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AND RETARDATION SPECTRA FOR LINEARLY VISCOELASTIC 
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ABSTRACT

Knowledge of the relaxation spectrum is important because 1) it provides an intrinsic characterization of the mechanical properties for linearly viscoelastic materials and 2) it offers a rational way to derive the coefficients for a Prony or Dirichlet series representation of the relaxation modulus of importance to some engineering analyses.

Although there are several ways of approximately determining the relaxation spectrum, it appears natural to examine numerical solutions of the definitive singular Fredholm integral equation.

It turns out that a solution based on Simpson quadrature leads to an unstable solution in the sense that an increase in integration intervals produces a progressively worse solution which oscillates between positive and negative values. This difficulty may be overcome by requiring that

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the curvature of the relaxation spectrum with respect to the relaxation times be minimized. The method is tested on the modified power law and good agreement with the exact and numerically determined relaxation spectrum is obtained. However, when the same method is used to determine the retardation spectrum, only the unstable solution is obtained, although the form of the integral equation is the same. This different behavior is attributed to the difference in the characteristics of the relaxation and retardation spectral functions.
INTRODUCTION

From the standpoint of polymer physics or polymer chemistry, the relaxation spectrum provides an intrinsic material characterization not modulated by particular laboratory test variations. Furthermore, it may be desirable to relate molecular parameters such as chain composition and conformation to the spectrum rather than a particular response curve.

While it is not always necessary from an engineering standpoint to determine the relaxation spectrum for stress analysis problems, it is at times convenient to characterize viscoelastic material functions by a finite Prony or Dirichlet series

\[ R(t) = R_\infty + \sum_{n=1}^{N} r_n e^{-t/\tau_n} \]  

where \( R \) is the response to a step stress or strain and \( R_\infty \) is the response at infinite time. Schapery [1] proposed a collocation method based on minimization of the square error for the determination of the coefficients \( r_n \) when the characteristic times \( \tau_n \) are chosen arbitrarily throughout the transition region of the material. It turns out that when the number of terms in the series (1) is increased in order to improve the smoothness of the representation some of the coefficients \( r_n \) turn out to be negative. The dynamic properties derived from such a series could be physically unrealistic. In such a case, knowledge of the spectral function would provide a rational means to derive from it positive coefficients by a straightforward integration.
MATHEMATICAL PRELIMINARIES

Because it is not possible to devise a test for the determination of the spectra, they must be calculated from material responses measured in particular test histories. In general, the material response \( R(t) \) can be represented in the form

\[
R(x) = \int_0^\infty H(\tau) B(x, \tau) \frac{d\tau}{\tau}
\]

where \( H(\tau) \) is the spectral function and \( B(x, \tau) \) is a function of relaxation time \( \tau \) and time measure \( x \) (time or frequency). Roesler, et al., [2,3,4] have treated the solution of (2) in terms of Fourier series synthesis with special application to dynamic viscoelastic responses. Twomey [5] and Philips [6] have considered the numerical solution of (2) for the Kernel \( B(x, \tau) = e^{-x/\tau} \). In this case the integral is of the Laplace type and its solution reduces to the determination of the Laplace inverse of an experimentally determined function. The special difficulty that arises in this computation is that the solution of the integral equation is not stable under reasonable perturbations [7]. This instability manifests itself in progressively worse solutions as one attempts to calculate the function at more and more points in the sense that the solution oscillates with ever wider excursions about the --presumably smooth--exact solution.

In order to arrive at a non-oscillating or meta-stable solution, it is possible [5,6] to solve the integral equation subject to the smoothness constraint that the curvature of the solution with respect to its variable be minimized. To demonstrate this let us write equation (2) in the form
R(x) = log_{e} 10 \int_{-\infty}^{\infty} H[\tau(y)] B[x, \tau(y)] dy \tag{3}

by virtue of the transformation \( y = \log_{10} \tau \). Assuming that \( H(\tau) \) contributes to the integral (3) over a finite domain of \( \tau^* \), one may use Simpson quadrature to write (3) as

\[ \sum_{i=1}^{N} W_{i} K_{i j} H_{i} = R_{j} + \varepsilon_{j} \tag{4} \]

where

\[ j = \text{integer such that } 1 \leq j \leq N_1 > N \]

and

\[ H_{i} = H(\tau_{i}) \quad 1 \leq i \leq N \]

\[ R_{j} = R(x_{j}) \quad 1 \leq j' \leq N_1 > N \]

\[ K_{ij} = \log_{e} 10 B(x_{j}, \tau_{i}) \]

\[ W_{i} = \text{Simpson quadrature coefficients} \]

\[ \{1, \frac{4}{3}, \frac{2}{3}, \ldots, \frac{4}{3}, \frac{1}{3}\} \]

