Questions About Relaxation Spectra Submitted by a Reader

G', G" for a single relaxation-time Maxwell model.

Kevin Penfield of Uniqema has submitted the following questions to the *Bulletin*:

"I have a vague sense of what relaxation spectra are, as a distribution of (Maxwell?) elements over a continuum of relaxation times. Could you provide me with a better definition, conceptually? What is a more accurate definition of the ordinate? And what pitfalls might there be in using frequency-sweep data covering finite frequency range to calculate a relaxation spectrum (especially, might the points at either end do weird things)?"

SOR member Professor John Dealy has provided the following answers.

These are very important questions that deal with the most fundamental aspects of the practical use of linear-viscoelastic material functions to describe the behavior of polymeric materials. I will deal with these under several headings in response to the issues raised by Kevin Penfield. A more detailed discussion of these subjects can be found in Ref. [1].

In brief, the *discrete relaxation-time spectrum* is a convenient artifice with no physical meaning. It can be calculated easily, but should only be used in a very limited way to interrelate linear-viscoelastic functions. The discrete spectra obtained from such curve-fitting are not unique.

The *continuous relaxation spectrum function* H(τ) is a true representation of linear-viscoelastic material properties. It cannot be calculated easily, but in the last two decades good techniques have been developed for calculating the continuous spectrum function from experimental data. The accurate calculation of H(τ) from experimental data requires choosing a data-inversion technique that properly accounts for the effect of experimental error. The continuous spectrum function obtained from these methods is unique, within the set of assumptions made about regularization parameters and about the distribution of errors.
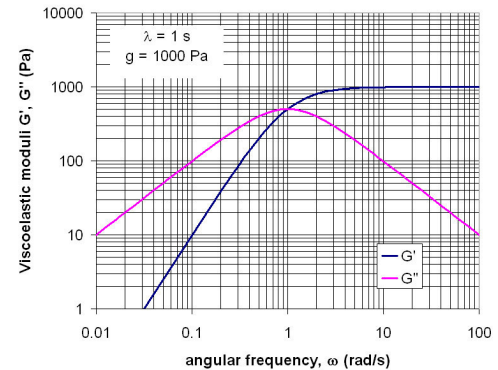
Finally, lack of information, especially at long relaxation times, compromises all calculations of linear-viscoelastic properties. Long relaxation-time information, such as is contained in accurate creep compliance data, is required to address this issue. Accurate techniques exist for combining G', G" and J(t) data in a way that allows for accurate calculation of the relaxation spectrum function.

The Discrete Relaxation Spectrum

The material function commonly used as the basis for discussing linear viscoelastic behavior is the relaxation modulus $G(t)$, although Don Plazek argues that the creep compliance is a better starting point [2]. In practice it is not possible to measure with good precision the relaxation modulus over the entire range of time from zero to infinity, but we wish to make the best use of the available data to arrive at an analytic function providing the truest possible representation of $G(t)$ within the limits imposed by the range, accuracy and precision of the data.

It is common practice to describe the relaxation moduli of polymers using a sum of exponentials, referred to as the generalized (multi-mode) Maxwell model.

$$G(t) = \sum_{i=1}^{N} G_i e^{-t/\tau_i} \qquad (1)$$

The set of constant, $\{\tau_i, G_i\}$, are said to constitute *a discrete relaxation spectrum*. While these empirical parameters have no physical significance, in the limit of large N, the sum should, in principle, approach the underlying function $G(t)$ that is a material property. The discrete spectrum lends itself to the conversion of one response functional into another, for example $G(t)$ to $J(t)$ or $G'(\omega), G''(\omega)$, and can be inferred from data in such a way that it describes these data with a precision limited only by that of the data themselves.

