

SIMPLE JOINT INVERSION LOCALIZED FORMULAE FOR RELAXATION SPECTRUM RECOVERY

R. S. ANDERSSSEN^{✉1}, A. R. DAVIES², F. R. de HOOG¹ and R. J. LOY³

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Abstract

In oscillatory shear experiments, the values of the storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, respectively, are only measured and recorded for a number of values of the frequency ω in some well-defined finite range $[\omega_{\min}, \omega_{\max}]$. In many practical situations, when the range $[\omega_{\min}, \omega_{\max}]$ is sufficiently large, information about the associated polymer dynamics can be assessed by simply comparing the interrelationship between the frequency dependence of $G'(\omega)$ and $G''(\omega)$. For other situations, the required rheological insight can only be obtained once explicit knowledge about the structure of the relaxation time spectrum $H(\tau)$ has been determined through the inversion of the measured storage and loss moduli $G'(\omega)$ and $G''(\omega)$. For the recovery of an approximation to $H(\tau)$, in order to cope with the limited range $[\omega_{\min}, \omega_{\max}]$ of the measurements, some form of localization algorithm is required. A popular strategy for achieving this is to assume that $H(\tau)$ has a separated discrete point mass (Dirac delta function) structure. However, this expedient overlooks the potential information contained in the structure of a possibly continuous $H(\tau)$. In this paper, simple localization algorithms and, in particular, a joint inversion least squares procedure, are proposed for the rapid recovery of accurate approximations to continuous $H(\tau)$ from limited measurements of $G'(\omega)$ and $G''(\omega)$.

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1. Introduction

In the study of the rheological properties of viscoelastic materials, the measured storage and loss moduli [8], $G'(\omega)$ and $G''(\omega)$, obtained from oscillatory shear

¹CSIRO Data61, GPO Box 664, Canberra, ACT 2601, Australia; e-mail: Bob.Anderssen@csiro.au, Frank.deHoog@csiro.au.

²Mathematics, University of Cardiff, Cardiff, UK; e-mail: DaviesR@cardiff.ac.uk.

³Mathematical Sciences Institute, Australian National University, Canberra, ACT 2601, Australia; e-mail: Rick.Loy@anu.edu.au.

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experiments, play fundamental roles. However, the values of $G'(\omega)$ and $G''(\omega)$ are only measured and recorded for a number of specific values of the frequency ω in some well-defined finite range $[\omega_{\min}, \omega_{\max}]$. Well-established and validated protocols [8, 10] have been developed and are utilized to directly obtain information about the associated polymer dynamics of the material under investigation. These protocols simply involve a visual inspection of the interrelationship between $G'(\omega)$ and $G''(\omega)$ as a function of ω [10, 14]. From the perspective of inverse problems, they correspond to the “direct use of indirect measurements” and thereby avoid the need to invoke some appropriate regularization to stabilize the associated ill-posedness of relaxation spectrum recovery.

Rheologically, the storage and loss moduli correspond to indirect measurements of the relaxation time spectrum $H(\tau)$ of the viscoelastic material being studied [6, 7]. In some situations, when decision making requires a comparison of $H(\tau)$ for different viscoelastic polymers, the required rheological insight can only be obtained once explicit knowledge about the structure of $H(\tau)$ has been determined through the inversion of $G'(\omega)$ and $G''(\omega)$.

Much theory has been developed for the recovery of approximations to $H(\tau)$ from the measurements of $G'(\omega)$ and $G''(\omega)$ under the assumption that they are known for all ω . In reality, only discrete values for the storage and loss moduli are, and indeed can be, measured. Consequently, for the recovery of an approximation to $H(\tau)$, some form of localization is required. A popular strategy for achieving this is to assume that $H(\tau)$ has a separated discrete structure [1]. However, this expedient overlooks the insight in the possible continuous structure of $H(\tau)$.