In principle, one would like to solve (4) with errors \( \varepsilon_{j} \equiv 0 \). One finds, however, that the inverse \([A]^{-1}\) of the matrix

\[ [A] = A_{ij} = W_{i} K_{ij} \tag{5} \]

becomes more ill conditioned as its size \( N \) increases [7] if \( B(x, \tau) \) has exponential character. The ill condition manifests itself in that its elements

* Practically speaking, it has been found that approximately two decades to either side of the transition region is sufficient.
alternate in size and become very large. In terms of the solution $H_i$ this means that small changes in the $R_j$ may result in large changes in the $H_i$ by virtue of the relation

$$H_i = A^{-1}_{ij} R_j$$

(6)

To improve this situation we define the square relative error

$$\varepsilon = \sum_{j=1}^{N_j} \left( \frac{\varepsilon_j}{R_j} \right)^2$$

(7)

and the second order difference

$$C = \sum_{i=1}^{N} \left\{ H_{i+1} - 2H_i + H_{i-1} \right\}^2$$

(8)

as a measure of the curvature of $H(\tau)$ with respect to $\tau$. It would be desirable to minimize the square error $\varepsilon$ with respect to the numbers $H_i$. If the curvature of the function $H(\tau)$ were known, this would lead to the well known variational problem with a constraint which can be treated by the method of Lagrange multipliers. Since the curvature is not known, one might still expect to obtain an improvement by minimizing the linear combination

$$F(H_i) = \varepsilon(H_i) + \lambda C(H_i)$$

(9)

and treat $\lambda$ as an unknown constant to be chosen more or less arbitrarily rather than through prescription of the curvature constraint. In effect one minimizes thus a linear combination of the square error and the local
curvature*. Under consideration of (4) and the definition (5), the minimization of (9)

\[ \frac{\partial F(H_i)}{\partial H_i} = 0 \quad j = 1, 2, 3, 4, \ldots, N \]  

(10)

leads to

\[ \sum_{j=1}^{N_1} \left( \frac{A_{jk} \epsilon_i}{R_j} \right)^2 + \lambda \sum_{i=1}^{N} S_{ki} H_i = 0 \]  

(11a)

or

\[ \sum_{i=1}^{N} \left( \sum_{j=1}^{N_1} \frac{A_{jk} A_{ki}}{R_j} \right) + \lambda S_{ki} \right) H_i = \sum_{j=1}^{N_1} \frac{A_{jk}}{R_j} \]  

(11b)

where \( S_{ki} \) represents the symmetric banded matrix

\[
\begin{bmatrix}
1 & -2 & 1 & 0 & 0 & 0 & 0 \\
-2 & 5 & -4 & 1 & 0 & 0 & 0 \\
1 & -4 & 6 & -4 & 1 & 0 & 0 \\
0 & 1 & -4 & 6 & -4 & 1 & 0 \\
& & & & & & \\
& & & & & & \\
0 & 0 & 0 & 1 & -4 & 6 & -4 & 1 \\
0 & 0 & 0 & 0 & 1 & -4 & 5 & -2 \\
0 & 0 & 0 & 0 & 0 & 1 & -2 & 1
\end{bmatrix}
\]

This may be written more compactly in matrix form as

\[ [M] [H] = [V] \]  

(12)

*Some further improvements may be obtained if for smooth functions \( H(\tau) \) the curvature is treated less locally by writing

\[ C = \sum_{i=1}^{N} \left( H_{i+2} - 2H_i + H_{i-2} \right)^2 \]
with

\[ M_{ki} = A_{ki} \sum_{j=1}^{N_1} \frac{A_{jk}}{R_j^2} + \lambda S_{ki} \]

\[ \nu_k = \sum_{j=1}^{N_1} \frac{A_{jk}}{R_j} \]

which equation has the formal solution

\[ \{H\} = [M]^{-1}\{V\} \quad (13) \]
SAMPLE CALCULATIONS FOR THE RELAXATION MODULUS

In order to test the solution method, it is necessary to obtain an exact solution of a typical response function for comparison. For this purpose we have chosen the function

\[ R(t) = \frac{E_g - E_e}{(1 - t/\tau_o)^n} = \int_0^\infty H(\tau) \, e^{-t/\tau} \, \frac{d\tau}{\tau} \]  

which equation has as the solution the modified power law for the relaxation modulus

\[ H(\tau) = \frac{E_g - E_e}{\Gamma(n)} \left( \frac{\tau_o}{\tau} \right)^n \, e^{-\tau_o/\tau} \]  

with \( E_g \) and \( E_e \) the glassy and equilibrium modulus, respectively.

In Figure 1 we show a comparison of results using (14) as the test data at \( N_1 = 43 \) points to calculate \( H(\tau) \) at \( N = 39 \) points, for different values of the smoothing factor \( \lambda \). If the curvature constraint is eliminated (\( \lambda = 0 \)) so that the procedure reduces to one of minimizing the square error, the solution oscillates considerably while even a small value of \( \lambda \) improves the solution considerably.

