Volterra kernels, Oldroyd models, and interconversion in superposition rheometry

D.J. Curtis[a], A.R. Davies[b,*]

[a] *Faculty of Science and Engineering, Swansea University Bay Campus, Fabian Way, Swansea SA1 8EN, UK.*
[b] *School of Mathematics, Cardiff University, Senghennydd Road, Cardiff CF24 4AG, UK.*

Abstract

The purpose of this paper is to demonstrate how the general problem of interconversion between parallel and orthogonal superposition protocols can be treated using the kernels in a Fréchet series expansion about the base viscometric flow. Such series differ from Fréchet series expanded about the rest history which are encountered in the theory of Green-Rivlin materials and the simple fluid theory of Coleman and Noll, in that nonlinear response of the material is captured at first order. Unlike first and second-order functional derivatives evaluated at the rest history, the derivatives we discuss require more than one kernel in their integral representation. However, all the kernels are inter-related. The strategy in the paper involves identifying the kernels which specify the components in the first and second order Fréchet derivatives for the nonlinear constitutive models to be used in the interconversion. Interconversion between parallel and orthogonal protocols can then be effected by establishing the relationships between the kernels. Step-strain perturbations are treated by allowing differentiation in the sense of distributions. The theory is illustrated throughout by evaluating the kernels and superposition moduli associated with the incompressible corotational Maxwell and Oldroyd models.

Keywords: superposition rheometry, Volterra kernels, Oldroyd constitutive equations, parallel and orthogonal superposition moduli, interconversion

1. Introduction

Superposition rheometry is a technique for probing the weakly-nonlinear characteristics of viscoelastic fluids by superposing on a steady simple shear flow a time-dependent perturbation either in parallel with or orthogonal to the bulk flow. Parallel measurements can be made using standard commercial rheometers, but the superposition moduli which are observed may not be monotonic and can display negative values. Parallel superposition moduli, in

*Corresponding author. Electronic mail: DaviesR@cf.ac.uk

general, do not share the conventional properties of linear relaxation moduli and complex moduli, and are consequently more difficult to interpret. Orthogonal measurements, on the other hand, have properties which are closer to their linear counterparts and are therefore easier to interpret. However, orthogonal measurements require non-standard, more costly, instrumentation which may not be found in every laboratory.

The general problem of interconversion between parallel and orthogonal protocols may be stated as follows:

Having measured a specific modulus or stress component in a parallel setting at a given temperature and pressure, and within a finite frequency range or time interval, we wish to predict under the same conditions
(i) the corresponding modulus or stress component in the orthogonal setting;
(ii) all other moduli and stress components in both parallel and orthogonal settings.

For example, having measured the superposition moduli $G'_{\parallel}(\dot{\gamma},\omega)$ and $G''_{\parallel}(\dot{\gamma},\omega)$ in parallel oscillatory shear superposed on a bulk shear flow with constant shear-rate $\dot{\gamma}$ in a given frequency range, we wish to predict the corresponding orthogonal moduli $G'_{\perp}(\dot{\gamma},\omega)$, $G''_{\perp}(\dot{\gamma},\omega)$ in the same frequency range, and the parallel and orthogonal relaxation moduli $G_{\parallel}(\dot{\gamma},t)$ and $G_{\perp}(\dot{\gamma},t)$ in the reciprocal time interval.

A solution to the general problem admits:
(iii) predictions in the reverse direction, from an orthogonal setting to a parallel setting;
(iv) interconversion of rate-dependent viscometric functions.

The general problem cannot be solved without recourse to a nonlinear constitutive equation capable of modelling the relevant flow properties of the fluid in question. Indeed, this requirement defines the primary scientific value of the problem, namely model validation [1]. Once a model has been validated by testing its predictions against data from both parallel and orthogonal experiments on a specific fluid, one has increased confidence in applying the model directly to predicting the properties of fluids in the same class, both in superposition flows and other, more complex, flows.

The ability to interconvert between parallel and orthogonal moduli offers the experimentalist the opportunity to obtain new information by comparing data in these configurations. One application in which such a comparison may be valuable lies in the study of flow induced anisotropy. Recent work on this phenomenon in colloidal gels employed the ratio of G' measured in orthogonal directions as a measure of anisotropy [2]. However, that study was limited to materials for which microstructural recovery was relatively slow, so that SAOS experiments probing anisotropic rheology could be performed following

cessation of the unidirectional flow; this approach being necessary to avoid "the problems associated with parallel superposition experiments" [2]. Dhont and Wagner [3] concluded that "the difference between the response to parallel and orthogonal superposition is due to the fact that the stationary sheared microstructure is anisotropic, and the two superposition experiments probe different parts of this anisotropic structure". A decade later, Mewis and Wagner [4] discussed the utility of a comparison of superposition moduli in studying microstructural anisotropy in suspensions, but also noted that "a quantitative interpretation of the results of rheological superposition measurements is still a challenge for active research".

There is a need for further study of superposition moduli, (i) to allow physical interpretation of the moduli and, (ii) facilitate the development of a quantitative interpretation of flow induced anisotropy probed by superposition rheometry [3]. In the latter, one would clearly not expect the theoretical conversion of $G^*_{\parallel}$ to $G^*_{\perp}$ to generate the measured data $G^*_{\perp}$ (or vice versa), rather, the converted moduli $G^*_{\parallel\to\perp}$ would provide an 'isotropic baseline' to which the measured data could be meaningfully compared. For given values of $\dot{\gamma}$ and ω, consider the discrepancy

$$\sigma(\dot{\gamma},\omega) = \sqrt{\Big(\frac{G'_{\perp}(\dot{\gamma},\omega)}{G'_{\parallel\to\perp}(\dot{\gamma},\omega)} - 1\Big)^2 + \Big(\frac{G''_{\perp}(\dot{\gamma},\omega)}{G''_{\parallel\to\perp}(\dot{\gamma},\omega)} - 1\Big)^2}.$$

For an isotropic fluid this quantity should be small, of the same order as the relative noise level in the measured data. Any significant deviation from this would provide a quantitative measure of anisotropy rooted in the underlying, direction dependent, stress relaxation characteristics of the sample. This presupposes that the isotropic model underlying the conversion has been adequately validated against experimental data from flows, rheometrical or otherwise, in which the isotropy of the material is conserved.

The use of step-strain parallel superposition rheometry (S-PSR) has previously been reported by Archer [5] and Li and Wang [6] who studied polymer disentanglement; the latter authors interpreted decreasing moduli with increasing $\dot{\gamma}$ in terms of convective constraint release (CCR). Later, Unidad and Ianniruberto (2014) [7] re-examined the data of Li and Wang [6] and suggested the alternative interpretation that accelerated stress relaxation under superposed flow could be "attributed to convection per se (not to be confused with CCR) and/or to a non-linear coupling between different components of the background and perturbation orientation tensors". In these studies [4-6], the oscillatory superposition moduli appear to have been interpreted as per their quiescent counterparts and there is no indication of negative moduli being observed. None of these works attempt interconversion between the S-PSR (step-PSR) and O-PSR (oscillatory-PSR) protocols. The rigorous strategy for interconversion between rheometric functions in superposition flows presented herein will also facilitate the meaningful implementation of broadband rheo-

metrical techniques, such as i-Rheo [8], in superposition rheometry.

In superposition flows, a perturbation $\epsilon\phi(t)$, of maximum value ϵ, is superposed on a steady shear flow with constant shear-rate $\dot{\gamma}$. The velocity fields in the parallel and orthogonal settings are, respectively,

$$\mathbf{u}_{\parallel} = ((\dot{\gamma} + \epsilon\dot{\phi}(t))y, 0, 0)^T, \quad \text{and} \quad \mathbf{u}_{\perp} = (\dot{\gamma}y, 0, \epsilon\dot{\phi}(t)y)^T. \tag{1.1}$$

Provided the perturbation amplitude, ϵ, is not too large, the associated stress tensor in each case may be represented as a power series

$$\boldsymbol{\tau}(t) = \boldsymbol{\tau}^{(0)}(t) + \epsilon\boldsymbol{\tau}^{(1)}(t) + \epsilon^2\boldsymbol{\tau}^{(2)}(t) + \cdots . \tag{1.2}$$

To a given order in ϵ, this series is equivalent to a tensor-valued Fréchet series evaluated to the same order in ϵ. In this paper we shall address the general problem of interconversion within the framework of such series. We shall be mainly concerned with small amplitudes, and will not proceed beyond second order terms, but it will be made clear how higher order terms may be treated.

In Section 2 of the paper we review the theory of Fréchet series and outline its relevance to superposition flows. In Section 3 we study the the restricted problem of interconversion of shear-stresses by means of the corotational Maxwell model, which is the simplest shear-thinning model among the class of Oldroyd models. In this section we also look at the rate-dependent response spectra associated with this model. In Section 4 we briefly discuss the modifications required in treating shear-thinning fluids with a Newtonian solvent. We restrict attention to the corotational Oldroyd model. In Section 5 we meet a simple class of models which lead to a solution of the general interconversion problem in terms of four rate-dependent Volterra kernels. In Section 6 we discuss second-order theory, and in Section 7 we end with a brief resumé of the results and their implications.

2. Volterra functionals and Fréchet series.

One of the earliest integral models of viscoelasticity after Boltzmann [9] is that of Vito Volterra (1860-1940). He conceived the theory of functionals [10], which Fréchet developed into a functional calculus. Volterra was keenly interested in applications, and proposed an integro-differential model for *hereditary elasticity* [11], in which he expresses strain as a tensor-valued functional of the stress history. Volterra was cited by Oldroyd in his classical 1950 paper [12]. Oldroyd offers an integro-differential constitutive equation in the style of Volterra, before confining his attention to differential models which were more receptive to the mathematical techniques of the time. The Dover publication, [13], is a translation of Volterra's lectures on the theory of functionals and applications, first published in 1927. It contains a complete bibliography of Volterra's works, and a brief biography.

2.1. Fréchet series expanded about the rest history.

The stress functionals associated with most, if not all, constitutive models, can be expanded as a series of functional derivatives (Fréchet series). Expanding the stress about the *rest history*, we have

$$\boldsymbol{\tau}(t) = \mathfrak{F}[\mathbf{G}(s)] = \mathfrak{F}_1[\mathbf{G}(s)] + \mathfrak{F}_2[\mathbf{G}(s)|\mathbf{G}(s)] + \mathfrak{F}_3[\mathbf{G}(s)|\mathbf{G}(s)|\mathbf{G}(s)] + \dots . \quad (2.1)$$

Here, $\mathfrak{F}_m$ denotes a multilinear functional of order m, of the strain history $\mathbf{G}(s) = \mathbf{G}(t, t-s)$, where s denotes the time lapse backwards from the current time t, $0 \leq s < \infty$. As a measure of strain we choose

$$\mathbf{G}(s) \equiv \mathbf{G}(t, t-s) = \mathbf{C}(t, t-s) - \mathbf{I}, \quad (2.2)$$

where $\mathbf{C}(t, t-s)$ is the right relative Cauchy-Green tensor. A multilinear functional of order m, *of polynomial form*, is given by

$$\int_0^\infty \cdots \int_0^\infty \kappa_{ijl_1k_1\cdots l_mk_m}(s_1, \cdots, s_m) G_{l_1k_1}(s_1) \cdots G_{l_mk_m}(s_m) ds_1 \cdots ds_m. \quad (2.3)$$

Functionals of polynomial form provide the basis for Fréchet series proposed by Green and Rivlin [14,15] in their treatment of materials with memory, and by Coleman and Noll [16] in their *simple fluid* theory.