Here, the focus is the recovery of continuous approximations to $H(t)$ when $G'(\omega)$ and $G''(\omega)$ are only known for a limited range of discrete values of ω . A localization algorithm is proposed for the recovery of a continuous approximation to $H(\tau)$ from limited measurements of the storage and loss moduli.

2. Background and preliminaries

The determination of approximations to relaxation time spectra $H(\tau)$ from oscillatory shear measurements of the storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, represents a way to characterize and compare linear viscoelastic materials [6, 7, 16, 18]. Computationally, this reduces to inverting the integral equations

$$G'(\omega) = G_e + \int_0^\infty \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} H(\tau) \frac{d\tau}{\tau}, \quad G''(\omega) = \int_0^\infty \frac{\omega \tau}{1 + \omega^2 \tau^2} H(\tau) \frac{d\tau}{\tau} \quad \omega \geq 0, \quad (2.1)$$

where $\omega \geq 0$ and $G_e = 0$ for a viscoelastic liquid and $G_e > 0$ for a viscoelastic solid. Various methods have been proposed for their inversion [6, 7, 16]. However, as far as we are aware, except for Davies and Anderssen [6] and Davies and Golding [7], the fact that the values of $G'(\omega)$ and $G''(\omega)$ are only measured on some finite interval $[\omega_{\min}, \omega_{\max}]$ has not been explicitly taken into account.

Equations (2.1) can be reformulated in terms of a Fourier deconvolution problem: for given data D and known kernel k , solve the (first-kind Fredholm) Fourier convolution integral equation

$$D = k * h, \quad (k * h)(x) = \int_{-\infty}^{\infty} k(x-y)h(y) dy = \int_{-\infty}^{\infty} h(x-y)k(y) dy \quad (2.2)$$

for h . For viscoelastic liquids, on applying the substitutions

$$h(x) = H(\exp(-x)), \quad g_1(x) = 2G'(\exp(x)), \quad g_2(x) = 2G''(\exp(x))$$

to the oscillatory shear equations (2.1), the corresponding counterparts of equation (2.2) become

$$g_1 = [1 + \tanh] * h, \quad (2.3)$$

$$g_2 = \operatorname{sech} * h. \quad (2.4)$$

Equation (2.3) is not often solved for h . Traditionally, attention has been focused on equation (2.4) because of the well-known fact that [8, 9]

$$H(\tau) \approx \frac{2}{\pi} G''(\tau^{-1}), \quad h(x) \approx \frac{1}{\pi} g_2(x).$$

However, both will be used in the subsequent work. In particular, we will make use of the following expressions, for which a formal derivation is given by Anderssen et al. [1],

$$h(x) = \frac{1}{\pi} \sum_{r=0}^{\infty} (-1)^r \left(\frac{\pi}{2}\right)^{2r+1} \frac{1}{(2r+1)!} \left[\frac{d^{2r+1} g_1}{dx^{2r+1}} \right] \quad (2.5)$$

$$= \frac{1}{\pi} \sum_{r=0}^{\infty} (-1)^r \left(\frac{\pi}{2}\right)^{2r} \frac{1}{(2r)!} \left[\frac{d^{2r} g_2}{dx^{2r}} \right]. \quad (2.6)$$

It is usually assumed, without proof, that convergence is guaranteed. Thereby, truncation of these series representations yields valid estimates for $h(x)$, [1]. An investigation of the regularity under which convergence is guaranteed has already been undertaken (Loy et al. "Convergence in relaxation spectrum recovery", unpublished).

3. Algorithms and validation

The advantage of the simple formulae examined below is their localization which is a direct consequence of the fact that numerical differentiation is a localized procedure [3]. They can be viewed as derivative recovery algorithms which have, and continue to play, a key role as nonparametric procedures in the construction of continuous approximations to $H(\tau)$, as explained by Anderssen et al. [1]. Derivative recovery algorithms are widely utilized in the recovery of information from observational data, including the use of derivative spectroscopy procedures to enhance the recovery of hidden structure in the measured values [5].

