Calculation of discrete retardation spectra from creep data
– I. Method

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Abstract: A new method is proposed for the calculation of discrete retardation spectra from creep and recovery data. The calculation of the spectrum is not restricted to a special region of consistency, e.g., the terminal region. In a retardation time window which has to correspond to the time window of the original data set a spectrum can always be calculated. A linear regression technique is applied to the measured data in the iterative calculation of a spectrum with a logarithmically equidistant spacing of retardation times. In this way the number of retardation times is limited and problems with ill-posedness are avoided. In order to obtain only positive retardation strengths it is necessary to shift the set of prescribed logarithmically equidistant retardation times on the logarithmic time scale. It can be shown that there is a retardation time interval for this shift, in which the retardation times may be varied without obtaining negative retardation strengths. While varying the retardation times in this interval the relative error of description of the data passes through a distinct minimum. In this way a spectrum is obtained which best describes the input data. Generally, one retardation time per decade will be sufficient to describe the data within the limits of experimental error. In the case of noisy data, the method is shown to work just as well and leads to a smoothing of the original data set. The method may be used for the conversion of creep and recovery data to storage and loss compliance. The error connected with this procedure is discussed.

Key words: Creep compliance – retardation spectrum – relaxation spectrum – linear viscoelastic theory

Introduction

When characterizing the mechanical properties of polymeric materials different measuring techniques are used. A torsional pendulum, for example, yields the complex shear modulus G^* as a function of angular frequency ω, while creep measurements in torsion yield the creep compliance J as a function of creep time t. All measurements apply to a well-defined excitation (stress or strain) which is a function of time. The observed response always combines the intrinsic material properties with the special characteristics of the excitation yielding the characteristic material response function for this case. When trying to characterize the viscoelastic material behavior in a very broad range of time or frequency, it is necessary to combine different measuring techniques yielding information in different time regimes. Thus the problem arises to convert viscoelastic response functions into each other. In this situation it is of common interest to know not only the material response on a special type of experiment, but to have a general function characterizing the material response independent of the method of excitation.

Restricting ourselves to the range of small stress, the relation between strain $\gamma(t)$ and stress $\sigma(t)$ can be described by a single constitutive equation which is based on the Boltzmann superposition principle (Boltzmann, 1874) using $J(t)$ as the only time dependent material function

$$\gamma(t) = \int_{-\infty}^{t} J(t-\xi)\dot{\sigma}(\xi)d\xi \, , \tag{1}$$

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where the dot indicates the derivative with respect to the argument. The integration is carried out over the history prior to the current time t. The evaluation of Eq. (1) yields for creep experiments ($\sigma = 0$ for $t<0$; $\sigma = \sigma_0$ for $t \geq 0$)

$$\gamma(t) = \sigma_0 \cdot J(t) \quad \text{for} \quad t \geq 0 , \tag{2}$$

and for experiments under prescribed harmonic stress ($\sigma = 0$ for $t<0$; $\sigma = \sigma_0 \cos \omega t$ for $t \geq 0$) in the steady state

$$\gamma(t) = \sigma_0 [J'(\omega) \cos (\omega t) + J''(\omega) \sin (\omega t)]$$
$$\text{for} \quad t \to \infty \tag{3}$$

involving the storage and loss compliance $J'(\omega)$ and $J''(\omega)$ respectively. The Boltzmann superposition principle allows a similar formulation for the conditions of prescribed strain involving the relaxation modulus $G(t)$:

$$\sigma(t) = \int_{-\infty}^{t} G(t-\xi)\dot{\gamma}(\xi)d\xi . \tag{4}$$

From the constitutive equations (1) and (4) it is possible to derive exact equations for the conversion of one measured viscoelastic function into any other measurable viscoelastic function, in shear. These equations are all integral transforms, which have to be evaluated over an infinite time or frequency regime extending from zero to infinity (Ferry, 1980). In practice the calculations often fail because of lack of information about the measured function to be transformed.

In order to overcome the above-mentioned problems, much work was done to establish easy to use approximation formulae to convert measured data from the frequency to the time domain and vice versa. If the method of conversion is sufficiently accurate and if the starting function is known with sufficient accuracy in a sufficiently wide time or frequency domain, the course of all material functions characterizing viscoelastic material behavior may be calculated from one experiment. For example, Schwarzl (Schwarzl, 1969, 1970, 1975) published a set of error-bound approximations for the interconversion of viscoelastic material functions, which are based on approximation of the kernel functions in the spectral representation of the mechanical properties, which will be mentioned in this paper.

The characteristic material functions which are independent of the method of excitation are the so called spectra. The relaxation and retardation spectra $g(\tau)$ and $j(\tau)$ are distribution functions for modulus

and compliance respectively. They express the contribution to the measurable response in stress relaxation or creep resulting from a relaxation or retardation time interval between τ and $\tau + d\tau$. It has to be noted that for reasons of physical interpretation all spectra have to have positive values only. The two spectra are interrelated; therefore it is sufficient to know one of them together with some viscoelastic constants. The spectra are related to the measurable response functions by Laplace, Stieltes or Fredholm integral equations of the first kind. From the relaxation spectrum the modulus functions $G(t)$, $G'(\omega)$ and $G''(\omega)$ may be calculated. The compliance functions $J(t)$, $J'(\omega)$ and $J''(\omega)$ are obtained from the retardation spectrum. Using spectra for the representation of the viscoelastic response functions has some advantages. First, a spectrum is a material function which is independent of the way of excitation. Second, knowing the spectrum, all other viscoelastic functions may be predicted. Third, many molecular theories yield distributions of relaxation times and strengths.