Functionals of polynomial form were studied by Volterra, and we shall refer to the kernels $\kappa(s_1, \cdots, s_m)$ as Volterra kernels. Under conditions (A) and (B) below, Fréchet's approximation theorem [17] can be applied to show that any continuous functional may be approximated as closely as we wish, in the uniform norm, by a Fréchet series of finite order of multilinear functionals of polynomial form. The conditions are
(A) the strain components are drawn from a compact topological space of continuous functions, and
(B) the strain components vanish outside a finite time interval $0 \leq s \leq T$.
Two important features of the Volterra kernels are that they are continuous functions of their arguments, and that they are completely independent of the strain history.

Fréchet's approximation theorem does not hold in the limit $T \to \infty$. Coleman and Noll [16] attempted to overcome this difficulty by employing the principle of fading memory. Their work marks a significant contribution to the theory of constitutive modelling, albeit with limitations. Rivlin [18] fiercely criticises their approach, stating "...the derivation by Coleman and Noll of the multiple integral representation from an assumption of Fréchet differentiability is fallacious, in that it relies on a nonexistent theorem in functional analysis." Saut and Joseph [19] in their comprehensive treatment of fading memory are more sanguine. They point out deficiencies in Coleman and Noll's approach without devaluing their contribution.

Experimentalists need not be unduly concerned with issues of convergence. In general, expansions of type (2.1) can be viewed as asymptotic, valid for small strains or strain-rates. Taking a pragmatic approach, it should always be possible to estimate the number of terms in a Fréchet series required in the interpretation of experimental data. For example, in a SAOS experiment only the first term is needed, while in MAOS or LAOS the number of terms is determined by the number of observable higher harmonics in the stress profiles.

Pipkin [20] provides a valuable review of the derivation of functional expansions in terms of multinomial forms of type (2.3). He concludes that for incompressible fluids which are initially isotropic, the number of kernels at any given order is dramatically reduced, with only four kernels needed for an expansion up to third order. Specifically

$$\begin{aligned}
\mathfrak{F}_1[\mathbf{G}] &= \int_0^\infty \kappa_1(s)\mathbf{G}(s)ds, \\
\mathfrak{F}_2[\mathbf{G}|\mathbf{G}] &= \int_0^\infty \int_0^\infty \kappa_2(s_1,s_2)\mathbf{G}(s_1)\mathbf{G}(s_2)ds_1ds_2, \\
\mathfrak{F}_3[\mathbf{G}|\mathbf{G}|\mathbf{G}] &= \int_0^\infty \int_0^\infty \int_0^\infty [\kappa_3(s_1,s_2,s_3)\mathbf{G}(s_1)\mathbf{G}(s_2)\mathbf{G}(s_3) \\
&+ \kappa_4(s_1,s_2,s_3)\mathbf{G}(s_1)tr\{\mathbf{G}(s_2)\mathbf{G}(s_3)\}]ds_1ds_2ds_3. \qquad (2.4)
\end{aligned}$$

Fréchet series, of the type described above, are often encountered in the rheological literature as *memory-integral expansions*. See, for example, Bird *et al* [43] and [44], who give an authoritative account of expansions for the stress tensor in various constitutive models in terms of n-fold integrals.

We end this summary of Fréchet expansions about the rest history by adding three remarks.

Remark 2.1. If the stress expansion (2.1) is viewed as a power series in some ordering parameter, $\dot{\gamma}$ say, then the functional $\mathfrak{F}_m$ will, in general, contain terms of order $\dot{\gamma}^m$ as well as terms of order higher than $\dot{\gamma}^m$. This is because $\mathbf{G}(s)$ is in general a nonlinear function of $\dot{\gamma}$. For example, in simple shear flow, $\mathfrak{F}_1$ has terms of orders $\dot{\gamma}$ and $\dot{\gamma}^2$, while $\mathfrak{F}_2$ has terms of orders $\dot{\gamma}^2, \dot{\gamma}^3$ and $\dot{\gamma}^4$.

Remark 2.2. The first order functional $\mathfrak{F}_1[\mathbf{G}(s)]$ represents the linear viscoelastic limit of the material or model. Thus, for an incompressible, initially isotropic fluid

$$\kappa_1(t) = -m(t) = \dot{G}(t), \qquad (2.5)$$

where $m(t)$ and $G(t)$ are the linear memory function and linear relaxation modulus, respectively. $\mathfrak{F}_1[\mathbf{G}(s)]$, therefore, offers no information on nonlinear properties of the material.

Remark 2.3. In [41], Lennon *et al* obtained experimental measurements of third-order complex moduli and complex compliances for a worm-like micelle solution with a three-tone sinusoidal strain (MAPS) input. The results were similar to theoretical predictions from a corotational Maxwell model in a series expansion about the rest state.

2.2. Fréchet series expanded about a viscometric flow history.

In superposition rheometry it is possible to capture nonlinear properties at first order by expanding about the base viscometric flow history. Let

$$\mathbf{G}(s) = \mathbf{G}_0(s) + \mathbf{E}(s), \tag{2.6}$$

where $\mathbf{G}_0(s)$ and $\mathbf{E}(s)$ denote the viscometric strain and perturbation strain measures, respectively. In the case of the flow fields (1.1), the perturbation strain measures are

$$\mathbf{E}_{\parallel}(s) = \begin{pmatrix} 0 & -\epsilon\Delta(s) & 0 \\ -\epsilon\Delta(s) & 2\epsilon\dot{\gamma}s\Delta(s) + \epsilon^2\Delta^2(s) & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{2.7}$$

$$\mathbf{E}_{\perp}(s) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \epsilon^2\Delta^2(s) & -\epsilon\Delta(s) \\ 0 & -\epsilon\Delta(s) & 0 \end{pmatrix}, \tag{2.8}$$

where $\Delta(s) = \phi(t) - \phi(t-s)$ is the relative perturbation strain history ($0 \leq s < \infty$). Then

$$\boldsymbol{\tau}(t) = \boldsymbol{\tau}^{(0)} + \mathfrak{F}_1[\dot{\gamma}|\mathbf{E}(s)] + \mathfrak{F}_2[\dot{\gamma}|\mathbf{E}(s)|\mathbf{E}(s)] + \dots, \tag{2.9}$$

where $\boldsymbol{\tau}^{(0)}$ is the stress associated with the base viscometric flow, and $\mathfrak{F}_1, \mathfrak{F}_2, \dots$ are again multilinear functionals. Pipkin [20] explains that the integral representations of these functionals are much more complicated than those for expansions about the rest history. $\mathfrak{F}_1$ and $\mathfrak{F}_2$ can no longer be represented by single Volterra kernels as in (2.4). We shall demonstrate that for superposition flows of simple Oldroyd fluids
(i) the kernels depend on the shear-rate $\dot{\gamma}$, as well as the direction of the superposed perturbation;
(ii) the kernels remain independent of the perturbation function $\phi(t)$ itself.

By an *Oldroyd fluid* we mean one of the models included within the Oldroyd 8-constant framework. These are tabulated in [43, Chapter 8], and in [44, Chapter 7]. We would expect features (i) and (ii) above to hold for *all* Oldroyd fluids, and also for a wide class of constitutive models of differential and integral type.

For an incompressible corotational Maxwell fluid with the velocity field $\mathbf{u}_{\parallel}$ given in (1.1) we shall show that, if ϕ is drawn from a suitable function space (Section 4), then

$$\mathfrak{F}_1[\dot{\gamma}|\mathbf{E}_{\parallel}(s)] = \epsilon \begin{pmatrix} \langle n, \Delta\rangle & \langle m, \Delta\rangle & 0 \\ \langle m, \Delta\rangle & -\langle n, \Delta\rangle & 0 \\ 0 & 0 & 0 \end{pmatrix} + \mathbf{O}(\epsilon^2), \tag{2.10}$$

where $m(\dot{\gamma}, s)$ and $n(\dot{\gamma}, s)$ are a pair of rate-dependent Volterra kernels, and the inner-products $\langle m, \Delta\rangle, \langle n, \Delta\rangle$ are linear functionals of the relative perturbation

strain history $\Delta(s)$. In contrast, with the velocity field $\mathbf{u}_\perp$ in (1.1), we have

$$\mathfrak{F}_1[\dot\gamma|\mathbf{E}_\perp(s)] = \epsilon \begin{pmatrix} 0 & 0 & \langle n_\perp, \Delta\rangle \\ 0 & 0 & \langle m_\perp, \Delta\rangle \\ \langle n_\perp, \Delta\rangle & \langle m_\perp, \Delta\rangle & 0 \end{pmatrix} + \mathbf{O}(\epsilon^2), \tag{2.11}$$

where $m_\perp(\dot\gamma, s)$ and $n_\perp(\dot\gamma, s)$ are a different pair of rate-dependent Volterra kernels. All four kernels $m, n, m_\perp$ and $n_\perp$ are inter-related, enabling interconversion between them. The $O(\epsilon^2)$ terms in (2.10) and (2.11) may be represented by a linear functional of $\dot\phi^2(t-s)$, (step-strain excluded), or by a linear functional of $\Delta^2(s)$, (step-strain included).

3. Shear-stress interconversion between parallel and orthogonal settings

3.1. Parallel superposition

The corotational Maxwell model is among the simplest of all Oldroyd models for modelling purely polymeric fluids. Consider the shear flow of an incompressible corotational Maxwell fluid with the velocity field

$$\mathbf{u}_\parallel = ((\dot\gamma + \epsilon\dot\phi(t))y, 0, 0)^T. \tag{3.1}$$

The Cauchy stress, $\boldsymbol{\sigma}$, may be written

$$\boldsymbol{\sigma} = -p\mathbf{I} + \boldsymbol{\tau}, \tag{3.2}$$

where p denotes an arbitrary pressure, and the extra-stress, $\boldsymbol{\tau}$, satisfies the constitutive equation

$$\boldsymbol{\tau} + \lambda_1 \frac{\mathfrak{D}\boldsymbol{\tau}}{\mathfrak{D}t} = \eta_0\dot{\boldsymbol{\gamma}}. \tag{3.3}$$

Here, λ_1 and η_0 are constants denoting a relaxation time and the zero shear-rate viscosity, respectively, while $\mathfrak{D}/\mathfrak{D}t$ denotes the corotational derivative defined in terms of the vorticity, $\boldsymbol{\omega}$, by

$$\frac{\mathfrak{D}\boldsymbol{\tau}}{\mathfrak{D}t} = \frac{D\boldsymbol{\tau}}{Dt} + \frac{1}{2}(\boldsymbol{\omega}\cdot\boldsymbol{\tau} - \boldsymbol{\tau}\cdot\boldsymbol{\omega}). \tag{3.4}$$

For the flow field in question, the material derivative $D\boldsymbol{\tau}/Dt$ reduces to the ordinary derivative with respect to time, while the vorticity and rate-of-deformation tensor, $\dot{\boldsymbol{\gamma}}$, are given by

$$\omega = \nabla\mathbf{u} - (\nabla\mathbf{u})^T, \qquad \dot{\boldsymbol{\gamma}} = \nabla\mathbf{u} + (\nabla\mathbf{u})^T. \tag{3.5}$$

Since the stress tensor, $\boldsymbol{\tau}$, is symmetric, the tensor equation (3.3) may be written as six component equations. For the flow field generated by (3.1) these admit the constraints

$$\tau_{13} = \tau_{23} = \tau_{33} = 0, \quad \tau_{11} + \tau_{22} = 0. \tag{3.6}$$

Eliminating the variable τ_{22}, the following pair of linear differential equations in τ_{11} and τ_{12} is obtained:

$$\begin{aligned} \tau_{11} + \lambda_1 \dot{\tau}_{11} - \lambda_1 \dot{\gamma} \tau_{12} - \epsilon \lambda_1 \dot{\phi}(t) \tau_{12} &= 0, \\ \tau_{12} + \lambda_1 \dot{\tau}_{12} + \lambda_1 \dot{\gamma} \tau_{11} + \epsilon \lambda_1 \dot{\phi}(t) \tau_{11} &= \eta_0 \dot{\gamma} + \epsilon \eta_0 \dot{\phi}(t). \end{aligned} \tag{3.7}$$