3.1. Direct utilization of truncation formulae Truncations of (2.5) and (2.6) in increasing order of the differentiation involved, up to the fourth order, are listed in Table 1. The choice of these simple approximations is motivated by the fact that the coefficients of the derivative terms in (2.5) decay rapidly, which implies that the contributions of the higher-order derivatives can often be neglected, especially when the structure within $h(x)$ only involves small and decreasing contributions from its higher derivatives.

TABLE 1. Tabulation of the simple localization formulae (the primes denote differentiation with respect to x).

Localization formula	Highest order differentiation
$h_1(x) = \frac{1}{\pi} g_2(x)$	0
$h_2(x) = \frac{1}{2} g_1'(x)$	1
$h_3(x) = \frac{1}{\pi} g_2(x) - \frac{\pi}{8} g_2''(x)$	2
$h_4(x) = \frac{1}{2} g_1'(x) - \frac{\pi^2}{48} g_1'''(x)$	3
$h_5(x) = \frac{1}{\pi} g_2(x) - \frac{\pi}{8} g_2''(x) + \frac{\pi^3}{384} g_2^{(iv)}(x)$	4

From the independent perspective of derivative spectroscopy [5], the derivative terms can be viewed as recovering information about the changing structure in $h(x)$ that is hidden in the oscillatory shear data. This engenders the opportunity of using derivatives of the oscillatory shear data to identify the locations for the kernel basis functions in the algorithms proposed by Davies and Golding [7]. Stable methods for the numerical differentiation of observational data can be found in the papers by Anderssen, de Hoog and Hegland [2–4].

3.2. Least squares joint inversion formulae Motivation for the use of *joint inversion* comes from the fact that different measurements of the same phenomena will contain different information about that phenomena. Joint inversion is a popular and widely utilized inversion ansatz within the analysis and interpretation of geophysical data with its origin in the seminal observations of Jupp and Vozoff [13]. However, its potential for application to other areas has yet to be fully exploited.

Since oscillatory shear measurements of the storage and loss moduli see different properties of the material being tested, it follows that the joint use of $g_1(x)$ and $g_2(x)$ for the recovery of the structure of $h(x)$ represents an alternative strategy for the generation of simple formulae.

Algebraic validation of this point follows from the following observation. Since

$$\begin{aligned}g_2(x) &= \pi h(x) + \frac{\pi^3}{8} h''(x) + O(h'''(x)), \\g_1'(x) &= 2h(x) + \frac{\pi^2}{12} h''(x) + O(h'''(x)),\end{aligned}$$

it follows that

$$h_6(x) = -\frac{g_2(x)}{2\pi} + \frac{3g_1'(x)}{4} = h(x) + O(h'''(x)). \quad (3.1)$$

Numerical validation for $h_6(x)$, which establishes that it yields a good approximation to $h(x)$, is given in Section 4.

Recall that $h_6(x)$, as shown algebraically above, neglects higher-order terms; a natural extension to this joint inversion formula is to allow the coefficients in equation (3.1) to be determined by the data. In particular, equation (3.1) is replaced with the generalization

$$h_7(x; a, b) = \left[ag_2 + b \frac{dg_1}{dx} \right], \quad (3.2)$$

where the parameters a and b are determined as the points α and β , respectively, which minimize

$$\left\| \frac{dg_1}{dx} - \text{sech} * h_7(x; a, b) \right\|_2. \quad (3.3)$$

Further justification for such an extension is the fact that other authors, such as Schwarzl and Staverman [15] and Tschoegl [17], have used similar formulae with different coefficients and obtained good approximations for $h(x)$.

Alternatively, the parameters a and b of $h_7(x; a, b)$ could be determined as the points α and β , respectively, which minimize

$$\min_{a,b} \|g_2 - \text{sech} * h_7(x; a, b)\|_2. \quad (3.4)$$

Although the least squares criterion (3.3) is a natural choice for the determination of the parameters a and b , the choice of other possibilities should be considered when the need arises.

