $\bar{H}_{\parallel}$. The shear viscosity is given by

$$\eta(\dot{\gamma}) = \int_0^{\infty} H_{\perp}(\tau,\dot{\gamma})d\tau = \lambda\eta_0 + \bar{\eta}(\dot{\gamma}),$$

where

$$\bar{\eta}(\dot{\gamma}) = \int_0^{\infty} \bar{H}_{\perp}(\tau,\dot{\gamma})d\tau, \tag{54}$$

where η_0 denotes the zero shear-rate viscosity. The constant λ is chosen to ensure

$$\eta(\dot{\gamma}) = \bar{\eta}(\dot{\gamma}) + \lambda\eta_0 \geq 0, \quad \dot{\gamma}_a < \dot{\gamma} < \dot{\gamma}_b. \tag{55}$$

We shall require that $\bar{H}_{\perp}(\tau,\dot{\gamma})$ is piecewise continuously differentiable with respect to both the variables τ and $\dot{\gamma}$. This enables the following:

(i) $\bar{H}_{\parallel}(\tau,\dot{\gamma})$ can be represented by a rate-dependent discrete spectrum and

(ii) if Γ_{ab} is a shear-thinning range, and $\bar{\eta} > 0$, we have

$$\lambda < 1 \quad \text{and} \quad \frac{d}{d\dot{\gamma}}\bar{\eta}(\dot{\gamma}) = \int_0^{\infty} \frac{\partial \bar{H}}{\partial \dot{\gamma}}(\tau,\dot{\gamma})d\tau < 0, \quad \dot{\gamma}_a < \dot{\gamma} < \dot{\gamma}_b. \tag{56}$$

On the other hand, if $\bar{\eta} < 0$, at least one of the inequalities in Eq. (56) is reversed.

Introduce a stretched variable $\xi = \tau\dot{\gamma}^{\alpha}$, where α is a constant. We then seek solutions of Eq. (48) in the form

$$\bar{H}_{\perp}(\tau,\dot{\gamma}) = \bar{H}_{\perp}(\xi), \quad \text{with} \quad \bar{H}_{\parallel}(\tau,\dot{\gamma}) = \bar{H}_{\parallel}(\xi), \quad \xi = \tau\dot{\gamma}^{\alpha}. \tag{57}$$

In the local range of shear-rates Γ_{ab}, the shear viscosity has the form

$$\eta(\dot{\gamma}) = \lambda\eta_0 + \kappa\dot{\gamma}^{-\alpha}, \quad \dot{\gamma}_a < \dot{\gamma} < \dot{\gamma}_b, \tag{58}$$

where $\kappa = \int_0^{\infty} \bar{H}_{\perp}(\xi)d\xi$ is a constant. The constants α and κ have the same sign if the viscosity over the range Γ_{ab} is shear-thinning but are of opposite sign if the viscosity over this range is shear-thickening.

If the range of shear-rates, Γ_{ab}, is sufficiently narrow, any continuous flow curve can be approximated to arbitrary accuracy by the form (58), with its three free parameters λ, κ, and α. By way of illustration, consider a single mode Wagner-type viscosity,

$$\frac{\eta_0}{(1+n\dot{\gamma}\tau_1)^2} \approx \lambda\eta_0 + \kappa\dot{\gamma}^{-\alpha}, \quad \dot{\gamma}_a < \dot{\gamma} < \dot{\gamma}_b. \tag{59}$$

Fitting by point collocation yields the following values for the parameters:

Range 1. $\dot{\gamma}_a = \frac{1}{4}(n\tau_1)^{-1}$, $\dot{\gamma}_b = \frac{1}{2}(n\tau_1)^{-1}$:

$$\lambda = 1.804, \quad \kappa = -1.588\eta_0(n\tau_1)^{-\alpha}, \quad \alpha = -0.224.$$

The maximum error in this range is approximately $10^{-4}\eta_0$.

