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Note on the Iterative Calculation of Relaxation Spectra

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Synopsis

The use of exact numerical methods for calculating spectra from dynamic moduli is shown to lead to acceptable results when a modified numerical method is employed. The modification avoids the wild oscillations encountered with existing methods when difficult experimental data containing sudden spectral cutoffs must be analyzed.

Methods of Calculation

Recently it has become possible, at least in principle, to solve the integral equations arising in relaxation spectrum calculations by numerical methods with the use of digital computers. Examples of this approach are found in the interesting work of Hopkins.[1,2] He has shown that it is most useful to start spectral calculations from the component $G''(\omega)$ of the complex modulus G^*. Accepting this, we have the following integral equation for the relaxation spectrum $H(\tau)$:

$$G''(\omega) = \int_0^\infty \omega H(\tau)\, d\tau/(1 + \omega^2\tau^2) \tag{1}$$

There is also a still expanding amount of work dealing with approximate rules for inversion of eq. (1). Ferry[3] reviews much of this. As an example, the rule of Ninomiya and Ferry[4] is

$$H(1/\omega) = (2/\pi)\{G''(\omega) + a/(a - 1)^2[G''(a\omega) + G''(\omega/a) - 2G''(\omega)]\} \tag{2}$$

where the data are tabulated at equal intervals on a logarithmic scale; each point is at a frequency a times the previous point. More accurate approximate rules can also be generated,[4,5] but for many typical experiments eq. (2) is quite adequate. Here we concentrate on exact numerical methods.

With iterative methods[2] it is known that some difficulties occur near the ends of the frequency scale, but these can easily be remedied. No physical $G''(\omega)$ data can terminate faster than a line spectrum (δ function), and this fact can be used to terminate data sets at the high-frequency end in a smooth manner. No terminations seem to be needed at the low-frequency end. For example, in Figure 1 the data beyond $\omega = 10^3$ rad/sec. is added to avoid the wild oscillations that would result if the data were suddenly stopped at this point. By contrast, nothing was added below $\omega = 2$ rad/sec., the other limit of the test data. Provided that these precautions

have been taken, one would expect that iterative numerical methods operating directly on eq. (1) would be capable of great accuracy. The direct methods[1,2] are simpler than some other[6–8] potentially exact schemes, and the latter seem to offer no substantial advantages.

Recently we attempted to analyze iteratively some experimental data obtained by Simmons[9] from a sample undergoing a steady shearing motion

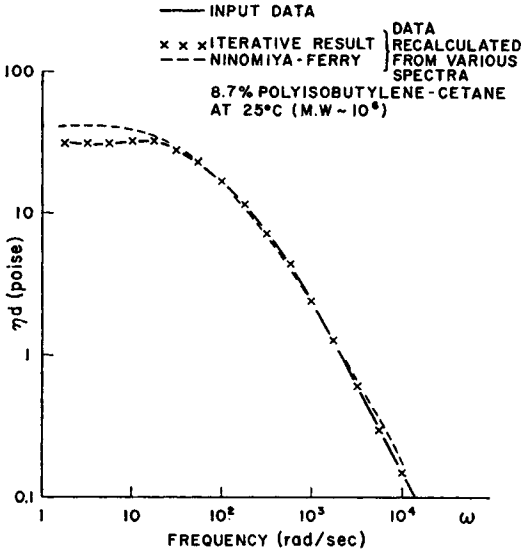

Fig. 1. Original and recalculated data for 8.7% polyisobutylene–cetane solution sheared at 102 sec.$^{-1}$.[9]

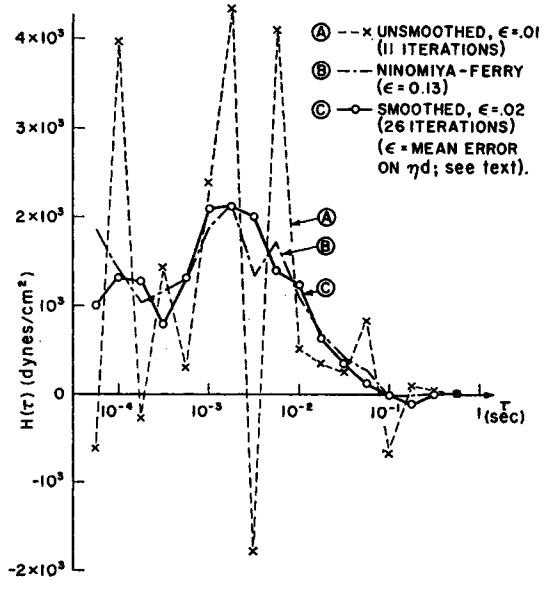

Fig. 2. Spectra for fluid of Figure 1 calculated by various methods.