Setting $\epsilon = 0$, we recover the viscometric solution for the corotational Maxwell model:

$$\begin{aligned} \tau_{11}^{(0)} &= \frac{\eta_0 \lambda_1 \dot{\gamma}^2}{1 + \lambda_1^2 \dot{\gamma}^2}, \\ \tau_{12}^{(0)} &= \frac{\eta_0 \dot{\gamma}}{1 + \lambda_1^2 \dot{\gamma}^2} = \eta(\dot{\gamma}) \dot{\gamma}, \\ \tau_{22}^{(0)} &= -\tau_{11}^{(0)}. \end{aligned} \tag{3.8}$$

Expanding the stress tensor, $\boldsymbol{\tau}$, as in (1.2), about the viscometric base (3.8), substitution in (3.7) gives, at first order in ϵ

$$\begin{aligned} \tau_{11}^{(1)} + \lambda_1 \dot{\tau}_{11}^{(1)} - \lambda_1 \dot{\gamma} \tau_{12}^{(1)} &= \alpha \dot{\phi}(t), \\ \tau_{12}^{(1)} + \lambda_1 \dot{\tau}_{12}^{(1)} + \lambda_1 \dot{\gamma} \tau_{11}^{(1)} &= \beta \dot{\phi}(t), \end{aligned} \tag{3.9}$$

where

$$\alpha = \frac{\eta_0 \lambda_1 \dot{\gamma}}{1 + \lambda_1^2 \dot{\gamma}^2}, \qquad \beta = \frac{\eta_0}{1 + \lambda_1^2 \dot{\gamma}^2}. \tag{3.10}$$

Eliminating the variable $\tau_{11}^{(1)}$ from (3.9), a particular solution for the shear stress is given in terms of a Green's function $\mathcal{G}(\dot{\gamma}, t - t')$:

$$\tau_{12}^{(1)}(t) = \int_{-\infty}^{t} \mathcal{G}(\dot{\gamma}, t - t') [(\beta - \alpha \lambda_1 \dot{\gamma}) \dot{\phi}(t') + \beta \lambda_1 \ddot{\phi}(t')] dt', \tag{3.11}$$

$$\mathcal{G}(\dot{\gamma}, t - t') = \begin{cases} \frac{1}{\lambda_1^2 \dot{\gamma}} e^{-(t-t')/\lambda_1} \sin(\dot{\gamma}(t - t')), & t' \le t, \\ 0, & t' > t. \end{cases} \tag{3.12}$$

The derivatives $\dot{\phi}$ and $\ddot{\phi}$ need only exist in the sense of distributions. Integration by parts then enables $\tau_{12}^{(1)}$ to be expressed as a linear functional of the relative strain history $\phi(t) - \phi(t - s), 0 \le s = t - t' < \infty$, as follows:

$$\tau_{12}^{(1)}(t) = \int_0^{\infty} m(\dot{\gamma}, s) [\phi(t) - \phi(t - s)] ds, \tag{3.13}$$

with a rate-dependent Volterra kernel (memory function), $m(\dot{\gamma}, s)$, given by

$$m(\dot{\gamma}, s) = \frac{\eta_0}{\lambda_1^2} e^{-s/\lambda_1} \cos(\dot{\gamma} s). \tag{3.14}$$

Note that the rate-dependent kernel reverts to its linear viscoelastic counterpart, $m(s) \equiv m(0, s)$, in the limit $\dot{\gamma} \to 0$. Note also that while $m(s)$ is always positive and completely monotonic, $m(\dot{\gamma}, s)$ is a damped oscillation, and must change sign when $\dot{\gamma} > 0$. This can lead to negative superposition moduli.

3.2. Parallel step-strain

In S-PSR, with the step applied at time $t = 0$, the perturbation is given by $\epsilon\phi(t)$, where $\phi(t) = \mathcal{H}(t)$ is the unit Heaviside step function. The shear-stress in (3.13) is then

$$\tau_{12}^{(1)}(t) = \int_t^\infty m(\dot\gamma, s)ds, \tag{3.15}$$

and the shear-stress to first order is

$$\tau_{12}(t) = \tau_{12}^{(0)} + \epsilon\tau_{12}^{(1)} = \frac{\eta_0\dot\gamma}{1+\lambda_1^2\dot\gamma^2} + \frac{\eta_0}{\lambda_1}\epsilon a\mathcal{H}(t)e^{-t/\lambda_1}\cos(\dot\gamma t + \theta), \tag{3.16}$$

$$a = \frac{1}{\sqrt{1+\lambda_1^2\dot\gamma^2}}, \qquad \theta = \tan^{-1}(\lambda_1\dot\gamma). \tag{3.17}$$

From (3.16) we identify the rate-dependent parallel superposition relaxation modulus for the corotational Maxwell fluid:

$$G_\parallel(\dot\gamma, t) = \frac{\eta_0}{\lambda_1}ae^{-t/\lambda_1}\cos(\dot\gamma t + \theta). \tag{3.18}$$

Note that $G_\parallel$ changes sign after a time $(\frac{1}{2}\pi - \theta)/\dot\gamma$. The identity

$$m(\dot\gamma, s) = -\frac{\partial}{\partial s}G_\parallel(\dot\gamma, s) \tag{3.19}$$

is readily verified, and is the rate-dependent version of the same relationship found in linear viscoelasticity. The phase angle, θ, in (3.16) - (3.18) plays an important role in describing the parallel response spectrum for the corotational Maxwell fluid (see Section 3.4 below).

3.3. Oscillatory parallel superposition rheometry

For the corotational Maxwell fluid the first order shear-stress $\tau_{12}^{(1)}$ in O-PSR may be written in the form

$$\tau_{12}^{(1)}(t) = G_\parallel^*(\dot\gamma, \omega)e^{i\omega t}, \tag{3.20}$$

where $G_\parallel^*(\dot\gamma, \omega)$ denotes a rate-dependent complex superposition modulus. Writing $\phi(t) = e^{i\omega t}$ in equations (3.10) we see that the first-order stresses take the forms

$$\tau_{11}^{(1)}(t) = A(\omega)e^{i\omega t}, \qquad \tau_{12}^{(1)}(t) = B(\omega)e^{i\omega t}, \tag{3.21}$$

where

$$\begin{aligned}(1+i\omega\lambda_1)A(\omega) - \lambda_1\dot\gamma B(\omega) &= \alpha i\omega,\\ (1+i\omega\lambda_1)B(\omega) + \lambda_1\dot\gamma A(\omega) &= \beta i\omega.\end{aligned} \tag{3.22}$$

In (3.21), the real part of the stresses represent the response to the real part of the strain. Solving (3.22) for $B(\omega)$ gives the required modulus in (3.20). We find

$$G_\parallel^*(\dot\gamma, \omega) = \frac{\eta_0 i\omega}{1+\lambda_1^2\dot\gamma^2}\Big[\frac{(1+i\omega\lambda_1) - \lambda_1^2\dot\gamma^2}{(1+i\omega\lambda_1)^2 + \lambda_1^2\dot\gamma^2}\Big], \tag{3.23}$$

which reduces to the linear viscoelastic modulus when $\dot{\gamma} = 0$. The complex modulus (3.23) also has the Fourier representation

$$G^*_{\parallel}(\dot{\gamma}, \omega) = \int_0^\infty m(\dot{\gamma}, s)(1 - e^{-i\omega s})ds.$$

Writing the modulus in (3.23) in terms of its real and imaginary parts, $G^*_{\parallel}(\dot{\gamma}, \omega) = G'_{\parallel}(\dot{\gamma}, \omega) + iG''_{\parallel}(\dot{\gamma}, \omega)$, we find

$$G'_{\parallel}(\dot{\gamma}, \omega) = \frac{\eta_0 \omega^2 \lambda_1 (1 + \omega^2 \lambda_1^2 - 3\lambda_1^2 \dot{\gamma}^2)}{(1 + \lambda_1^2 \dot{\gamma}^2)[(1 + \lambda_1^2 \dot{\gamma}^2 - \omega^2 \lambda_1^2)^2 + 4\omega^2 \lambda_1^2]}, \tag{3.24}$$

$$G''_{\parallel}(\dot{\gamma}, \omega) = \frac{\eta_0 \omega (1 + \omega^2 \lambda_1^2 - \lambda_1^2 \dot{\gamma}^2)}{(1 + \lambda_1^2 \dot{\gamma}^2 - \omega^2 \lambda_1^2)^2 + 4\omega^2 \lambda_1^2}, \tag{3.25}$$

from which we can deduce that both $G'_{\parallel}$ and $G''_{\parallel}$ will become negative at sufficiently high shear-rates. In what follows we shall say that $G'_{\parallel}$ or $G''_{\parallel}$ is *globally positive* if and only if it is positive for all positive frequencies.

Result 3.1
(i) The condition for $G'_{\parallel}(\dot{\gamma}, \omega)$ to be globally positive is $\lambda_1^2 \dot{\gamma}^2 < \frac{1}{3}$. Otherwise $G'_{\parallel}(\dot{\gamma}, \omega) < 0$ whenever $\omega^2 \lambda_1^2 < 3\lambda_1^2 \dot{\gamma}^2 - 1$.
(ii) The condition for $G''_{\parallel}(\dot{\gamma}, \omega)$ to be globally positive is $\lambda_1^2 \dot{\gamma}^2 < 1$. Otherwise $G''_{\parallel}(\dot{\gamma}, \omega) < 0$ whenever $\omega^2 \lambda_1^2 < \lambda_1^2 \dot{\gamma}^2 - 1$.
(iii) The moduli $G'_{\parallel}$ and $G''_{\parallel}$ in (3.24)-(3.25) satisfy the Kramers-Kronig relations. This is because, apart from at its poles, the modulus $G^*_{\parallel}(\dot{\gamma}, \omega)$ in (3.23) is an analytic function of ω throughout the complex frequency plane. This modulus has two poles in the upper-half of the complex frequency plane, given by $\omega = \pm\dot{\gamma} + i\lambda_1^{-1}$.

It is evident that $G'_{\parallel}$ is more likely to be negative than $G''_{\parallel}$. Equations (3.24) - (3.25) and Result 3.1(i) were first derived by Booij [42].

3.4. Parallel spectral representation

In linear viscoelasticity, the relaxation spectrum, $H(\tau)$, can be defined as the inverse Laplace transform of the memory function, where it is understood that the forward transform is taken with respect to the reciprocal variable τ^{-1}. If $m(t)$ denotes the linear memory function, then

$$H(\tau) = \mathcal{L}^{-1}[m(t)](\tau), \qquad m(t) = \int_0^\infty H(\tau) e^{-t/\tau} \frac{d\tau}{\tau^2}. \tag{3.26}$$

We refer to the second equation in (3.26) as the *spectral representation* of the linear memory function. In the case of a corotational Maxwell fluid we have, in non-dimensional form,

$$H(\tau) = \frac{\eta_0}{\lambda_1} \delta(\frac{\tau}{\lambda_1} - 1), \tag{3.27}$$

where $\delta(.)$ denotes the Dirac point measure or delta-distribution.