It is important to note that this choice of a sum of exponentials is arbitrary and does not have a solid foundation in polymer physics. It is thus an empirical description; there is no unique discrete spectrum, and

the fitting parameters $\{\tau_i, G_i\}$ have no physical significance. It is true that there are theories of polymer behavior that lead to relaxation moduli of the form of Eq 1, and this seems to imply that there is a basis at the molecular level for the use of a sum of exponentials. These theories , however, are based on a much simplified picture in which the molecule is replaced by a chain of N beads connected by N-1 connecting springs [3, p. 157]. Unlike the actual molecule, this chain is freely-jointed, which dramatically reduces the mathematical complexity of the model. The number of springs is much less than the number of backbone bonds, is arbitrary within certain limits, and thus has no physical significance. For example, the Rouse-Bueche model for an unentangled melt predicts that

$$G(t) = \frac{\rho RT}{M} \sum_{p=1}^{N} e^{-tp^2/\tau_R} \quad \tau_R = \frac{6\eta_0 M}{\pi^2 \rho RT} \qquad (2)$$

The Doi-Edwards model for an entangled chain is also based on the freely-jointed chain picture and predicts the following relaxation moldulus for an entangled, monodisperse melt in the plateau and terminal zones.

$$G(t) = \frac{8}{\pi^2} G_N^0 \sum_{i,odd} \frac{1}{i^2} e^{-i^2 t/\tau_d} \qquad (3)$$

where τ_d is the reptation or disengagement time. The upper limit of the summation is generally not indicated, because it converges very rapidly, but the empirical picture of the freely-jointed chain still lurks in the background.

We conclude that there is little basis at the level of molecular physics for the use of a sum of exponentials to describe the relaxation modulus. Thus, the use of a discrete spectrum should be seen as a convenient empirical representation of experimental data.

Continuous relaxation spectrum functions

If the number of elements in the generalized Maxwell model is increased toward infinity, one arrives at the continuous spectrum function, $F(\tau)$, where $F(\tau)d\tau$ is the contribution to $G(t)$ due to Maxwell elements having relaxation times between τ and $\tau + d\tau$. The relaxation modulus is related to the spectrum function as shown by Eq 4.

$$G(t) = \int_0^\infty F(\tau)[\exp(-t/\tau)]d\tau \qquad (4)$$

However, because of the concentration of relaxation information at very short times, it is generally preferable to work with a logarithmic time scale. This leads to a relaxation spectrum function, $H(\tau)$, which is a time-weighted spectrum function defined as $F\tau$, so that the relaxation modulus is given by:

$$G(t) = \int_{-\infty}^\infty H(\tau)[\exp(-t/\tau)]d(\ln \tau) \qquad (5)$$

Relationships between the various material functions describing linear behavior and methods for converting among them are discussed by Ferry [4]. The continuous functions $F(\tau)$ and $H(\tau)$ are not empirical fittings as is the discrete spectrum, as they are integral transforms that contain all the information that is in the modulus itself.

The degree to which a discrete spectrum approaches the continuous spectrum that is a true material characteristic depends on the density of data points and the technique used to infer the set of spectrum parameters $\{\tau_i, G_i\}$. Obviously, the greater the density of data points the better the characterization, but the method used to infer the parameters is also of crucial importance.

Methods of Inferring a Discrete Spectrum From Experimental Data

Whether using a discrete or a continuous spectrum function to represent $G(t)$, the practical problem is how to use experimental data to determine it. We must first recognize that it is not possible to determine the relaxation modulus with good precision and accuracy over the entire range of relevant times, which may run from microseconds to hours or days. Furthermore, the classical step strain experiment is not a popular method for determining $G(t)$ because of the difficulties involved in generating an instantaneous deformation and tracking the very rapid initial decay of the stress following the strain. The experiment most often used to characterize linear behavior is small amplitude oscillatory shear. Oscillatory shear data are usually reported as a table of the storage and loss moduli at a series of frequencies, i.e, the set $\{G'_k, G''_{k,} \omega_k\}$, Using the Boltzmann superposition principle, one can show that these are Fourier transforms of the relaxation modulus:

$$G'(\omega) = \omega \int_0^\infty G(s)\sin(\omega s)ds \qquad (6a)$$

$$G''(\omega) = \omega \int_0^\infty G(s)\cos(\omega s)ds \qquad (6b)$$

These transforms can, in principle, be inverted to give $G(s)$, given the storage and loss moduli [4, p.68]. However, to carry out the inversion in a precise way, these moduli must be known as continuous functions of frequency over the range of frequencies from zero to a value at which they have reached their high-frequency limiting behaviors, whereas what is available are G' and G'' values at discrete frequencies whose range is limited by the capabilities of the instrument used.