4. The synthetic data and validation

The validation was performed with synthetic oscillatory shear data corresponding to $h(x)$ consisting of the two Gaussian density functions

$$h(x) = \frac{1}{\sqrt{\pi}} \exp\left(-\frac{(x+2)^2}{8}\right) + \frac{3}{4\sqrt{\pi}} \exp\left(-\frac{(x-3)^2}{8}\right).$$

The importance of this choice can be seen in Figure 1 as it shows that the oscillatory shear data can often hide a multiple hump structure in $h(x)$. Such data is representative of that which would be obtained for polystyrene and polybutadiene samples [11, 12].

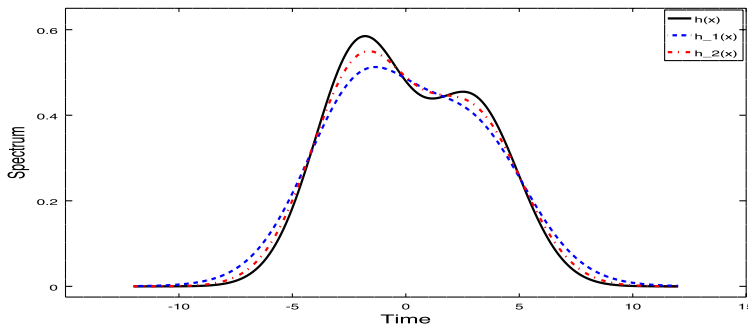


FIGURE 1. A comparison of approximations of $h(x)$ by $h_1(x)$ and $h_2(x)$ (colour available online).

However, the synthetic data is more challenging in that, unlike the $g_2(x)$ data for polystyrene and polybutadiene samples, there is little evidence in the synthetic $g_2(x)$ data that there are peaks in $h(x)$.

The peaks are visible in the red curve (online) in Figure 1, which corresponds to $g'_1(x)/2$. This comes at the expense of having to perform a numerical differentiation. It represents an example, in terms of a derivative spectroscopy [5] application, of how only a single differentiation can highlight the hidden structure in the nondifferentiated data [5]. Here, this relates to the fact that the sech^2 -kernel generator of $g'_1(x)/2$ is more strongly peaked than the sech .

4.1. The truncation formulae This is clear from Figure 1, where the black curve is the exact $h(x)$, while the blue (online) curve is the measured oscillatory shear data $h_1(x) = g_2(x)$ and the red curve is the approximation $h_2(x) = g'_1(x)/2$. It confirms that $h_1(x)$ corresponds to an over-smoothed approximation as it gives no indication of the bumps in $h(x)$ and that the derivative spectroscopic nature of $h_2(x)$, even though it only involves a single differentiation, yields a good indicative approximation that highlights the existence of the bumps.

Although the approximation $h_2(x)$ is reasonable in that it recovers the double hump structure of $h(x)$, it is marginal from an accuracy perspective as there are local regions where there is a clear difference between $h_2(x)$ and $h(x)$. More accurate results are plotted in Figure 2. The improvement in going from $h_2(x)$ to $h_3(x)$ and $h_4(x)$ is clear. The plot of $h_5(x)$ is not shown since, due to graphical accuracy, it is indistinguishable from the exact solution, $h(x)$.

However, from a practical numerical perspective, using either the $h_4(x)$ and $h_5(x)$ derivative spectroscopic approximations to improve the accuracy of the recovery of $h(x)$ may not be optimal because of the higher levels of differentiation involved.