Consider the rate-dependent parallel response spectrum defined by

$$H_{\parallel}(\dot{\gamma},\tau) = \mathcal{L}^{-1}[m(\dot{\gamma},t)](\tau), \tag{3.28}$$

where $m(\dot{\gamma},t)$ is given by (3.14). This may be represented by the distribution

$$H_{\parallel}(\dot{\gamma},\tau) = \frac{1}{2}\frac{\eta_0}{\lambda_1}\Big[\frac{\bar{\lambda_1^*}}{\lambda_1}\delta(\frac{\tau}{\bar{\lambda_1^*}}-1) - \frac{\lambda_1^*}{\lambda_1}\delta(\frac{\tau}{\lambda_1^*}-1)\Big], \tag{3.29}$$

where τ is complex, and $\lambda_1^*, \bar{\lambda_1^*}$ are complex conjugate relaxation times defined by

$$\lambda_1^* = \frac{\lambda_1}{1-i\lambda_1\dot{\gamma}}, \quad \bar{\lambda_1^*} = \frac{\lambda_1}{1+i\lambda_1\dot{\gamma}}, \quad |\lambda_1^*| = |\bar{\lambda_1^*}| = \frac{\lambda_1}{\sqrt{1+\lambda_1^2\dot{\gamma}^2}}. \tag{3.30}$$

For fixed $\dot{\gamma}$, the relaxation time λ_1^* occupies a point in the first quadrant of the complex τ-plane, with its conjugate in the fourth quadrant. In (3.29) the delta-distribution with complex argument is defined by its inner product

$$\int_{\Lambda} f(\tau)\delta(\frac{\tau}{\lambda^*}-1)\frac{d\rho}{\lambda^*} = \pm f(\lambda^*),$$

where Λ is a line in the complex τ-plane passing through the point λ^* once and only once, with line element $d\rho$. The plus sign is required when Λ is positively orientated, and the negative sign when Λ is negatively orientated.

As the shear-rate increases from zero, the linear relaxation time λ_1 in (3.27) splits into the rate-dependent times λ_1^* and $\bar{\lambda_1^*}$, each of which decrease in magnitude with increasing shear-rate. The argument of λ_1^* is the phase angle θ in (3.17), i.e.

$$\arg(\lambda_1^*) = \theta = \tan^{-1}(\lambda_1\dot{\gamma}). \tag{3.31}$$

This angle increases with increasing shear-rate. It is interesting to examine the loci of λ_1^* and $\bar{\lambda_1^*}$ as parametrized by $\dot{\gamma}$. As $\dot{\gamma}$ increases from 0 to infinity, λ_1^* and $\bar{\lambda_1^*}$ traverse a circle, C, in the complex τ-plane. C has its centre on the real axis at $\tau = (\frac{1}{2}\lambda_1, 0)$ and intersects the real axis at the two points $\tau = (\lambda_1, 0)$ and $\tau = (0,0)$. As $\dot{\gamma}$ increases, λ_1^* traverses C in the first quadrant of the complex plane in an anti-clockwise direction, reaching the highest point $\tau = (\frac{1}{2}\lambda_1, \frac{1}{2}\lambda_1)$ when $\dot{\gamma} = \lambda_1^{-1}$. As $\dot{\gamma} \to \infty$, λ_1^* reaches the Newtonian limit $\lambda_1^* = (0,0)$. Similarly, $\bar{\lambda_1^*}$ traverses C in the fourth quadrant in a clockwise direction.

Consider a constant λ_1^*, i.e. constant λ_1 and constant $\dot{\gamma}$. Taking an integral transform of the distribution (3.29) involves choosing a contour in the complex τ-plane. For convenience we choose a contour which includes two conjugate rays, Λ (negatively orientated), and $\bar{\Lambda}$ (positively orientated):

$$\Lambda = \{\tau = \rho e^{i\theta}, \infty > \rho \geq 0\}, \quad \bar{\Lambda} = \{\tau = \rho e^{-i\theta}, 0 \leq \rho < \infty\}, \tag{3.32}$$

where θ is the constant phase angle given in (3.17). $\bar{\Lambda}$ emanates from the origin and passes through the point $\bar{\lambda}_1^*$, while Λ joins its point at infinity to the origin, passing through the point λ_1^*. The punctilious reader may request that the contour be closed by joining the two points at infinity by a circular arc of infinite radius. While aesthetically pleasing, this has no practical value since integration along such an arc cannot activate either delta-distribution in (3.29).

In taking integral transforms of the complex distributions we denote by $\int_0^\infty$ the sum of the two line integrals. Thus

$$\int_0^\infty f(\tau)H_\parallel(\dot\gamma,\tau)d\rho = (\int_{\bar\Lambda}+\int_\Lambda)f(\tau)H_\parallel(\dot\gamma,\tau)d\rho. \tag{3.33}$$

Integration along $\bar{\Lambda}$ activates the first distribution in (3.29) while integration along Λ activates the second with a change of sign due to its negative orientation. Consequently, we may write

$$m(\dot\gamma,t) = \int_0^\infty H_\parallel(\dot\gamma,\tau)e^{-t/\tau}\frac{d\rho}{\tau^2} = \frac{\eta_0}{\lambda_1^2}\Re(e^{-t/\lambda_1^*}), \tag{3.34}$$

in keeping with (3.26). Equation (3.34) is the spectral representation of the rate-dependent memory function. The spectral representations of the rate-dependent relaxation modulus, $G_\parallel$, and rate-dependent complex modulus, $G_\parallel^*$, are

$$G_\parallel(\dot\gamma,t) = \int_0^\infty H_\parallel(\dot\gamma,\tau)e^{-t/\tau}\frac{d\rho}{\tau} = \frac{\eta_0}{\lambda_1}\Re(\frac{\lambda_1^*}{\lambda_1}e^{-t/\lambda_1^*}), \tag{3.35}$$

$$\begin{aligned} G_\parallel^*(\dot\gamma,\omega) &= \int_0^\infty \frac{i\omega\tau}{1+i\omega\tau}H_\parallel(\dot\gamma,\tau)\frac{d\rho}{\tau} \\ &= \frac{1}{2}\frac{\eta_0}{\lambda_1}\Big(\frac{\lambda_1^*}{\lambda_1}\frac{i\omega\lambda_1^*}{1+i\omega\lambda_1^*}+\frac{\bar\lambda_1^*}{\lambda_1}\frac{i\omega\bar\lambda_1^*}{1+i\omega\bar\lambda_1^*}\Big). \end{aligned} \tag{3.36}$$

3.5. Orthogonal superposition and interconversion

In othogonal superposition the flow field is given by

$$\mathbf{u} = (\dot\gamma y, 0, \epsilon\dot\phi(t)y)^T. \tag{3.37}$$

Expanding the stress tensor as in (3.9) yields the same viscometric base, $\tau^{(\mathbf{0})}$, as previously, while the constitutive equation (3.3), at first order in ϵ, can be reduced to the pair of linear differential equations in $\tau_{13}^{(1)}$ and $\tau_{23}^{(1)}$ given by

$$\begin{aligned} \tau_{13}^{(1)}+\lambda_1\dot\tau_{13}^{(1)}-\tfrac{1}{2}\lambda_1\dot\gamma\tau_{23}^{(1)} &= \tfrac{1}{2}\alpha\dot\phi(t), \\ \tau_{23}^{(1)}+\lambda_1\dot\tau_{23}^{(1)}+\tfrac{1}{2}\lambda_1\dot\gamma\tau_{13}^{(1)} &= \tfrac{1}{2}(\eta_0+\beta)\dot\phi(t). \end{aligned} \tag{3.38}$$

Employing the Green's function $\mathcal{G}(\frac{1}{2}\dot\gamma, t-t')$, the first-order shear-stress may again be written as a linear functional of the perturbation strain history:

$$\tau_{23}^{(1)}(t) = \int_0^\infty m_\perp(\dot\gamma,s)[\phi(t)-\phi(t-s)]ds, \tag{3.39}$$

with a rate-dependent Volterra kernel

$$m_\perp(\dot\gamma, s) = \frac{\eta_0}{\lambda_1^2} b e^{-s/\lambda_1} \cos(\tfrac{1}{2}\dot\gamma s - \theta_M), \tag{3.40}$$

$$b = \frac{1 + \frac{1}{4}\lambda_1^2\dot\gamma^2}{\sqrt{1+\lambda_1^2\dot\gamma^2}}, \qquad \theta_M = \tan^{-1}\Big(\frac{\lambda_1^3\dot\gamma^3}{4+3\lambda_1^2\dot\gamma^2}\Big). \tag{3.41}$$

In comparing the orthogonal memory kernel in (3.40) with its parallel counterpart in (3.14) we note that the damped oscillation has its frequency reduced by the factor $\frac{1}{2}$ while shifted by a phase θ_M.

At first order, therefore, interconversion between *any* parallel protocol and *any* orthogonal protocol is effected by the transition

$$m(\dot\gamma, s) \leftrightarrow m_\perp(\dot\gamma, s). \tag{3.42}$$

The consistency of this transition will be discussed in Section 6. For the integral constitutive models studied in Curtis and Davies [21,22], the orthogonal and parallel memory kernels are related explicitly by differential equations. For Oldroyd differential models, the relationship between the two kernels is implicit rather than explicit. The model parameters are determined using one protocol and implemented in the other. The special case of the corotational Maxwell model is particularly simple in that, in theory, it would appear that there is no need for a parallel or orthogonal experiment. It suffices to determine the discrete linear relaxation spectrum $\{\eta_{0j}, \lambda_{1j}\}$ for as many modes as required. In practice, the determination of a spectrum from linear data alone is unlikely to be sufficient to predict accurately the results of a superposition experiment. We discuss this point further in Section 5.2.

The orthogonal relaxation modulus, $G_\perp(\dot\gamma, t)$, for the corotational Maxwell fluid takes the form

$$G_\perp(\dot\gamma, t) = \frac{\eta_0}{\lambda_1} c e^{-t/\lambda_1} \cos(\tfrac{1}{2}\dot\gamma t + \theta_G), \tag{3.43}$$

$$c = \sqrt{\frac{1+\frac{1}{4}\lambda_1^2\dot\gamma^2}{1+\lambda_1^2\dot\gamma^2}}, \qquad \theta_G = \tan^{-1}\Big(\frac{\lambda_1\dot\gamma}{2+\lambda_1^2\dot\gamma^2}\Big), \tag{3.44}$$

while the orthogonal complex modulus, $G_\perp^*(\dot\gamma, t)$, takes the form

$$G_\perp^*(\dot\gamma, \omega) = \frac{\eta_0 i\omega}{1+\lambda_1^2\dot\gamma^2}\Big[\frac{(1+i\omega\lambda_1) + \frac{1}{4}\lambda_1^2\dot\gamma^2(1+2i\omega\lambda_1)}{(1+i\omega\lambda_1)^2 + \frac{1}{4}\lambda_1^2\dot\gamma^2}\Big]. \tag{3.45}$$

The real and imaginary parts are given by

$$G'_\perp(\dot\gamma, \omega) = \frac{\eta_0\omega^2\lambda_1}{1+\lambda_1^2\dot\gamma^2}\Big[\frac{(1+\frac{1}{2}\lambda_1^2\dot\gamma^2)\omega^2\lambda_1^2 + (1+\frac{1}{4}\lambda_1^2\dot\gamma^2)(1-\frac{1}{2}\lambda_1^2\dot\gamma^2)}{(1+\frac{1}{4}\lambda_1^2\dot\gamma^2-\omega^2\lambda_1^2)^2 + 4\omega^2\lambda_1^2}\Big], \tag{3.46}$$

$$G''_\perp(\dot\gamma, \omega) = \frac{\eta_0\omega}{1+\lambda_1^2\dot\gamma^2}\Big[\frac{(1+\frac{1}{4}\lambda_1^2\dot\gamma^2)^2 + \omega^2\lambda_1^2(1+\frac{3}{4}\lambda_1^2\dot\gamma^2)}{(1+\frac{1}{4}\lambda_1^2\dot\gamma^2-\omega^2\lambda_1^2)^2 + 4\omega^2\lambda_1^2}\Big]. \tag{3.47}$$

We note that the relaxation modulus $G_\perp$ changes sign after a time $t = (\pi - 2\theta_G)/\dot\gamma$. Also, $G'_\perp$ can be negative at sufficiently high shear-rates, whereas $G''_\perp$ cannot. Specifically, we have

Result 3.2
(i) The condition for $G'_\perp(\dot\gamma,\omega)$ to be globally positive is $\lambda_1^2\dot\gamma^2 < 2$. Otherwise $G'_\perp(\dot\gamma,\omega) < 0$ whenever $\omega^2\lambda_1^2 < (1+\frac{1}{4}\lambda_1^2\dot\gamma^2)(\lambda_1^2\dot\gamma^2-2)/(2+\lambda_1^2\dot\gamma^2)$.
(ii) $G''_\perp(\dot\gamma,\omega)$ is globally positive.
(iii) The moduli $G'_\perp$ and $G''_\perp$ in (3.46)-(3.47) satisfy the Kramers-Kronig relations.