Range 2. $\dot{\gamma}_a = (n\tau_1)^{-1}$, $\dot{\gamma}_b = 3(n\tau_1)^{-1}$:

$$\lambda = -0.046, \quad \kappa = 0.296\eta_0(n\tau_1)^{-\alpha}, \quad \alpha = 0.915.$$

The maximum error in this range is approximately $10^{-3}\eta_0$. The error can be reduced by narrowing the range of $\dot{\gamma}$, with a corresponding variation in parameter values.

In Range 1, κ and α are both negative, whereas in Range 2 they are both positive. In any given range, κ and α must have the same sign in shear-thinning. If the single mode viscosity is changed to a multimode viscosity, the parameter values will also change.

In terms of the stretched variable ξ, Eq. (48) reduces to the first-order ordinary differential equation:

$$\bar{H}_{\perp}(\xi) + \alpha\xi\bar{H}'_{\perp}(\xi) = \bar{H}_{\parallel}(\xi), \tag{60}$$

where the symbol prime ($'$) denotes differentiation with respect to ξ. This has the solution

$$\bar{H}_{\perp}(\xi) = \beta\int^{\xi}\left(\frac{x}{\xi}\right)^{\beta}\bar{H}_{\parallel}(x)\frac{dx}{x}, \quad \text{with} \quad \beta = 1/\alpha, \tag{61}$$

$$= \beta\int^{\ln\xi}\exp[\beta(\ln x - \ln\xi)]\bar{H}_{\parallel}(x)d(\ln x). \tag{62}$$

The boundary conditions on $\bar{H}_{\perp}$, which are necessary conditions for the viscosity to remain finite, are as follows:

$$\bar{H}_{\perp}(0) = 0 \quad \text{and} \quad \lim_{\xi\to\infty}\bar{H}_{\perp}(\xi) = 0. \tag{63}$$

The same conditions will be asked for $\bar{H}_{\parallel}$. Finally, to ensure regularity in Eq. (60), we impose

$$\lim_{\xi\to\infty}\xi\bar{H}'_{\perp}(\xi) = 0. \tag{64}$$

We now establish a result which is complementary to Result II.8 for the Wagner I model.

Result IV.1. *In a shear-thinning region, $\bar{H}_\parallel(\xi)$ must be negative for some values of the relaxation time τ.*

To prove Result IV.1, it is enough to consider the case $\alpha > 0$, otherwise κ must be negative, and so $\bar{H}_\parallel$ must be negative for some values of the relaxation time. Using Liebniz rule for integrals to differentiate (62), we find

$$\bar{H}'_\perp(\xi) - \xi^{-1}\bar{H}_\parallel(\xi) = -\beta^2\xi^{-1}\int^{\ln\xi} \exp[\beta(\ln x - \ln\xi)]\bar{H}_\parallel(x)d(\ln x). \tag{65}$$

It is clear that if $\bar{H}_\parallel$ is everywhere positive, then $\xi\bar{H}'_\perp(\xi) - \bar{H}_\parallel(\xi)$ is everywhere negative. Furthermore, $\bar{H}_\parallel(\xi) \to 0$ as $\xi \to \infty$. So, there exists either a finite constant $-C < 0$ such that $\xi\bar{H}'_\perp(\xi) \to -C$ as $\xi \to \infty$ or $\xi\bar{H}'_\perp(\xi) \to -\infty$ as $\xi \to \infty$. In either case, condition (64) cannot hold, and so Result IV.1 follows immediately.

B. Discrete and piecewise continuous response spectra

We may infer from (47) that, as in the case of the linear relaxation spectrum, $\bar{H}_\parallel$ is representable as a discrete spectrum. However, this spectrum does not share the properties of a linear relaxation spectrum. Result IV.1 informs us that at least one of the discrete modes must carry a negative coefficient. Complete monotonicity of the associated nonlinear memory function in PSR is thus lost. On the other hand, complete monotonicity is retained by the corresponding OSR memory function. In this section, we explore the nature of a discrete spectral representation for $\bar{H}_\parallel$ and the corresponding spectral representation for $\bar{H}_\perp$.

