Fast Determination of the Complex Modulus Function

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ABSTRACT
An algorithm which determines the complex modulus in roughly half the
experiment time needed for a reliable
analysis by Fourier transformation has been
developed. The algorithm is based on
Boltzmann's superposition principle and the
existence of a relaxation time spectrum.

INTRODUCTION
The use of computers for the generation of arbitrary stress or strain inputs and
subsequent analysis of rheological data raises the
question of how to extract maximum information about a material in a given
experiment time.

Measuring the complex modulus over a
range of frequencies is a time consuming process and the measurements at the lowest
frequency typically takes about half of the
total measurement time. Holly et al.¹ have
shown how to shorten the total measurement
time by applying a strain which is a sum of sinusoids of different frequencies to the sample and extracting the complex modulus from steady state data by Fourier
transformation.

For measurements at low frequencies, the
absolute time to obtain the steady state
needed for Fourier transformation is long. However, the data taken before steady state also reflect the material properties and an
analysis algorithm capable of extracting the complex modulus from these data has been
developed.

The algorithm can determine the complex modulus in about half the experiment time needed for a reliable analysis by Fourier transformation provided the signal-to-noise ratio is sufficiently high to avoid averaging over many periods. This is usually the case for measurements on solids and melts but not for dilute solutions.

DERIVATION OF THE ALGORITHM
The algorithm is derived with a strain input but analogous equations can be written for a stress input.

The stress response from a linear material subjected to a strain is given by Boltzmann's superposition principle:

$$\sigma(t) = - \int_0^\infty G(t') \frac{d\gamma(t-t')}{dt'} \, dt'.$$  \hspace{1cm} (1)

The stress relaxation modulus, $G(t)$, is often expressed by the discrete relaxation time spectrum as

$$G(t) = \sum_{j=1}^{\infty} G_j e^{-q_j t}. \hspace{1cm} (2)$$

Discretization of Eq. 1 with a time step $\Delta t$ and insertion of Eq. 2 yields

$$\sigma_{p\ell}(k\Delta t) = \sum_{j=1}^{\infty} G_j f(j,k), \hspace{1cm} (3)$$
where

\[ f(j,k) = e^{-\Delta q(2\tau_j)} \gamma(k\Delta t) - 2 \sinh(\frac{\Delta t}{2\tau_j}) \sum_{m=1}^{\infty} e^{-m\Delta q} \gamma((k-m)\Delta t). \] (4)

The subscript \( pr \) is used with the stress because Eq. 3 yields the predicted stress from a given set of the coefficients, \( G_j \), and relaxation times, \( \tau_j \).

The relaxation times are fixed in order to obtain a simple algorithm. The corresponding optimum coefficients, \( G_j \), are determined by a least squares fit to experimental data, i.e. the following equation is solved:

\[ \frac{\partial}{\partial G_i} \sum_{p=-\infty}^{\infty} \left[ \sigma(p\Delta t) - \sigma_{\text{exp}}(p\Delta t) \right]^2 = 0. \] (5)

Substituting Eqs. 3 and 4 into Eq. 5 yields

\[ \sum_{j=1}^{n} A_j(k) G_j = b_j(k), \] (6)

where

\[ A_j(k) = \sum_{p=-\infty}^{\infty} f(i,p) f(j,p) \] (7)

\[ b_j(k) = \sum_{p=-\infty}^{\infty} f(i,p) \sigma(p\Delta t). \]

Both the matrix \( A_j(k) \) and the vector \( b_j(k) \) can be evaluated by adding the \( k \)th term to the previous quantity. Furthermore the quantity \( f(j,k) \) can also be evaluated recursively from the previous value, \( f(j,k-1) \).

Therefore it is unnecessary to store all stress and strain values during the experiment. Only the quantities \( A_j(k), b_j(k) \) and \( f(j,k) \) need to be stored.