The rate-dependent orthogonal response spectrum for the corotational Maxwell fluid is given by the inverse Laplace transform of (3.42):

$$H_\perp(\dot\gamma,\tau) = \frac{1}{2}\frac{\eta_0}{\lambda_1}\Big[\bar{c}^\bullet\delta(\frac{\tau}{\bar\lambda_1^\bullet}-1) - c^\bullet\delta(\frac{\tau}{\lambda_1^\bullet}-1)\Big], \tag{3.48}$$

where $\lambda_1^\bullet$ and $\bar\lambda_1^\bullet$ are complex conjugate relaxation times, with

$$\lambda_1^\bullet = \frac{\lambda_1}{1-\frac{1}{2}i\lambda_1\dot\gamma}, \quad c^\bullet = \frac{4+3\lambda_1^2\dot\gamma^2 - i\lambda_1^3\dot\gamma^3}{(4-2i\lambda\dot\gamma)(1+\lambda^2\dot\gamma^2)} = b\frac{\lambda_1^\bullet}{\lambda_1}e^{-i\theta_M}. \tag{3.49}$$

Integral transforms of this distribution can be evaluated by integrating along the rays through $\bar\lambda_1^\bullet$ and $\lambda_1^\bullet$ in the complex plane, as previously.

For certain isotropic constitutive models of integral type it has been shown that the shear viscosity can be expressed as the integral of the orthogonal response spectrum, which is analogous to the corresponding result in linear viscoelasticity. This strengthens the view that orthogonal superposition moduli share certain features in common with their linear viscoelastic counterparts, unlike parallel moduli. The shear viscosity of the (isotropic) cororotational Maxwell fluid can also be expressed as an integral of its orthogonal response spectrum (3.48):

$$\eta(\dot\gamma) = \int_0^\infty H_\perp(\dot\gamma,\tau)d\rho = \frac{\eta_0}{1+\lambda_1^2\dot\gamma^2}. \tag{3.50}$$

The spectral representations of the rate-dependent relaxation modulus, $G_\perp$, and rate-dependent complex modulus, $G^*_\perp$ are given by the integrals

$$G_\perp(\dot\gamma,t) = \int_0^\infty H_\perp(\dot\gamma,\tau)e^{-t/\tau}\frac{d\rho}{\tau} = \frac{\eta_0}{\lambda_1}\Re(c^\bullet e^{-t/\lambda_1^\bullet}), \tag{3.51}$$

$$G^*_\perp(\dot\gamma,\omega) = \int_0^\infty \frac{i\omega\tau}{1+i\omega\tau}H_\perp(\dot\gamma,\tau)\frac{d\rho}{\tau} = \frac{1}{2}\frac{\eta_0}{\lambda_1}\Big(c^\bullet\frac{i\omega\lambda_1^\bullet}{1+i\omega\lambda_1^\bullet} + \bar{c}^\bullet\frac{i\omega\bar\lambda_1^\bullet}{1+i\omega\bar\lambda_1^\bullet}\Big). \tag{3.52}$$

It may also be shown that

$$\begin{aligned} m_\perp(\dot\gamma, s) &= -\frac{\partial}{\partial s} G_\perp(\dot\gamma, s), \\ \text{and} \quad G^*_\perp(\dot\gamma, \omega) &= \int_0^\infty m_\perp(\dot\gamma, s)(1 - e^{-i\omega s})ds. \end{aligned} \tag{3.53}$$

4. Function spaces and Newtonian solvents.

Let $L^2_h(0,\infty)$ denote a weighted L^2-Hilbert space with positive weight $h(s)$ satisfying $h(0) = 1, h(s) \to 0$ as $s \to \infty$. In dealing with the Oldroyd models in this paper, a suitable weight function (not unique) is $h(s) = e^{-s/\lambda_1}$, where, in a multimode treatment, λ_1 denotes the smallest relaxation time. $H^k_h(0,\infty), k > 0$, denotes the Sobolev space of functions in $L^2_h(0,\infty)$ with derivatives up to order k in the sense of distributions also in $L^2_h(0,\infty)$. $\overset{o}{H}{}^k_h(0,\infty)$ is the closed subspace of $H^k_h(0,\infty)$ whose elements vanish at $s = 0$, while $H^{-k}_h(0,\infty)$ is the space of distributions which is the topological dual of $H^k_h(0,\infty)$. Finally, if H is a space of functions in R or C, defined on $(0,\infty)$, then $\mathbb{H}$ is the corresponding symmetric tensor-valued space in R^6 or C^6.

Oldroyd [23] was critical of the simple fluid theory of Coleman and Noll on the grounds that, in that theory, stress in a material can only be generated by strain and not by strain-rate. This means that neither the Newtonian fluid nor a polymeric material in a Newtonian solvent can be accomodated in the Coleman and Noll theory. Coleman and Noll express the idea of fading memory by drawing strain histories from a weighted Hilbert space, $\mathbb{L}^2_h$. This means that all linearized stresses, $\mathfrak{F}_1[\mathbf{G}(s)]$ are continuous tensor-valued linear functionals of $\mathbf{G}(s)$ and can be represented as the inner product of $\mathbf{G}(s)$ against a fixed element of $\mathbb{L}^2_h$. In a Newtonian fluid, the stresses are proportional to the strain-rate, and cannot be represented in this way.

Wang [24] and Saut and Joseph [19] propose theories of fading memory which address this situation. Saut and Joseph draw their strain histories from a weighted Sobolev space, $\overset{o}{\mathbb{H}}{}^1_h(0,\infty) \cap \mathbb{H}^k_h(0,\infty)$ and show that the stresses in its topological dual can have integral representations with kernels which are Dirac measures and their derivatives.

Applying the Saut and Joseph theory to the parallel superposition flow in (3.1), if the perturbation strain history $\Delta(s)$ is drawn from a scalar Sobolev space H^1_h, then the shear-stress in a Newtonian fluid may be expressed as

$$\tau_{12}(t) = \eta_0\dot\gamma + \epsilon\eta_0\dot\phi(t) = \eta_0\dot\gamma - \epsilon\int_0^\infty \frac{\eta_0}{\lambda_0}\dot\delta(s)[\phi(t) - \phi(t-s)]ds, \tag{4.1}$$

where $\dot\delta(s)$ denotes the first derivative of the Dirac delta-distribution, and $\lambda_0 = 1$ is the unit relaxation time. We interpret derivatives of the Dirac delta in the

sense of Green and Rivlin [15]:

$$\int_0^\infty \delta^{(n)}(s)f(s)\frac{ds}{\lambda_0} \equiv \lim_{\epsilon_1\to 0}\int_{-\epsilon_1}^\infty \delta^{(n)}(s)f(s)\frac{ds}{\lambda_0} = (-1)^n f^{(n)}(0).$$

In the case of a step-strain perturbation history, $\Delta(s)$ is in $L^2_h(0,\infty)$ but not in $H^1_h(0,\infty)$. By regularization and passage to the limit, it can be shown that equation (4.1) holds in the sense of distributions with the integral term replaced by $\epsilon(\eta_0/\lambda_0)\delta(t)$.

For the orthogonal superposition flow in (3.37), equation (4.1) is replaced by

$$\tau_{12}(t) = \eta_0\dot\gamma, \quad \tau_{23}(t) = -\epsilon\int_0^\infty \frac{\eta_0}{\lambda_0}\dot\delta(s)[\phi(t)-\phi(t-s)]ds.$$

It is now a straightforward matter to adapt the theory in Section 3 above to polymeric materials in a Newtonian solvent. The Volterra kernels m in (3.14) and $m_\perp$ in (3.40) are simply augmented with a distributional derivative. Technically, Volterra kernels are by nature continuous. We shall therefore refer to the new kernels as *augmented kernels*.

Consider the incompressible corotational Oldroyd model

$$\boldsymbol{\tau} + \lambda_1\frac{\mathfrak{D}\tau}{\mathfrak{D}t} = \eta_0[\dot\gamma + \lambda_2\frac{\mathfrak{D}\dot\gamma}{\mathfrak{D}t}], \tag{4.2}$$

where λ_2 denotes a constant retardation time. Let

$$\eta_1 = \frac{\eta_0}{\lambda_1}(\lambda_1-\lambda_2), \quad \eta_2 = \eta_0\frac{\lambda_2}{\lambda_1}, \quad \eta_0 = \eta_1+\eta_2. \tag{4.3}$$

Then equation (4.2) may be rewritten in the form

$$\boldsymbol{\tau} = \boldsymbol{\pi} + \eta_2\dot\gamma, \quad \boldsymbol{\pi} + \lambda_1\frac{\mathfrak{D}\boldsymbol{\pi}}{\mathfrak{D}t} = \eta_1\dot\gamma. \tag{4.4}$$

The parallel Volterra kernel for the corotational Maxwell fluid is therefore replaced by the augmented kernel

$$m(\dot\gamma,s) = \frac{\eta_1}{\lambda_1^2}e^{-s/\lambda_1}\cos(\dot\gamma s) - \frac{\eta_2}{\lambda_0}\dot\delta(s), \tag{4.5}$$

and the orthogonal Volterra kernel by

$$m_\perp(\dot\gamma,s) = \frac{\eta_1}{\lambda_1^2}be^{-s/\lambda_1}\cos(\tfrac{1}{2}\dot\gamma s-\theta_M) - \frac{\eta_2}{\lambda_0}\dot\delta(s). \tag{4.6}$$

The superposition moduli are amended in similar fashion. The relaxation moduli $G_\parallel(\dot\gamma,t)$ and $G_\perp(\dot\gamma,t)$ carry the additional distribution $(\eta_2/\lambda_0)\delta(t)$, while the complex moduli $G^*_\parallel(\dot\gamma,\omega)$ and $G^*_\perp(\dot\gamma,\omega)$ carry the additional Newtonian term $\eta_2 i\omega$. Results 3.1(i), 3.2(i) and 3.2(ii) are unaffected, but the condition for the global positivity of $G''_\parallel$ is much more complicated.

5. Four-kernel interconversion

5.1. Single mode interconversion

Consider a class of models which solve the general problem of interconversion, to order ϵ, by means of four inter-related rate-dependent Volterra kernels, $m(\dot\gamma, s), n(\dot\gamma, s), m_\perp(\dot\gamma, s)$ and $n_\perp(\dot\gamma, s)$. The stress components are written

$$\textit{Parallel} \quad \tau_{11}^{(1)}(t) = \langle n, \Delta\rangle \equiv \int_0^\infty n(\dot\gamma, s)[\phi(t) - \phi(t-s)]ds, \quad (5.1)$$

$$\tau_{12}^{(1)}(t) = \langle m, \Delta\rangle \equiv \int_0^\infty m(\dot\gamma, s)[\phi(t) - \phi(t-s)]ds, \quad (5.2)$$

$$\textit{Orthogonal} \quad \tau_{13}^{(1)}(t) = \langle n_\perp, \Delta\rangle \equiv \int_0^\infty n_\perp(\dot\gamma, s)[\phi(t) - \phi(t-s)]ds, \quad (5.3)$$

$$\tau_{23}^{(1)}(t) = \langle m_\perp, \Delta\rangle \equiv \int_0^\infty m_\perp(\dot\gamma, s)[\phi(t) - \phi(t-s)]ds. \quad (5.4)$$

The corotational Maxwell model belongs to this class. Solving equations (3.9) and (3.38) completely, the four kernels are

$$m(\dot\gamma, s) = \frac{\eta_0}{\lambda_1^2} e^{-s/\lambda_1} \cos(\dot\gamma s), \quad (5.5)$$

$$n(\dot\gamma, s) = \frac{\eta_0}{\lambda_1^2} e^{-s/\lambda_1} \sin(\dot\gamma s), \quad (5.6)$$

$$m_\perp(\dot\gamma, s) = \frac{\eta_0}{\lambda_1^2} b e^{-s/\lambda_1} \cos(\tfrac{1}{2}\dot\gamma s - \theta_M), \quad (5.7)$$

$$n_\perp(\dot\gamma, s) = \frac{\eta_0}{\lambda_1^2} b e^{-s/\lambda_1} \sin(\tfrac{1}{2}\dot\gamma s - \theta_M). \quad (5.8)$$

Other models within the class can have Fréchet series of the form

$$\boldsymbol{\tau}(t) = \boldsymbol{\tau}^{(0)} + \mathfrak{F}_1[I_1, I_2|\mathbf{E}(s)] + \mathfrak{F}_2[I_1, I_2|\mathbf{E}(s)|\mathbf{E}(s)] + \ldots, \quad (5.9)$$

where I_1, I_2 are the first and second invariants of the strain measure $\mathbf{G}(s)$, or alternatively, of the Cauchy-Green tensor $\mathbf{C}(t, t-s)$. The Volterra kernels representing $\mathfrak{F}_1$ will depend on I_1 and I_2. Such models establish a link with the K-BKZ and Rivlin-Sawyer class of models.