Following Ref. 18, we first examine the spectral representation for $\bar{H}_\perp$ resulting from a single constituent mode in $\bar{H}_\parallel$. Consider

$$\bar{H}_\parallel(\xi) = c_1\delta(\xi - \xi_1), \tag{66}$$

where $\delta(\cdot)$ is the Dirac point impulse function and c_1 and ξ_1 are constants, with $\xi_1 > 0$. The rate-dependence becomes clear by associating with ξ_1 the rate-dependent relaxation time $\tau_1 = \xi_1\dot{\gamma}^{-\alpha}$. Equation (66) may then be written as

$$\bar{H}_\parallel(\xi) = c_1\dot{\gamma}^{-\alpha}\delta(\tau - \tau_1), \tag{67}$$

From (61), we deduce

$$\bar{H}_\perp(\xi) = \beta c_1\xi_1^{-1}\left(\frac{\xi_1}{\xi}\right)^\beta\mathscr{H}(\xi - \xi_1) = \beta c_1\xi_1^{-1}\left(\frac{\tau_1}{\tau}\right)^\beta\mathscr{H}(\tau - \tau_1), \tag{68}$$

where $\mathscr{H}(.)$ denotes the Heaviside unit step function.

If $0 < \alpha < 1$ ($\beta > 1$), then $\bar{H}_\perp(\xi)$ is integrable and is compliant with a finite viscosity. However, if $\alpha < 0$ ($\beta < 0$), then $|\bar{H}_\perp(\xi)| \to \infty$ as $\xi \to \infty$ and is not compliant with a finite viscosity. This situation can easily be rectified by taking a pair of Dirac functions with coefficients of opposite sign.

Definition. Let ξ_1 and ξ_2 be two positive constants with $0 < \xi_1 < \xi_2$. We define a *compliant Dirac pair* as a pair of the form

$$D(\xi;\xi_1,\xi_2) = c_1\delta(\xi - \xi_1) + c_2\delta(\xi - \xi_2), \tag{69}$$

where the coefficients c_1 and c_2 are chosen in the ratio

$$\frac{c_1}{c_2} = -\left(\frac{\xi_1}{\xi_2}\right)^\beta = -\left(\frac{\tau_1}{\tau_2}\right)^\beta. \tag{70}$$

For modeling purposes, each pair has three free parameters: c_1, ξ_1, ξ_2, or c_1, τ_1, τ_2, with β fixed for the range of shear-rates Γ_{ab}.

With coefficients in the ratio (70), it follows from (61) that

Result IV.2. The compliant Dirac pair (69) has a corresponding orthogonal response spectrum $E(\xi;\xi_1,\xi_2)$, which is a hyperbolic spline of order 1, with knots ξ_1 and ξ_2. Specifically, E takes the form

$$E(\xi;\xi_1,\xi_2) = \beta c_1\xi_1^{-1}\left(\frac{\xi_1}{\xi}\right)^\beta[\mathscr{H}(\xi - \xi_1) - \mathscr{H}(\xi - \xi_2)], \tag{71}$$

$$= \begin{cases} 0, & 0 \le \xi \le \xi_1, \\ \beta c_1\xi_1^{-1}\left(\frac{\xi_1}{\xi}\right)^\beta, & \xi_1 \le \xi \le \xi_2, \\ 0, & \xi > \xi_2. \end{cases} \tag{72}$$

The two functions D and E form a basis for interconversion between parallel and orthogonal response spectra. E is piecewise continuously differentiable and is integrable for all nonzero values of α and β.