in addition to a small sinusoidal shear. Figure 1 shows the original dynamic viscosity data ($\eta_d \equiv G''/\omega$) and the data recalculated from various spectral estimates. To make the recalculation of $G''(\omega)$, given discrete points of $H(\tau)$ spaced at logarithmic intervals (interval a), we supposed that $H(\tau)$ consisted of blocks of width log a and of varying height. Hopkins[2] used delta functions in his recalculations, but with our closely spaced data (about a quarter-decade) there is a negligible difference between the two methods. The Ninomiya-Ferry spectrum, eq. (2), does not yield an adequate fit upon recalculation, as the dashed line in Figure 1 shows. The cause of most of the error seems to be the sharp cutoff in the spectrum at about $\tau = 3/\gamma$, where γ is the shearing rate. The spectrum is also not very smooth; see Figure 2, curve B.

Iteration until the mean error ϵ in the dynamic viscosity (defined as the sum of the absolute errors in η_d, divided by the sum of the given η_d) was 0.01, and required 11 iterations with eq. (2) as an algorithm. The result was the extraordinary curve, (curve A) in Figure 2, which is worse than the Ninomiya-Ferry result, curve B. Although curve A was the worst one found out of about 16 sets of data, it was not obvious a priori that it would be the most troublesome. To deal with this problem a slightly modified procedure was adopted.

Smoothing Procedure

The cure for the wildly oscillating spectrum was to use an algorithm much less sophisticated than eq. (2). To ensure smoothing we initially set

$$H(1/\omega) = (2/3\pi)[G''(\omega/a) + G''(\omega) + G''(a\omega)] \tag{3}$$

This form was evolved from trial and error and seems to be an acceptable compromise between allowing smoothing and preventing information loss. At the end points of the frequency interval we take

$$H(1/\omega) = (2/\pi)G''(\omega) \tag{4}$$

From this initial $H(\tau)$ [with the use of eqs. (3) and (4)] the new values of $G''(\omega)$ ($=G''_{(1)}$, say) are calculated by assuming block spectra centered on $1/\omega_i$, where ω_i are the data points. The corrections to the spectra, ΔH, are found by replacing G'' with $G'' - G''_{(1)}$ and H with ΔH in eqs. (3) and (4). From the sum of H and ΔH new values of $G''_{(1)}$ are calculated; the process is continued until sufficient accuracy is attained. It was found that it was impossible to achieve an arbitrarily high accuracy; after 80 iterations about 1.3% mean error on η_d persisted; only 26 iterations were required to attain 2% accuracy. This result is shown in Figure 2, curve C. It appears that the residual errors left over with the present method are probably indicative of the size of the random errors in the input data.

Due to the interest in detecting sudden spectral cutoffs with this data, a box spectrum reaching from $\tau = 0$ to $\tau = 0.0562$ and of unit height was analyzed. The input-data set was "perfect" (three-figure) values of η_d at quarter-decade intervals. At $\tau = 0.1$ the calculated $H(\tau)$ was 0.11 (in-

stead of zero), and at $\tau = 0.0316$ the $H(\tau)$ was 0.88 (instead of 1.00). Overshoots and undershoots of about 0.06 occurred in a typical way.[2] Thus it appears that quite sharp cutoffs can be detected; a drop from a maximum to zero can be detected in about 2 frequency intervals ($=2 \log a$) with the present method. No significant information loss has occurred; no better result was ever obtained with any algorithm.

Conclusion

We found that very smooth spectra were computed with most input-data sets by using the present method[10] and that acceptable results were found even in difficult cases such as the example given here. Although the present scheme is satisfactory, we expect that further improvements may be made by using various numerical smoothing devices iteratively, if required.[11]

A point of interest seems to be that the more exact the inversion from the standpoint of the usual approximate methods,[5] the worse the iterative result; we emphasize that if an acceptable iterative result is ultimately obtained, the algorithm is of no importance except for speed of convergence. Although the Ferry-Ninomiya formula, eq. (2), avoids the derivative notation, it is clear that the terms in the square brackets are proportional to the finite-difference approximation[11] of the logarithmic second derivative, and they inevitably accentuate "noise" in the data. By contrast, eq. (3) continually smooths the data. This feature seems more important than the speed of convergence with digital methods. Using an IBM 360 computer we found that the input–output time was more important than the iteration time, and each inversion took 1 or 2 min. at most. Finally there seems to be no difficulty in applying the present ideas to the inversion of other integral relations arising in viscoelastic studies.

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