Returning to the corotational Maxwell model, once the model parameters η_0 and λ_1 are known, it is clear that, using equations (5.1) - (5.4), interconversion between any parallel or orthogonal protocol is immediate. Of course, a single mode representation is unlikely to prove effective in general. The inner products in (5.1) - (5.4) should be viewed as basis elements for a multimode treatment.

5.2. Multimode interconversion

The key issue here is the effective determination of the discrete linear spectrum $\{\eta_{0j}, \lambda_{1j}\}$. In Boltzmann's formulation of linear viscoelasticity it

is an inherent premise that, for shear deformations at fixed temperature and pressure, every material has a unique continuous relaxation spectrum. This is not the case for discrete spectra, as can be discerned immediately from the fact that continuous spectra can be discretised in a number of different ways [26]. The problem of determining the spectrum from linear data is ill-posed, and different methods of regularization invariably lead to different results, despite fitting the data equally well [28]. There is an extensive literature covering a variety of available methods, a selection of which are treated in [25-35]. Malkin [36] states that: "The discrete relaxation spectrum is just a convenient way of representing experimental data... It has no basic physical meaning". Chow and Zukoski [37,38] state: "No line spectrum - produced by whatever method - is ever the true spectrum".

It can be readily verified that determination of a linear spectrum by fitting the experimental dynamic moduli $G'(\omega)$ and $G''(\omega)$ separately does not generally enable effective interconversion between the two [39]. Under separate fitting, the model parameters adjust to different distributions of statistical noise in the data. The spectrum should be fitted to both moduli simultaneously so that the parameters adjust to the overall distribution of noise. This phenomenon is exacerbated when fitting superposition moduli. Let us assume that the real and imaginary parts of the parallel superposition moduli $G^*_{\parallel}(\dot{\gamma}_k, \omega), k = 0, 1, 2, 3$, have been measured under the same ambient conditions over a finite frequency range, for four separate shear-rates $\dot{\gamma}_k$, where $\dot{\gamma}_0 = 0$ corresponds to the quiescent state $G^*(\omega)$. The spectrum is best determined by fitting all four pairs of moduli simultaneously, using Maxwell elements for G^* and the basis elements (3.24) and (3.25) for $G^*_{\parallel}$. A good fit to the full set of data establishes confidence in the multimode model, whereas on the other hand, an inability to find a good fit indicates that the model is inadequate for the material concerned.

We make two final remarks in regard to multimode interconversion.

Remark 5.1. Consider Results 3.1. and 3.2 above. In a multimode scenario it only requires one of the modes to satisfy the condition for global positivity of the superposition modulus to weaken the overall constraint on global positivity. In particular, admitting several modes increases the probability that $\Sigma G'_{\perp}(\dot{\gamma}, \omega)$ is globally positive.

Remark 5.2. The constitutive equation (3.3) is linear in stress, as are all of Oldroyd's models. [This is not, in general, the case for differential models such as those of Phan-Thien Tanner (PTT) and Giesekus]. Linearity enables each mode to be treated separately in the series (1.2).

6. Second-order theory

It is well known than in MAOS and LAOS only odd-order harmonics appear as the strain amplitude is increased. The same is true for O-OSR (orthogonal superposition of oscillatory shear on a bulk simple shear flow) should the amplitudes be increased above the linear range. However, in O-PSR (parallel

superposition of oscillatory shear), both even and odd order harmonics will appear, as pointed out by Lennon *et al* [40, 41]. We begin with a general treatment of second order terms in parallel superposition.

6.1. Second-order kernels. Parallel superposition.

Second-order viscoelasticity conventionally refers to the truncation of the Fréchet series at the second functional derivative [16]. Coleman and Noll give conditions under which the second derivative has an integral representation for which the second-order Volterra kernels are continuous functions of their arguments. As we pointed out in Section 4, to extend this theory to Oldroyd models we must work in an appropriate weighted Sobolev space. We choose a space $\mathbb{H}^2_h$, in which the scalar strain histories and their derivatives up to order two in the sense of distributions are in the space L^2_h. Step-strain histories require a slight modification. We shall show that the kernels contributing to $O(\epsilon^2)$ terms are no longer continuous Volterra kernels. Instead, their role are played by distributions.

We remind the reader that the functional derivative $\mathfrak{F}_1$ contains both $O(\epsilon)$ and $O(\epsilon^2)$ terms, whereas $\mathfrak{F}_2$ contains $O(\epsilon^2)$, $O(\epsilon^3)$ and $O(\epsilon^4)$ terms. In our second-order theory we shall restrict attention to those kernels which contribute to $O(\epsilon^2)$ terms, and which identify the stress $\boldsymbol{\tau}^{(2)}(t)$ in the series (1.2).

Consider the corotational Maxwell model. All higher-order kernels may be constructed from the four basic Volterra kernels $m, n, m_\perp, n_\perp$, and the two Green's functions $\mathcal{G}(\dot\gamma, s)$ and $\mathcal{G}(\frac{1}{2}\dot\gamma, s)$. Let us first consider the parallel setting. For orders $r \geq 2$, equations (3.9) are replaced by

$$\begin{aligned} \tau_{11}^{(r)} + \lambda_1 \dot\tau_{11}^{(r)} - \lambda_1 \dot\gamma \tau_{12}^{(r)} &= \lambda_1 \dot\phi(t) \tau_{12}^{(r-1)}, \\ \tau_{12}^{(r)} + \lambda_1 \dot\tau_{12}^{(r)} + \lambda_1 \dot\gamma \tau_{11}^{(r)} &= -\lambda_1 \dot\phi(t) \tau_{11}^{(r-1)}. \end{aligned} \tag{6.1}$$

Let us assume, first, that ϕ is twice continuously differentiable, so that $\dot\phi$ and $\ddot\phi$ are not distributions. Choosing $r = 2$ and eliminating $\tau_{11}^{(1)}$, we find

$$(1 + \lambda_1^2 \dot\gamma^2)\tau_{12}^{(2)} + 2\lambda_1 \dot\tau_{12}^{(2)} + \lambda_1^2 \ddot\tau_{12}^{(2)} = -\lambda_1^2 \dot\gamma \dot\phi \tau_{12}^{(1)} - \lambda_1^2 \ddot\phi \tau_{11}^{(1)} - \lambda_1 \dot\phi (\tau_{11}^{(1)} + \lambda_1 \dot\tau_{11}^{(1)}). \tag{6.2}$$

We may then use (3.9) to rewrite the right-hand side of (6.2) as

$$-\alpha \lambda_1 \dot\phi^2 - 2\lambda_1^2 \dot\gamma \dot\phi \tau_{12}^{(1)} - \lambda_1^2 \ddot\phi \tau_{11}^{(1)}, \tag{6.3}$$

where

$$\dot\phi^2(t) = -\int_0^\infty \frac{\dot\delta(s)}{s} [\phi(t) - \phi(t-s)]^2 \frac{ds}{\lambda_0}, \tag{6.4}$$

$$\dot\phi(t) = -\int_0^\infty \dot\delta(s) [\phi(t) - \phi(t-s)] \frac{ds}{\lambda_0}, \tag{6.5}$$

$$\ddot\phi(t) = -\int_0^\infty \ddot\delta(s) [\phi(t) - \phi(t-s)] \frac{ds}{\lambda_0}. \tag{6.6}$$

Introducing the distributions

$$\kappa(\dot\gamma,t,s_1) = \frac{\eta_0}{1+\lambda_1^2\dot\gamma^2}\frac{\lambda_1}{\lambda_0}\mathcal{G}(\dot\gamma,t)\frac{\dot\delta(s_1)}{s_1}, \tag{6.7}$$

$$\kappa_{12}(\dot\gamma,t,s_1,s_2) = \frac{\lambda_1^2}{\lambda_0}\mathcal{G}(\dot\gamma,t)[2\dot\gamma m(\dot\gamma,s_1)\dot\delta(s_2)+n(\dot\gamma,s_1)\ddot\delta(s_2)], \tag{6.8}$$

the solution to (6.2) may be expressed as

$$\tau_{12}^{(2)}(t)=\lambda_1\dot\gamma\langle\kappa,\Delta^2\rangle_t+\langle\kappa_{12},\Delta,\Delta\rangle_t, \tag{6.9}$$

where $\langle\kappa,\Delta^2\rangle_t$ is a linear functional of Δ^2 and $\langle\kappa_{12},\Delta,\Delta\rangle_t$ is a bilinear functional of Δ defined by

$$\langle\kappa,\Delta^2\rangle_t \equiv \int_{-\infty}^{t}\int_0^\infty \kappa(\dot\gamma,t-t_1,s_1)\Delta_1^2(s_1)dt_1ds_1, \tag{6.10}$$

$$\langle\kappa_{12},\Delta,\Delta\rangle_t \equiv \int_{-\infty}^{t}\int_0^\infty\int_0^\infty \kappa_{12}(\dot\gamma,t-t_1,s_1,s_2)\Delta_1(s_1)\Delta_1(s_2)dt_1ds_1ds_2, \tag{6.11}$$

with $\Delta_1(s)=\phi(t_1)-\phi(t_1-s)$.