C. Interconversion

Under the splitting (52) and (53), one has a corresponding splitting of the superposition moduli:

$$G^*_\parallel(\omega,\dot{\gamma}) = \lambda G^*(\omega) + \bar{G}^*_\parallel(\omega,\dot{\gamma}), \tag{73}$$

$$G^*_\perp(\omega,\dot{\gamma}) = \lambda G^*(\omega) + \bar{G}^*_\perp(\omega,\dot{\gamma}), \tag{74}$$

where $G^*(\omega)$ is the linear complex modulus. If $\bar{H}_\parallel$ is the Dirac pair in (69), the corresponding expressions for $\bar{G}_\parallel{}'$ and $\bar{G}''_\parallel$ are as follows:

$$\bar{G}'_\parallel(\omega,\dot{\gamma};c_1,\xi_1,\xi_2) = c_1\left[\frac{\omega^2\xi_1}{\dot{\gamma}^{2\alpha} + \omega^2\xi_1^2} - \left(\frac{\xi_2}{\xi_1}\right)^\beta\frac{\omega^2\xi_2}{\dot{\gamma}^{2\alpha} + \omega^2\xi_2^2}\right], \tag{75}$$

$$\bar{G}''_\parallel(\omega,\dot{\gamma};c_1,\xi_1,\xi_2) = c_1\dot{\gamma}^\alpha\left[\frac{\omega}{\dot{\gamma}^{2\alpha} + \omega^2\xi_1^2} - \left(\frac{\xi_2}{\xi_1}\right)^\beta\frac{\omega}{\dot{\gamma}^{2\alpha} + \omega^2\xi_2^2}\right]. \tag{76}$$

The corresponding expressions for $\bar{G}'_\perp$ and $\bar{G}''_\perp$ are as follows:

$$\bar{G}'_\perp(\omega,\dot{\gamma};c_1,\xi_1,\xi_2) = c_1\beta\xi_1^{-1}\int_{\xi_1}^{\xi_2}\left(\frac{\xi_1}{\xi}\right)^\beta\frac{\omega^2\xi}{\dot{\gamma}^{2\alpha} + \omega^2\xi^2}d\xi, \tag{77}$$

$$\bar{G}''_\perp(\omega,\dot{\gamma};c_1,\xi_1,\xi_2) = c_1\beta\xi_1^{-1}\dot{\gamma}^\alpha\int_{\xi_1}^{\xi_2}\left(\frac{\xi_1}{\xi}\right)^\beta\frac{\omega}{\dot{\gamma}^{2\alpha} + \omega^2\xi^2}d\xi. \tag{78}$$

In terms of unknown parameters $\{c_{2j-1}, \xi_{2j-1}, \xi_{2j}, j = 1\cdots n\}$, the models for the parallel and orthogonal moduli are then given by

$$G'_\parallel(\omega,\dot{\gamma}) = \lambda G'(\omega) + \sum_{j=1}^n \bar{G}'_\parallel(\omega,\dot{\gamma};c_{2j-1},\xi_{2j-1},\xi_{2j}), \tag{79}$$

$$G''_\parallel(\omega,\dot{\gamma}) = \lambda G''(\omega) + \sum_{j=1}^n \bar{G}'_\parallel(\omega,\dot{\gamma};c_{2j-1},\xi_{2j-1},\xi_{2j}), \tag{80}$$

$$G'_\perp(\omega,\dot{\gamma}) = \lambda G'(\omega) + \sum_{j=1}^n \bar{G}'_\perp(\omega,\dot{\gamma};c_{2j-1},\xi_{2j-1},\xi_{2j}), \tag{81}$$

$$G''_{\perp}(\omega,\dot{\gamma}) = \lambda G''(\omega) + \sum_{j=1}^{n} \bar{G}''_{\perp}(\omega,\dot{\gamma};c_{2j-1},\xi_{2j-1},\xi_{2j}), \qquad (82)$$

and the process of converting parallel data to orthogonal moduli can be described as follows:

- Obtain measurements of the linear moduli over a range of frequencies.
- Obtain a flow curve and hence estimate the parameters λ and β for a suitable range of shear-rates, Γ_{ab}.
- Select one value of $\dot{\gamma}$ in Γ_{ab} and determine the unknown parameters $\{c_{2j-1}, \xi_{2j-1}, \xi_{2j}, j = 1\cdots n\}$ by fitting models (79) and (80) to parallel data for this value of $\dot{\gamma}$.
- Using (81) and (82), calculate the orthogonal moduli for this value of $\dot{\gamma}$ over the same range of frequencies as for the parallel data.