Another factor which influences the solution is the range of relaxation times. This range must be large enough to include the range over which the spectrum is essentially non-zero, yet one may not be too liberal in this choice, particularly at small values for \( \tau \). The reason for this limitation is the behavior of the inverse of the matrix \([ M] \), equation (13). In this region the function \( R(t) \) has a plateau and the problem becomes one of determining
locally the solution for \( H(\tau) \) which renders \( R(t) \) nearly a constant. This solution is very sensitive to round-off errors in \( [M]^{-1} \) and the accuracy of the prescribed values of \( R(t) \). Indeed, in the case of experimentally determined functions \( R(t) \) it may be necessary to locally smooth the data numerically.

Figure 2 gives a comparison of the numerical solution \( (\lambda = 10^{-6}) \) with the exact one along with two approximations of the Widder-Post formula. Note that although the approximate solutions are close to the exact one to the right of the maximum where the numerical solution is locally less adequate though close on the average. The latter compares very well with the exact solution near the peak, whereas the approximate solutions achieve peak values considerably lower than either of the other solutions. It appears thus that a combination of the two solution methods might give good results. A calculation of the error as presented in Figure 3 shows further that the numerical solution has a nearly vanishing mean error while the two approximations have small but constant errors.
APPLICATION TO CREEP COMPLIANCE

The creep compliance may be written in spectral form as

\[ D_{\text{crp}}(t) = D_g + \int_0^\infty L(\tau) (1 - e^{-t/\tau}) \frac{d\tau}{\tau} \]  

or alternately

\[ R'(t) = D_e - D_{\text{crp}}(t) = \int_0^\infty L(\tau) e^{-t/\tau} \frac{d\tau}{\tau} \]  

with \( D_e = D_g + \int_0^\infty L(\tau) \frac{d\tau}{\tau} \) as the long time elastic compliance and \( D_g \) the glassy compliance. Equation (17) is of the same form as (14) and could, therefore in principle, be solved in the same way as before. As a first test case we have chosen the mathematical relation

\[ D_{\text{crep}}(t) = \frac{1}{E_{\text{rel}}(\tau)} \]  

which, physically speaking is only an approximation, \( E_{\text{rel}}(\tau) \) being given by the power law (14)

\[ E_{\text{rel}}(t) = E_e + R(\tau) \]

The solution to (17) is shown as a strongly unstable, oscillating function in Figure 4; no variation of the smoothness coefficient \( \lambda \) changed the character of the solution. A second attempt was made using the measured properties for the equivoluminal composition of Solithane 113 [8] with the same result of an unstable solution. Inasmuch as the integral equations (14) and (17) are the same and the function \( R(t) \) decreases in both cases monotonically.
with time in a very similar manner, the distinction between solvable and unsolvable equations may be rather fine. It is generally accepted that relaxation spectra increase rapidly with $\tau$ and decrease slowly after the peak is passed whereas the converse is true for the retardation spectrum. From the standpoint of the cited experiments with the numerical inversion scheme presented here, it appears that the determination of the relaxation spectra is feasible and is not feasible if the spectrum has the characteristics of the retardation spectrum.
CONCLUSION

We have attempted to automate the determination of spectral distribution functions from experimental data using relatively simple numerical techniques. Although the straightforward numerical solution of the singular integral equations always leads to unstable solutions the introduction of a smoothness constraint leads to acceptable solutions if the spectra are of the relaxation type but not if they are of the retardation type. While the quality of the numerical solution may not be much better than that of standard approximate methods, it should be borne in mind that the current method lends itself, where applicable, to routine calculation and circumvents to a large degree the guess work and subjective interpretation associated with other approximate methods.
REFERENCES


Fig. 1 COMPARISON OF RELAXATION SPECTRUM FOR DIFFERENT SMOOTHNESS CONSTRAINTS $\lambda$
\[ H(\tau) = \frac{E_g - E_e}{I_n} \left( \frac{\tau_0}{\tau} \right)^n \exp\left( -\frac{\tau_0}{\tau} \right) \]

\[ n = \frac{1}{2}, \quad \tau_0 = 1 \]

Numerical Result

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Widder-Post; \( N = 1 \)

Widder-Post; \( N = 2 \)

**FIG. 2** COMPARISON OF EXACT, NUMERICAL, AND APPROXIMATE RELAXATION SPECTRA
FIG. 3 ERROR IN RELAXATION SPECTRUM AS DETERMINED NUMERICALLY AND BY THE WIDDER-POST METHOD
Fig. 4  UNSTABLE SOLUTION FOR THE RETARDATION SPECTRUM $L(\tau)$