Now consider the case where ϕ is differentiable only in the sense of distributions. For many distributions, equations (6.1) and (6.2) can be treated by regularization. In particular, the formulation (6.9) can be derived by regularizing the distribution $\dot\phi$, solving the regularized equation (6.2), and then passing to the limit. The stress in (6.9) is well-defined if

$$\int_0^\infty f(s)[\phi(t-s)-\phi(t-s-s_1)]^n ds$$

is twice right differentiable at $s_1=0$ for certain well-defined functions $f(s)$, with $n=1$ or 2 as required. This condition holds for the step-strain perturbation $\phi(t)=\mathcal{H}(t)$. The stress in (6.9) is then $\tau_{12}^{(2)}(t)=\mathcal{H}(t)G_{2\|}(\dot\gamma,t)$, with second-order relaxation modulus

$$G_{2\|}(\dot\gamma,t)=-\frac{\eta(\dot\gamma)}{2\lambda_1}\sqrt{9\lambda_1^2\dot\gamma^2+1}e^{-t/\lambda_1}\cos(\dot\gamma t-\theta_{2G}),\quad \theta_{2G}=\cot^{-1}(3\lambda_1\dot\gamma).$$

The normal stress, $\tau_{11}^{(2)}(t)$, may be written as

$$\tau_{11}^{(2)}(t)=-\langle\kappa,\Delta^2\rangle_t+\langle\kappa_{11},\Delta,\Delta\rangle_t, \tag{6.12}$$

where

$$\kappa_{11}(\dot\gamma,t,s_1,s_2)=\frac{\lambda_1^2}{\lambda_0}\mathcal{G}(\dot\gamma,t)[2\dot\gamma n(\dot\gamma,s_1)\dot\delta(s_2)-m(\dot\gamma,s_1)\ddot\delta(s_2)]. \tag{6.13}$$

This means that the second order term in the first functional derivative $\mathfrak{F}_1[\dot\gamma|\mathbf{E}_\parallel(s)]$ in (2.10) takes the form

$$\epsilon^2\langle\kappa,\Delta^2\rangle_t\begin{pmatrix}-1 & \lambda_1\dot\gamma & 0\\ \lambda_1\dot\gamma & 1 & 0\\ 0 & 0 & 0\end{pmatrix}, \tag{6.14}$$

while the second functional derivative is given by

$$\mathfrak{F}_2[\dot\gamma|\mathbf{E}_\parallel(s)|\mathbf{E}_\parallel(s)] = \epsilon^2\begin{pmatrix}\langle\kappa_{11},\Delta,\Delta\rangle_t & \langle\kappa_{12},\Delta,\Delta\rangle_t & 0\\ \langle\kappa_{12},\Delta,\Delta\rangle_t & -\langle\kappa_{11},\Delta,\Delta\rangle_t & 0\\ 0 & 0 & 0\end{pmatrix}+\mathbf{O}(\epsilon^3). \tag{6.15}$$

In general both (6.14) and (6.15) contribute non-zero components to the shear-stress $\tau_{12}^{(2)}(t)$. These give rise to second harmonics in parallel oscillatory shear perturbations, and we discuss this next.

6.2. Second order complex moduli. Parallel superposition.

Let $\phi = e^{i\omega t}$. We shall seek stress components in the complex form

$$\begin{aligned}\tau_{11}^{(2)}(t) &= A_0(\omega)+A_2(\omega)e^{2i\omega t},\\ \tau_{12}^{(2)}(t) &= B_0(\omega)+B_2(\omega)e^{2i\omega t},\end{aligned} \tag{6.16}$$

where the real parts of the equations are implied. To this end, we employ the identity

$$(\Re\dot\phi)(\Re\tau) = \Re[(\Re\dot\phi)\tau],$$

and replace equations (6.1) by

$$\begin{aligned}\tau_{11}^{(2)}+\lambda_1\dot\tau_{11}^{(2)}-\lambda_1\dot\gamma\tau_{12}^{(2)} &= \lambda_1[\Re\dot\phi(t)]\tau_{12}^{(1)},\\ \tau_{12}^{(2)}+\lambda_1\dot\tau_{12}^{(2)}+\lambda_1\dot\gamma\tau_{11}^{(2)} &= -\lambda_1[\Re\dot\phi(t)]\tau_{11}^{(1)}.\end{aligned} \tag{6.17}$$

Substituting (6.16) into (6.17) yields the equations

$$\begin{aligned}A_0(\omega)-\lambda_1\dot\gamma B_0(\omega) &= -\tfrac{1}{2}i\omega\lambda_1 B(\omega),\\ B_0(\omega)+\lambda_1\dot\gamma A_0(\omega) &= \tfrac{1}{2}i\omega\lambda_1 A(\omega),\\ (1+2i\omega\lambda_1)A_2(\omega)-\lambda_1\dot\gamma B_2(\omega) &= \tfrac{1}{2}i\omega\lambda_1 B(\omega),\\ (1+2i\omega\lambda_1)B_2(\omega)+\lambda_1\dot\gamma A_2(\omega) &= -\tfrac{1}{2}i\omega\lambda_1 A(\omega),\end{aligned}$$

where $A(\omega)$ and $B(\omega)$ are given by (3.22). Solving for B_0 and B_2 then leads to the expansion

$$\tau_{12}(t) = \eta(\dot\gamma)\dot\gamma[1+\epsilon^2C_0(\dot\gamma,\omega)]+\epsilon G_\parallel^*(\dot\gamma,\omega)e^{i\omega t}+\epsilon^2G_{2\parallel}^*(\dot\gamma,\omega)e^{2i\omega t}+O(\epsilon^3), \tag{6.18}$$

which displays the first and second harmonics. The coefficient C_0 is given by

$$C_0(\dot\gamma,\omega) = -\tfrac{1}{2}\frac{\omega^2\lambda_1^2(3+\lambda_1^2\dot\gamma^2-\omega^2\lambda_1^2)}{(1+\lambda_1^2\dot\gamma^2-\omega^2\lambda_1^2)^2+4\omega^2\lambda_1^2} \tag{6.19}$$

and has the limiting value $C_0(\dot\gamma,\omega)\to\frac12$ as $\omega\to\infty, \lambda_1\dot\gamma$ fixed. The first-order complex modulus $G^*_\parallel$ is given by (3.23), while the second-order modulus is given by

$$G^*_{2\parallel}(\dot\gamma,\omega)=-\tfrac12\eta(\dot\gamma)\dot\gamma\frac{\omega^2\lambda_1^2[2\omega^2\lambda_1^2+\lambda_1^2\dot\gamma^2-3(1+2i\omega\lambda_1)]}{[(1+i\omega\lambda_1)^2+\lambda_1^2\dot\gamma^2][(1+2i\omega\lambda_1)^2+\lambda_1^2\dot\gamma^2]}. \tag{6.20}$$

6.3. Second-order kernels. Orthogonal superposition.

In orthogonal superposition of oscillatory shear, it is the stress component $\tau_{23}(t)$ which is measured. This takes the form

$$\tau_{23}(t)=\epsilon G^*_\perp(\dot\gamma,\omega)e^{i\omega t}+O(\epsilon^3). \tag{6.21}$$

Both expressions (6.18) and (6.21) are correct to second order, and interconversion between them should be second-order consistent. We discuss this issue in Section 6.4 below. In this section we complete the description of the second-order terms in the functional derivatives $\mathfrak{F}_1[\dot\gamma|\mathbf{E}_\perp(s)]$ and $\mathfrak{F}_2[\dot\gamma|\mathbf{E}_\perp(s)|\mathbf{E}_\perp(s)]$.

The second-order stress components satisfy

$$\begin{aligned}
\tau^{(2)}_{13}=\tau^{(2)}_{23} &= 0, &(6.22)\\
\tau^{(2)}_{11}+\tau^{(2)}_{22}+\tau^{(2)}_{33} &= 0, &(6.23)\\
\tau^{(2)}_{12}+\lambda_1\dot\tau^{(2)}_{12}+\lambda_1\dot\gamma\nu^{(2)} &= -\tfrac12\lambda\dot\phi\tau^{(1)}_{13},\\
\nu^{(2)}+\lambda_1\dot\nu^{(2)}-\lambda_1\dot\gamma\tau^{(2)}_{12} &= \tfrac12\lambda\dot\phi\tau^{(1)}_{23},\\
\tau^{(2)}_{33}+\lambda_1\dot\tau^{(2)}_{33} &= \lambda_1\dot\phi\tau^{(1)}_{23}, &(6.24)
\end{aligned}$$

where $\nu^{(2)}=\frac12(\tau^{(2)}_{11}-\tau^{(2)}_{22})$. Solving equations (6.24) and using (6.23) we find that the $\mathbf{O}(\epsilon^2)$ term in (2.11) is

$$\tfrac14\epsilon^2\langle\kappa,\Delta^2\rangle_t\begin{pmatrix}-(2+\lambda_1^2\dot\gamma^2) & \lambda_1\dot\gamma & 0\\ \lambda_1\dot\gamma & 2+\lambda_1^2\dot\gamma^2 & 0\\ 0 & 0 & 0\end{pmatrix}, \tag{6.25}$$

while the second functional derivative is given by

$$\mathfrak{F}_2[\dot\gamma|\mathbf{E}_\perp(s)|\mathbf{E}_\perp(s)]=\tfrac14\epsilon^2\begin{pmatrix}\langle\kappa^\perp_{11},\Delta,\Delta\rangle_t & \langle\kappa^\perp_{12},\Delta,\Delta\rangle_t & 0\\ \langle\kappa^\perp_{12},\Delta,\Delta\rangle_t & \langle\kappa^\perp_{22},\Delta,\Delta\rangle_t & 0\\ 0 & 0 & \langle\kappa^\perp_{33},\Delta,\Delta\rangle_t\end{pmatrix}+\mathbf{O}(\epsilon^3), \tag{6.26}$$

with $\kappa^\perp_{ij}=\kappa^\perp_{ij}(\dot\gamma,t,s_1,s_2)$,

$$\begin{aligned}
\kappa^\perp_{11} &= \frac{\lambda_1^2}{\lambda_0}\mathcal{G}(\dot\gamma,t)[3\dot\gamma n_\perp(\dot\gamma,s_1)\dot\delta(s_2)-2m_\perp(\dot\gamma,s_1)\ddot\delta(s_2)]-\tfrac12\kappa^\perp_{33}, &(6.27)\\
\kappa^\perp_{12} &= \frac{\lambda_1^2}{\lambda_0}\mathcal{G}(\dot\gamma,t)[3\dot\gamma m_\perp(\dot\gamma,s_1)\dot\delta(s_2)+2n_\perp(\dot\gamma,s_1)\ddot\delta(s_2)], &(6.28)\\
\kappa^\perp_{22} &= -(\kappa^\perp_{11}+\kappa^\perp_{33}), &(6.29)\\
\kappa^\perp_{33} &= -\frac{1}{\lambda_1}e^{-t/\lambda_1}m_\perp(\dot\gamma,s_1)\dot\delta(s_2). &(6.30)
\end{aligned}$$

6.4. Second-order consistent model parameterization

The discussion in this section is not necessarily confined to Oldroyd models. We shall be concerned with the restricted problem of interconversion between the two stress profiles $\tau_{12}(t)$ and $\tau_{23}(t)$. We shall say that a set of model parameters is *second-order consistent* if, in a parallel setting, it correctly characterizes the first- and second-order terms in the Fréchet expansion of $\tau_{12}(t)$. If the perturbation is an oscillatory shear, the model parameters must fit both first and second harmonics. On the other hand, if the perturbation is a step-strain, the model parameters must characterize both first and second superposition relaxation moduli $G_{\parallel}(\dot{\gamma}, t)$ and $G_{2\parallel}(\dot{\gamma}, t)$. Second order consistency is an essential element of interconversion, and consequently, of model validation.

In the case of a multimode corotational Maxwell model, the set of model parameters is the discrete linear relaxation spectrum. A linear spectrum determined by fitting both linear data $G^*(\omega)$ and first-order parallel data $G^*_{\parallel}(, \dot{\gamma}, \omega)$, together, may well require more parameters than the spectrum determined from linear data alone. However, due to ill-posedness and non-uniqueness issues, the extended spectrum need not be second-order consistent, even if the model is valid. The linear spectrum, therefore, should be chosen to characterize the linear data, and first-order and second-order data collectively, by means of the appropriate first and second order moduli.

The above remarks refer to conversion from parallel to orthogonal settings. In the reverse direction, determining the linear spectrum from $G^*(\omega)$ and $G^*_{\perp}(\dot{\gamma}, \omega)$ together should provide a second-order consistent set of parameters. If the model is valid, subsequent conversion to the parallel setting should offer satisfactory estimates of both $G^*_{\parallel}(\dot{\gamma}, \omega)$ and $G^*_{2\parallel}(\dot{\gamma}, \omega)$. This can obviously be checked by increasing the amplitude in a parallel experiment above the linear range.