V. A MODEL EXAMPLE

When β is an integer, the integrals in (77) and (78) may be evaluated in closed form, involving logarithmic or inverse tangent functions. As an illustration of the above theory, we choose a model example with $\alpha = \frac{1}{2}$, $\beta = 2$, and $0 < \kappa = 2c\eta_s < 2c\eta_0$, $0 < c < 1$. The following parallel moduli satisfy the Kramers-Kronig relations:

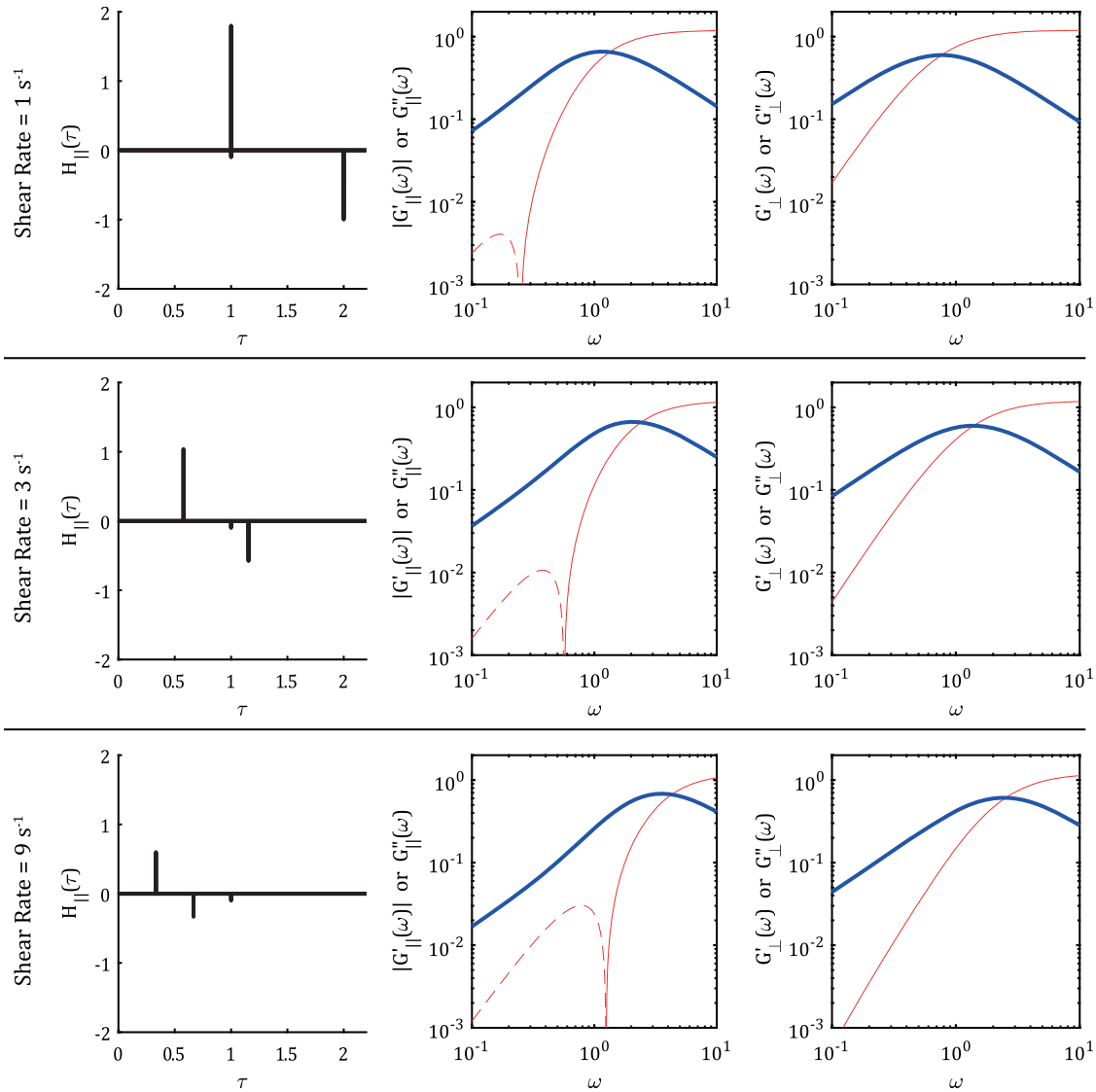

FIG. 1. Model data for parallel response spectra (column 1), parallel superposition moduli (column 2), and orthogonal superposition moduli (column 3), for three shear-rates $\dot{\gamma} = 1, 3, 9s^{-1}$. Parameter values: $\beta = 2$, $\lambda\eta_0 = -0.1$, $\eta_s = 1$, and $c = 0.8$. Real and imaginary parts of the superposition moduli are shown as red (thin) and blue (bold) lines, respectively. Negative $G'_{\parallel}(\omega,\dot{\gamma})$ are shown as red dashed (thin) lines.

$$G'_{\parallel}(\omega,\dot\gamma)=\frac{\eta_s\omega^2(2\omega^2-\dot\gamma)}{(\dot\gamma+\omega^2)(\dot\gamma+4\omega^2)}+\frac{c\eta_s\omega^2}{\dot\gamma+\omega^2}+\frac{\lambda\eta_0\omega^2}{1+\omega^2},\tag{83}$$

$$G''_{\parallel}(\omega,\dot\gamma)=\frac{3\eta_s\sqrt{\dot\gamma}\omega^3}{(\dot\gamma+\omega^2)(\dot\gamma+4\omega^2)}+\frac{c\eta_s\sqrt{\dot\gamma}\omega}{\dot\gamma+\omega^2}+\frac{\lambda\eta_0\omega}{1+\omega^2}.\tag{84}$$