The conversion of a data set $\{G'_k, G''_k, \omega_k\}$ into a relaxation modulus function is usually carried out by representing $G(t)$ in terms of a discrete relaxation spectrum $\{G_i, \tau_i\}$. This requires the inversion of the summations:

$$G'(\omega) = \sum_{i=1}^{N} \frac{G_i (\omega\tau_i)^2}{[1+(\omega\tau_i)^2]} \tag{7a}$$

$$G''(\omega) = \sum_{i=1}^{N} \frac{G_i (\omega\tau_i)}{[1+(\omega\tau_i)^2]} \tag{7b}$$

It is very important to note that the success of this transformation is limited by the following inevitable features of oscillatory shear data.

1. Data are obtained only at a certain number of discrete frequencies.
2. Data are available only between maximum and minimum frequencies that are imposed by the capabilities of the instruments used. This range of frequencies is called the "experimental window".
3. There is always some imprecision (called scatter or noise) in the data.

There may also be systematic error (bias) in the data, but there is no way of correcting for this if it cannot be modeled explicitly. As a result of these nonidealities, the inference of a discrete spectrum using Eqs. 7a,b is an ill-posed problem. Although a set of parameters can be found that provides an approximate description of the rheological behavior that is suitable for some purposes, there is no unique discrete spectrum corresponding to a given set of data.

There are two approaches to this problem, depending on one's objectives. If one wants only an empirical equation that fits the data, it is a relatively simple matter of curve fitting. The most straightforward method for accomplishing this is linear regression, an example of which is the work of Laun [5]. Laun started by selecting one relaxation time parameter τ_i

per decade and determined the G_i values corresponding to them by linear regression based on both G' and G''. When Laun used the resulting discrete spectrum to recalculate the storage and loss moduli, he found that spurious oscillations were present. It is also possible using this technique to arrive at a parameter set that includes one or more negative values of G_i, which is obviously nonphysical. Of course, the number N of empirical constants fitted should not exceed the number of data points available. Furthermore, in this approach, one ends up modeling the scatter in the data along with the underlying "true" values of the moduli.

A more sophisticated approach to this curve fitting is that of Baumgaertel and Winter [6]. Using nonlinear regression, they developed an algorithm that converges to a "parsimonious" spectrum, *i.e.*, one having the fewest possible Maxwell modes consistent with the level of random error in the data. They do not smooth or filter the data. In other words, they are careful not to model the error. A commercial software package, IRIS [7], is based on their method. This technique yields the simplest possible fitting of the data but contains much less information than was in the data set and has very little if any relationship to the "true" relaxation spectrum.

The second approach to the problem of inferring a spectral function from dynamic data is directed at establishing as accurately as possible the spectrum that is a material property of the material under study rather than simply fitting experimental data. To accomplish this, it is necessary to overcome the ill-posedness of the problem by providing information in addition to the experimental data. A general approach to the problem of arriving at a spectrum that approximates a true material property is the use of regularization. Here the additional information introduced is the specification that the spectrum be a smooth function of time and an estimate of the error in the data. Honerkamp and Weese [8] accomplished this by assuming that the spectrum and its first and second derivatives are continuous and that the second derivative is small. To avoid modeling the noise (random error) in the data, they employ Tikhonov regularization. Provencher [9] has described an algorithm for treating data using this technique, and a commercial version of this code, CONTIN, is available [10]. Tikhonov regularization requires the selection of a value for the regularization parameter, and Honerkamp and Weese [11] have proposed a reliable method for doing this. They use regularization with linear regression to arrive at a spectrum that converges to a unique material function as the number of terms in the discrete spectrum, N,