7. Summary

When the stress in a material is expressed as a tensor-valued functional of the strain history, then if the strain history is drawn from a suitable function space, the stress functional can be expanded as a Fréchet series of functional derivatives. These derivatives can be evaluated at a base strain history of choice. In the theory of Green-Rivlin materials, and the simple fluid theory of Coleman and Noll, the derivatives are evaluated at the rest history, and we say that the Fréchet series is expanded about the rest history. For infinite time histories, the series should be viewed as asymptotic, i.e. valid for sufficiently small strains or strain-rates. The first functional derivative in such series represents the linear viscoelastic limit of the material, and only contains information about the linear properties of the material. For an incompressible, initially isotropic fluid, the first derivative has an integral representation in terms of a single kernel (the linear viscoelastic memory kernel). Pipkin [20]

has shown that for such a fluid, the second derivative has a double integral representation in terms of another single kernel. Both kernels are independent of the strain history generating the stress.

For perturbation flows superposed on a base simple shear flow, it is expedient to expand the Fréchet series about the base viscometric strain history. The first functional derivative then probes the nonlinear response of the material to the imposed strains. For an incompressible, initially isotropic fluid, the first derivative now requires at least one kernel to characterize each component of its integral representation. Similarly for the higher derivatives. For the incompressible corotational Maxwell model we have shown that the kernels depend on the base rate of shear and on the direction of the superposed perturbation, i.e. whether parallel or orthogonal to the base flow. They are independent, however, of the actual perturbation function itself. For Oldroyd constitutive models within the 8-constant framework, all the kernels of all orders are implicitly inter-related.

The purpose of this paper is to demonstrate how the general problem of interconversion between parallel and orthogonal superposition protocols can be treated using the kernels in a Fréchet series expansion about the base viscometric flow. The strategy involves identifying the kernels which specify the components in the first and second order Fréchet derivatives for the nonlinear constitutive models to be used in the interconversion. Interconversion between parallel and orthogonal protocols can then be effected by establishing the relationships between the kernels. We anticipate that this strategy may be invoked for a wide class of constitutive models of differential and integral type, with different inter-relationships between the kernels. Step-strain perturbations are treated by allowing differentiation in the sense of distributions.

It is helpful to re-order the Fréchet series as a power series in the perturbation amplitude, ϵ. We have chosen the incompressible corotational Maxwell model as a template to illustrate a class of models in which four inter-related rate-dependent Volterra kernels characterize the stresses at $O(\epsilon)$, while an additional seven kernels are required at $O(\epsilon^2)$. In a multimode treatment, the steps required in converting from one protocol to another may be summarized as follows:

- Determine a second-order consistent relaxation spectrum from available data. In O-PSR, the real and imaginary parts of the basis elements (3.23) and (6.20) are fitted to the first- and second-order data, respectively, while in S-PSR, a stress-profile modelled by the basis elements $G_{\parallel}(\dot{\gamma}, t)$ and $G_{2\parallel}(\dot{\gamma}, t)$ is fitted.
- Select the perturbation protocol to which conversion is to be made.
- If a stress component is required, calculate the appropriate linear and bilinear functionals. For $G_{\perp}(\dot{\gamma}, t)$, the basis elements (3.43) are needed.

- If a superposition modulus is required, calculate the appropriate basis representation. For $G^*_\perp(\dot\gamma,\omega)$, the basis elements consisting of the real and imaginary parts of (3.45) are needed.

In recent articles we have treated first order kernels for a Lodge-type integral constitutive model [21] and for the K-BKZ integral model [22]. At first order these models fall into the four-kernel interconversion class outlined in Section 5. In both cases the first order kernels are Laplace transforms of parallel or orthogonal response spectra $H_\parallel(\dot\gamma,\tau)$ or $H_\perp(\dot\gamma,\tau)$. If $H_\parallel(\dot\gamma,\tau)$ is represented as a compliant rate-dependent spectrum we have shown that $H_\perp(\dot\gamma,\tau)$ is a first-order hyperbolic spline in the case of the K-BKZ model, and a second-order hyperbolic spline in the case of the Lodge model. The linear functional representations we have presented in Section 5 can be used to interconvert between any parallel and any orthogonal shear-stresses $\tau^{(1)}_{12}(t)$ and $\tau^{(1)}_{23}(t)$, the model parameters being the parameters of the appropriate response spectrum. Our comments on second-order consistent model parameterization should be taken into consideration.

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9. References

1. Yamamoto M (1971). *Rate-dependent relaxation spectra and their determination.* Trans. Soc. Rheol. 15:331-344.
2. Colombo G, Sunhyung K, Schweizer T, Schroyen B, Clasen C, Mewis J, Vermant J (2017). *Superposition rheology and anisotropy in rheological properties of sheared colloidal gels.* J Rheol 61:1035-1048.
3. Dhont J, Wagner N (2001). *Superposition Rheology.* Phys. Rev. E 63, 021406.
4. Mewis J, Wagner N (2013). *Colloidal Suspension Rheology, 1st Ed.* Cambridge University Press.
5. Archer LA (1999). *Polymer disentanglement in steady-shear flow.* J Rheol 43:1617-1633
6. Li X, Wang S-Q (2010). *Studying steady shear flow characteristics of entangled polymer solutions with parallel mechanical superposition.* Macromolecules 43: 5904-5908.

7. Unidad H, Ianniruberto G (2014). *The role of convective constraint release in parallel superposition flows of nearly monodispoerse entangled polymer solutions.* Rheol Acta 53:191-198.
8. Tassieri M, Laurati M, Curtis DJ, Auhl DW, Coppola S, Scalfati A, Hawkins K, Williams PR, Cooper JM (2016). *i-Rheo: Measuring the materials' linear viscoelastic properties "in a step"!* J Rheol 60: 649-660.
9. Boltzmann L (1874). *Zur theorie der elastichen nachwirkung.* Sitzber Kgl Akad Wiss Wien, Math-Naturw Classe 70:725-306.
10. Volterra V (1887). *Sopra le funzioni che dipendono da altra funzioni.* R. C. Accad. Lincei (4) 3:97-105 and 153-158.
11. Volterra V (1909). *Equationi integro-differenziale della teoria dell'elasticà.* R. C. Accad. Lincei (5) 18:577-586.
12. Oldroyd JG (1950). *On the formulation of rheological equations of state.* Proc. Roy. Soc. A200:523-541.
13. Volterra V (1959). *Theory of functionals and of integral and integro-differential equations.* Dover, New York.
14. Green AE, Rivlin RS (1957). *The mechanics of non-linear materials with memory.* Part I. Arch. Rational Mech. Anal. 1:1-27.
15. Green AE, Rivlin RS (1960). *The mechanics of non-linear materials with memory.* Part III. Arch. Rational Mech. Anal. 4:387-404.
16. Coleman BD, Noll W (1961). *Foundations of linear viscoelasticity.* Rev. Mod. Physics 33:239-249. Erratum (1964) *op. cit.* 36:1103.
17. Fréchet M (1910), *Sur les functionnelles continues.* Annales Scientifiques de l'É.N.S. 3e série, 27:193-216.
18. Rivlin RS (1983). *Integral representations of constitutive equations.* Rheol Acta 22:260-267.
19. Saut JC, Joseph DD (1983). *Fading memory.* Arch. Rational. Mech. Anal. 81:53-95.
20. Pipkin AC (1964). *Small finite deformations of viscoelastic solids.* Rev. Mod. Phys. 36:1034-1041.
21. Curtis DJ, Davies AR (2019). *On shear-rate dependent relaxation spectra in superposition rheometry: A basis for comparison/interconversion of orthogonal and parallel superposition moduli.* J non-Newtonian Fluid Mech. 274,104198. https://doi.org/10.1016/j.jnnfm.2019.104198
22. Curtis DJ, Davies A R (2019). *On response spectra and Kramers-Kronig relations in superposition rheometry.* Physics of Fluids 31, 127105. https://doi.org/10.1063/1.5133885.
23. Oldroyd JG (1965). *Some steady solutions of the general elasticoviscous liquid.* Proc. Roy. Soc. A283:115-133.
24. Wang CC (1965). *The principle of fading memory.* Arch. Rational Mech. Anal. 18: 343-366.
25. Baumgaertel M, Winter HH (1989). *Determination of discrete relaxation and retardation time spectra from dynamic mechanical data.* Rheol Acta 28:511-519.

26. Honerkamp J, Weese J (1989). *Determination of the relaxation spectrum by a regularization method.* Macromolecules 22:4372-4377.
27. Honerkamp J, Weese J (1990) *Tikhonov's regularization method for ill-posed problems - a comparison of different methods for the determination of the regularization parameter.* Continuum Mechanics and Thermodynamics 2, 17–30.
28. Baumgaertel M, Winter HH (1992). *Interrelation between continuous and discrete relaxation time spectra.* J non-Newtonian Fluid Mech 44:15-36.
29. Honerkamp J, Weese, J (1993) *A nonlinear regularization method for the calculation of relaxation spectra.* Rheol Acta 32:65–73.
30. Emri I, Tscheogl NW (1993). Generating line spectra from experimental responses. Part I. relaxation modulus and creep compliance. Rheol Acta 32:321-331.
31. Carrot C, Verney V (1996). *Determination of a discrete relaxation spectrum from dynamic experimental data using the Pade-Laplace method.* European Polymer Journal 32:69-77.
32. Macdonald JR (2000). *On relaxation-spectrum estimation for decades of data: accuracy and sampling-localization considerations.* Inverse Problems 16:1561-1583.
33. Malkin A.Ya., Masalova I (2001).*From dynamic moduli via different relaxation spectra to relaxation and creep functions.* Rheol Acta 40:262-271.
34. Davies AR, Douglas RJ (2019) *A kernel approach to deconvolution of the complex modulus in linear viscoelasticity.* Inverse Problems https://doi.org/10.1088/1361-6420/ab2944
35. Shanbhag S (2020). *Relaxation spectra using nonlinear Tikhonov regularization with a Bayesian criterion.* Rheol Acta 59:509–520.
36. Malkin A.Ya. (2002). *The sense of a relaxation spectrum and methods for its calculation.* Vysokomol. Soedin. Ser B. 44:1598. (Polymer Science Ser B. 44:247).
37. Chow MK, Zukoski CF (1995). *Gap size and shear history dependencies in shear thickening of a suspension ordered at rest.* J Rheol 39:15-32.
38. Chow MK, Zukoski CF (1995). *Nonequilibrium behavior of dense suspensions of uniform particles - volume fraction and size dependence of rheology and microstructure.* J Rheol 39:33-59.
39. Winter HH (1997). *Analysis of dynamic mechanical data: inversion into a relaxation time spectrum and consistency check.* J. non-Newtonian Fluid Mech. 68:225 –239.
40. Lennon KR, McKinley GH, Swan JW (2020). *Medium amplitude parallel superposition (MAPS). Part 1: Theoretical framework and mathematical examples.* J Rheol. 64:551-579.
41. Lennon KR, Geri M, McKinley GH, Swan JW (2020). *Medium amplitude parallel superposition (MAPS). Part 2: Experimental protocols and data analysis.* J Rheol. 64. https//doi.org/10.1122/8.0000104.
42. Booij HC (1966). *Influence of superimposed steady shear flow on the dynamic properties of non-Newtonian fluids. II. Theoretical approach based on the Oldroyd theory.* Rheol Acta 5: 222-227.

43. Bird RB, Armstrong RC, Hassager O (1977). Dynamics of Polymeric Liquids, Vol. 1, *1st ed.* Wiley, New York.
44. Bird RB, Armstrong RC, Hassager O (1987). Dynamics of Polymeric Liquids, Vol. 1, *2nd ed.* Wiley, New York.

Volterra kernels, Oldroyd models, and interconversion in superposition rheometry.

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Highlights

- Treats interconversion between protocols in superposition rheometry.
- Explores non-monotonicity and changes of sign in superposition moduli.
- Treats oscillatory and step-strain perturbations.
- Analyses Fréchet series expanded about viscometric flow history.
- Explains second-order consistency of model parameterization.

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We confirm that there is no conflict of interest in submitting this article for publication in the Journal of Non-Newtonian Fluid Mechanics.

A Russell Davies

Daniel J Curtis.