The model is restricted to a range of shear-rates away from zero. We choose $1\le\dot\gamma<10$. The associated response spectrum is given by

$$H_{\parallel}(\tau,\dot\gamma)=\frac{\eta_s}{\sqrt{\dot\gamma}}\left[(1+c)\delta\left(\tau-\frac{1}{\sqrt{\dot\gamma}}\right)-\delta\left(\tau-\frac{2}{\sqrt{\dot\gamma}}\right)\right]+\lambda\eta_0\delta(\tau-1),\tag{85}$$

which has a negative part and is compliant with a finite shear viscosity. Since the value of α lies in the integrable range $0<\alpha<1$, it is not necessary that the coefficients in the Dirac pair are in the ratio (70).

The rate-dependent part of $G'_{\parallel}$ in (83) is negative for frequencies

$$0<\omega<\sqrt{\frac{(1-c)\dot\gamma}{2(1+2c)}},$$

whereas the corresponding part of $G''_{\parallel}$ in (84) is positive for all frequencies $\omega>0$. Figure 1 (column 1) shows plots of the parallel response spectra for three values of the shear-rate: $\dot\gamma=1,3,9$. Here, $\lambda\eta_0=-0.1$, $c=0.8$, and $\eta_s=1$. Figure 1 (column 2) shows the corresponding plots of $|G'_{\parallel}|$ for frequencies in the range $0.1<\omega<10$. The range of frequencies for which $G'_{\parallel}$ is negative increases with increasing shear-rate. The plateau moduli $G'_{\parallel}(\infty,\dot\gamma)$ have a value of 1.2, independent of $\dot\gamma$. Figure 1 (column 2) also shows the corresponding plots for $G''_{\parallel}$.