Once the coefficients \( G_j \) have been determined, the complex modulus, \( G^*(\omega) \), can be calculated \(^2\) by inserting steady state sinusoidal data in Eq. 3:

\[ G^*(\omega) = \frac{\sum_{j=1}^{n} G_j e^{-\Delta q(2\tau_j)} \frac{1 - e^{-i\omega\Delta t}}{1 - e^{-\Delta q(2\tau_j)} e^{-i\omega\Delta t}}}{G^0(2\omega_0)} \sin(2\omega_0 \omega t) \] (8)

**TEST OF THE ALGORITHM**

In order to make a thorough study of the applicability of the algorithm, it was decided to try it in all the different regions of an amorphous polymer, i.e. from the melt to the glass.

A series of computer simulated experiments has therefore been carried out on a material with a box and wedge relaxation time spectrum which models an amorphous polymer well \(^2\).

A strain of the following form is applied to the material:

\[ \gamma(t) = \sum_{i=0}^{\infty} \frac{\sigma_0}{G^0(2i\omega_0)} \sin(2i\omega_0 \omega t) \] (9)

i.e. a fundamental frequency, \( \omega_0 \), and seven of its harmonics covering approximately two decades. The amplitudes of the individual frequencies are adjusted so that the stress amplitudes become equal to \( \sigma_0 \). This ensures that all frequencies are affected equally by white noise which is added to the stress in some of the simulations.

The frequency content of the strain input determines which of the relaxation times in the material are excited. It turns out that it is sufficient to include relaxation times so that

\[ \omega_{\text{max}} \tau_{\text{min}} = 0.1 \]
\[ \omega_{\text{min}} \tau_{\text{max}} = 10. \] (10)

Furthermore, 3.3 relaxation times per decade are needed to give good results. Finally, the quantity \( f(j,k) \) in Eq. 4 quickly vanishes as \( \Delta t/\tau_j \rightarrow \infty \) so the smallest possible \( \tau_{\text{min}} \) is of the order of the sampling interval, \( \Delta t \).

Use of the strain in Eq. 9 therefore requires
15 relaxation times in the fit, and thus 15 coefficients, \( G_j \), as fitting parameters.

RESULTS AND DISCUSSION

The complex modulus is obtained from the simulated stress and strain data both by the algorithm described above and by conventional Fourier transformation.

Analysis of noise-free data from the first period of the fundamental frequency, \( \omega_0 \), by the new algorithm gives the storage and loss moduli well within 1.5 % for the applied frequencies and well within 7 % for frequencies which are about half a decade lower than the lowest applied frequency, i.e. 0.5 \( \omega_0 \). In the liquid region only the loss modulus, which is several orders of magnitude larger than the storage modulus, can be determined but in this region the viscosity is usually sufficient to characterize the material.

Fourier transformation of the same data gives errors of up to 30 % in the moduli because the data do not represent steady state. The errors are negligible only in the liquid and glassy regions. Data from the first period of the lowest applied frequency must therefore be discarded and only data from the second period analyzed by Fourier transformation to obtain the moduli within 0.8 %.

When Gaussian white noise with a dispersion of 2 % of the maximum stress value is added to the stress, the new algorithm is no longer capable of determining the moduli down to 0.5 \( \omega_0 \). However, the moduli are still determined within 5 % for all of the eight applied frequencies - except in the liquid and glassy regions where neither the new algorithm nor Fourier transformation can determine the smaller of \( G'(\omega) \) and \( G''(\omega) \). The new algorithm therefore reduces the experiment time needed to determine the complex modulus by a factor of two compared to conventional Fourier transformation.

Flexibility of the new algorithm

Another advantage of the new algorithm is its flexibility with respect to the form of the strain input. Successful analysis by Fourier transformation requires periodic data which cover an integral number of periods. In contrast, no assumptions of periodicity or an integral number of periods are made in the derivation of the new algorithm.

For example, analysis of noise-free data from 1/3 of the period of the lowest frequency, \( \omega_0 \), gives the moduli within 3 % for angular frequencies down to at least \( 2\pi/T \), where \( T \) is the experiment time. Fourier transformation of the same data does not make sense.

Determined coefficients

The coefficients, \( G_j \), determined by the algorithm only represent a discrete relaxation time spectrum when the relaxation times included in the fit are those giving the largest contributions to the complex modulus at the applied frequencies. The coefficients start to fluctuate between positive and negative values if the dominant relaxation times are not included. However, the complex modulus calculated from Eq. 8 is still well determined by the fluctuating coefficients.

REFERENCES