4.2. The least squares joint inversion formulae The joint inversion approximation $h_6(x)$ is plotted in blue (online) in Figure 3 with its least squares counterpart, corresponding to (3.2) and (3.3), plotted in red. These two approximations are even better than the ones plotted in Figure 2. They represent validation for extending the

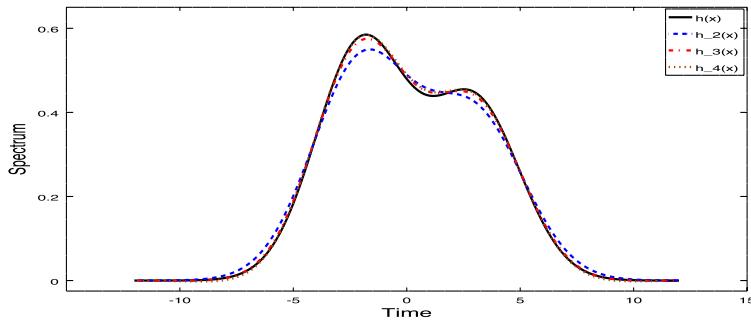


FIGURE 2. A comparison of approximations of $h(x)$ by $h_2(x)$, $h_3(x)$ and $h_4(x)$, which overlays $h(x)$ for most values of x (colour available online).

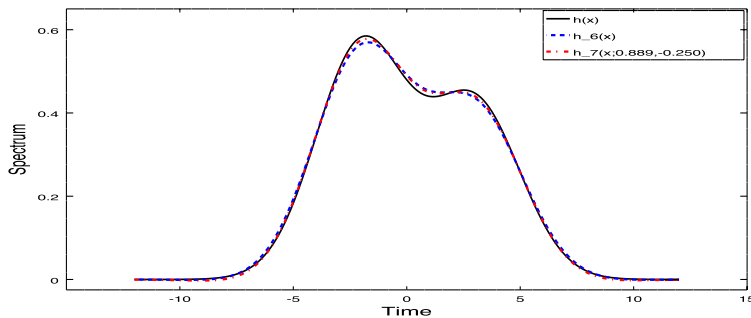


FIGURE 3. A comparison of $h(x)$ with $h_6(x)$ and the least squares solution $h_7(x; 0.889, -0.250)$, generated using the minimization (3.3) (colour available online).

joint inversion methodology to the recovery of approximations for $h(x)$ jointly from $g'_1(x)$ and $g_2(x)$.

Further support for this approach of generating least squares joint inversion approximations is given in Figure 4, in which the red curve in Figure 3 is replaced by the red curve for the least squares joint inversion approximation corresponding to (3.2) and (3.4).

It is clear from a comparison of Figures 3 and 4 that both least squares joint inversion approximations are equally good. The only limitation on the utilization of the least squares procedure is the need to have a comprehensive set of data for both $g_1(x)$ and $g_2(x)$.

5. Conclusions

In the practical recovery of estimates of the relaxation spectrum from oscillatory shear data, it is necessary to work with limited data. This leads to a need for local formulae to perform the recovery. Here, advantage is taken of the fact that simple truncations of the formulae (2.5) and (2.6) often yield good approximations for $h(x)$

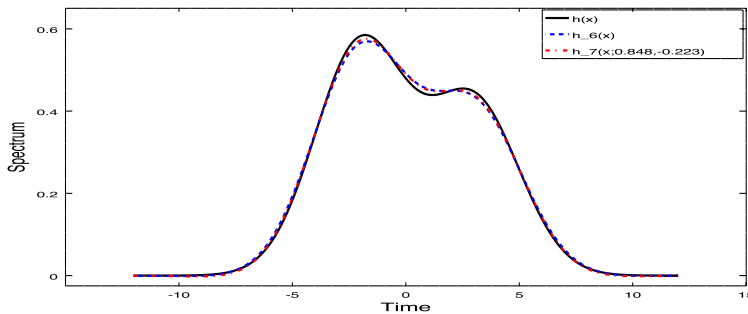


FIGURE 4. A comparison of $h(x)$ with $h_6(x)$ and the least squares solution $h_7(x; 0.848, -0.223)$, generated using the minimization (3.4) (colour available online).

and, in particular, g_2 and dg_1/dx . Their accuracy is improved by applying the joint inversion methodology to both g_2 and dg_1/dx within the least squares framework of the minimization of either (3.3) or (3.4). Such joint inversion least squares procedures represent rapid ways for the practical rheologist to quickly obtain good approximations to the relaxation spectrum when it is continuous.