Using the K-BKZ interconversion theory developed in Sec. IV, the corresponding orthogonal moduli can be derived in the form

$$G'_{\perp}(\omega,\dot\gamma)=(1+c)\frac{\eta_s\omega^2}{\dot\gamma}\ln(1+\frac{\dot\gamma}{\omega^2})-\frac{2\eta_s\omega^2}{\dot\gamma}\ln(1+\frac{\dot\gamma}{4\omega^2})+\frac{\lambda\eta_0\omega^2}{1+\omega^2},\tag{86}$$

$$G''_{\perp}(\omega,\dot\gamma)=\frac{2\eta_s\omega^2}{\dot\gamma}\left[\frac{(1-c)\pi}{2}+(1+c)\tan^{-1}\left(\frac{\omega}{\sqrt{\dot\gamma}}\right)-2\tan^{-1}\left(\frac{2\omega}{\sqrt{\dot\gamma}}\right)\right]+\frac{\kappa\omega}{\sqrt{\dot\gamma}}+\frac{\lambda\eta_0\omega}{1+\omega^2},\qquad\kappa=2c\eta_s.\tag{87}$$

These orthogonal moduli satisfy the Kramers-Kronig relations and are plotted in Fig. 1 (column 3). By expanding the argument of the logarithmic term in (86), as $\omega\to\infty$, it can be shown that the plateau moduli $G'_{\perp}(\infty,\dot\gamma)$ have a value independent of $\dot\gamma$, which is equal to the value of the parallel plateau moduli. This is a manifestation of the following general result for the K-BKZ model:

Result V.1. If the parallel plateau modulus $G'_{\parallel}(\infty,\dot\gamma)=\int_0^\infty H_{\parallel}(\tau,\dot\gamma)\frac{d\tau}{\tau}$ is independent of the shear-rate, then so is the orthogonal plateau modulus, $G'_{\perp}(\infty,\dot\gamma)$. Moreover, the two moduli have the same value.

The result follows immediately from (26).

VI. CONCLUSIONS

In parallel superposition rheometry, the problem of how to interpret and utilize dynamic moduli has been mainly unresolved. It has been assumed many times in the rheological literature that dynamic moduli associated with certain integral constitutive models do not satisfy the classical Kramers-Kronig relations, even within the confines of linear perturbation theory. In this paper, we have shown that, in the case of the Wagner I and, more generally, K-BKZ models, the superposition moduli do satisfy the classical Kramers-Kronig relations. We have also shown how to interpret the parallel response spectra for the general K-BKZ model by relating them to their orthogonal counterparts. Special bases have been introduced which enable the interconversion of parallel and orthogonal response spectra and of parallel and orthogonal dynamic moduli.

The K-BKZ model has several important special cases, for example, the Doi-Edwards model [Ref. 24, Appendix B]. Our results carry over to all such cases, whether the memory kernels are separable or not. Interested readers may ask whether the results of this paper hold for a wider class of Rivlin-Sawyer models, where the elastic energy potential, U, is replaced by two independent scalar functions of time-lapse and the invariants I_1 and I_2. Expanding to first order in γ_0, we would anticipate that the Kramers-Kronig relations hold for a wider class of models for both OSR and PSR. It may be that, for some members of the wider class, the Bernstein formula relating the parallel and orthogonal superposition moduli no longer holds true. Should this be the case, a different method of proof would be needed to establish the Kramers-Kronig relations.

Yamamoto[3] derived the superposition moduli in OSR and PSR mainly for the purpose of testing the response of a nonlinear integral constitutive model to small perturbations about shear flow. Interconverting between the moduli on the basis of the model, and comparing with experimental measurements, tests the potential applicability of the model to different flow settings. The linear viscoelastic limit cannot, in general, shed light on the nonlinear aspects of the response. The Wagner I model is an interesting special case since the exponential damping function dictates that the orthogonal response spectrum is a recalibration, or nonlinear contraction, of relaxation times in the linear spectrum. The nonlinear response, here, is imparted through this nonlinear contraction.

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