References

- [1] R. S. Anderssen, A. R. Davies, F. R. de Hoog and R. J. Loy, “Derivative based algorithms for continuous relaxation spectrum recovery”, *J. Non-Newtonian Fluid Mech.* **222** (2015) 132–140; doi:10.1016/j.jnnfm.2014.10.004.
- [2] R. S. Anderssen and F. R. de Hoog, “Finite-difference methods for the numerical differentiation of non-exact data”, *Computing* **33** (1984) 259–267; doi:10.1007/BF02242272.
- [3] B. Anderssen, F. de Hoog and M. Hegland, “A stable finite difference ansatz for higher order differentiation of non-exact data”, *Bull. Aust. Math. Soc.* **58** (1998) 223–232; doi:10.1017/S0004972700032196.
- [4] R. S. Anderssen and M. Hegland, “For numerical differentiation, dimensionality can be a blessing!”, *Math. Comput.* **68** (1999); doi:10.1090/S0025-5718-99-01033-9.
- [5] R. S. Anderssen and M. Hegland, “Derivative spectroscopy - An enhanced role for numerical differentiation”, *J. Integral Equations Appl.* **22** (2010) 355–367; doi:10.1216/JIE-2010-22-3-355.
- [6] A. R. Davies and R. S. Anderssen, “Sampling localization in determining the relaxation spectrum”, *J. Non-Newtonian Fluid Mech.* **73** (1997); doi:10.1016/S0377-0257(97)00056-6.
- [7] A. R. Davies and N. J. Goulding, “Wavelet regularization and the continuous relaxation spectrum”, *JNNFM* **189** (2012) 19–30; doi:10.1016/j.jnnfm.2012.09.002.
- [8] J. D. Ferry, *Viscoelastic properties of polymers* (Wiley, New York, 1980).
- [9] R. M. Fuoss and J. G. Kirkwood, “Electrical properties of solids. VIII. Dipole moments in polyvinyl chloride-diphenyl systems”, *J. Amer. Chem. Soc.* **63** (1941) 385–394; doi:10.1021/ja01847a013.
- [10] R. D. Groot and W. G. M. Agterof, “Dynamic viscoelastic modulus of associative polymer networks – off-lattice simulations, theory and comparison to experiments”, *Macromolecules* **28** (1995) 6284–6295; doi:10.1021/ma00122a041.
- [11] J. Honerkamp and J. Weese, “Determination of the relaxation spectrum by a regularization method”, *Macromolecules* **22** (1989) 4372–4377; doi:10.1021/ma00201a036.
- [12] J. Honerkamp and J. Weese, “A nonlinear regularization method for the calculation of relaxation spectra”, *Rheologica Acta* **32** (1993) 65–73; doi:10.1007/BF00396678.

- [13] D. L. B. Jupp and K. Vozoff, “Stable iterative methods for the inversion of geophysical data”, *Geophys. J. R. Astro. Soc.* **42** (1975) 957–976; doi:10.1111/j.1365-246X.1975.tb06461.x.
- [14] A. Ya. Malkin, “The use of a continuous relaxation spectrum for describing the viscoelastic properties of polymers”, *Polymer Sci. A* **48** (2006) 39–45; doi:10.1134/S0965545X06010068.
- [15] F. Schwarzl and A. J. Staverman, “Higher approximation methods for the relaxation spectrum from static and dynamic measurements of visco-elastic materials”, *Appl. Sci. Res. A* **4** (1953) 127–141; <http://link.springer.com/article/10.10072FBF03184944>.
- [16] R. I. Tanner and K. Walters, *Rheology: an historical perspective* (Elsevier, Amsterdam, 1998).
- [17] N. W. Tschoegl, *The phenomenological theory of linear viscoelastic behavior: an introduction* (Springer, Berlin, 1989).
- [18] K. Walters, *Rheometry* (Chapman and Hall, London, 1975).