The advantages in using spectra are responsible for the broad interest in deriving approximations and algorithms for their calculation which can be found in literature. The difficulty with this task is that the determination of a spectrum has been recognized to constitute an illposed problem (Tanner, 1968; Friedrich and Hoffmann, 1983; Honerkamp, 1989). This means that for each set of experimental data a large number of different spectra can be found, each of them describing the data with the same accuracy. Therefore, the problem of calculating the spectrum from an experimentally obtained response function, does not seem to have a unique solution, but an (infinite) number of solutions, each of them fitting the original data equally well. There have been several attempts to overcome this difficulty. They all remove some degree of freedom from the system either by prescribing values for some of the parameters or by adding constraints to the calculation.

Most of the methods published in the 1950s and 1960s were set up to yield continuous spectra. Ferry and Williams (Ferry and Williams, 1952) proposed to assume the special form for the logarithmic spectra $H(\tau)$ and $L(\tau)$ in the shape of a wedge, containing some parameter values, which can be determined from the experimental response. This spectrum is modified in a second step by a correction term. Schwarzl and Staverman (Schwarzl and Staverman, 1952) published approximations for the course of the continuous logarithmic spectra using derivatives of the experimentally accessible functions. The approximations of Tschoegl (Tschoegl, 1971) and Yasuda

(Yasuda and Ninomiya, 1966) use finite differences of the measured functions to evaluate the information about the course of $L(\tau)$ or $H(\tau)$ respectively. These (and other approximations) are nicely reviewed in a book by Tschoegl (Tschoegl, 1989).

We will restrict ourselves to the problem of the calculation of a discrete retardation spectrum from creep curves.

Basic equations

The creep compliance $J(t)$ can be calculated from the non-negative retardation spectrum $j(\tau)$ by the equation

$$J(t) = J_0 + \int_{-\infty}^{\infty} L(\tau)\cdot[1 - e^{-t/\tau}]\,d\ln\tau + t/\eta_0 \ , \qquad (5)$$

where J_0 is the elastic compliance and η_0 the shear viscosity. In Eq. (5) $L(\tau) = \tau j(\tau)$ denotes the non-negative logarithmic retardation spectrum as a function of the retardation time τ. $L(\tau)$ is the contribution to the compliance from the retardation time interval between $\ln\tau$ and $\ln\tau + d\ln\tau$. If $L(\tau)$, J_0 and η_0 are known, the dynamic behavior under prescribed sinusoidal stress can be easily calculated

$$J'(\omega) = J_0 + \int_{-\infty}^{\infty} L(\tau)\cdot\frac{1}{1+\omega^2\tau^2}\,d\ln\tau \qquad (6)$$

$$J''(\omega) = \frac{1}{\omega\eta_0} + \int_{-\infty}^{\infty} L(\tau)\cdot\frac{\omega\tau}{1+\omega^2\tau^2}\,d\ln\tau \ . \qquad (7)$$

The experimental functions can be described with the same precision by a discrete retardation spectrum $\{J_k\,|\,\tau_k\}$, which is a set of $2N$ positive constants J_k and τ_k, by means of the equations

$$J(t) = J_0 + \sum_{k=1}^{N} J_k\cdot[1 - e^{-t/\tau_k}] + t/\eta_0 \qquad (8)$$

$$J'(\omega) = J_0 + \sum_{k=1}^{N} J_k\cdot\frac{1}{1+\omega^2\tau_k^2} \qquad (9)$$

$$J''(\omega) = \frac{1}{\omega\eta_0} + \sum_{k=1}^{N} J_k\cdot\frac{\omega\tau_k}{1+\omega^2\tau_k^2} \ . \qquad (10)$$

The equations involving the logarithmic relaxation spectrum $H(\tau) = \tau g(\tau)$ or the discrete relaxation spectrum $\{G_k\,|\,\bar\tau_k\}$ are quite similar. We only mention the equations for the stress relaxation modulus $G(t)$:

$$G(t) = G_\infty + \int_{-\infty}^{\infty} H(\tau)\cdot e^{-t/\tau}\,d\ln\tau \qquad (11)$$

$$G(t) = G_\infty + \sum_{k=1}^{\bar N} G_k\cdot e^{-t/\bar\tau_k} \ . \qquad (12)$$

G_∞ will be zero for a viscoelastic fluid having a finite viscosity $(1/\eta_0 \neq 0)$. For a viscoelastic solid the viscosity is infinite and G_∞ is a measure for the value of $G(t)$ in the limit $t\to\infty$. This value is connected to the network density in chemically or physically crosslinked networks.

Equations (5) – (7) and (11) are integral transforms (Tschoegl, 1989) and may be summarized by

$$Y_i(z) = \int_{-\infty}^{\infty} X_i(\tau)\cdot K_i(z,\tau)\,d\ln\tau + \sum_{n=-1}^{1} C_{i,n}\cdot z^n \ . \qquad (13)$$

In this relation Y_i is a measurable viscoelastic function (viz. J, J', J'', G, G', G'') which is a function of z (representing time t or angular frequency ω). $X_i(\tau)$ is the corresponding logarithmic spectrum and $K_i(z,\tau)$ is a characteristic kernel function. The additional constants $C_{i,n}$ depend on the excitation, too. Equation (13) can also be written using a discrete spectrum

$$Y_i(z) = \sum_{m=1}^{N} X_i(\tau_m)\cdot K_i(z,\tau_m) + \sum_{n=-1}^{1} C_{i,n}\cdot z^n \ . \qquad (14)$$

Here, $X_i(\tau_m)$ denotes the value of the discrete spectrum at the retardation or relaxation time τ_m.

For physical reasons not only the spectrum, but also all constants in the Eqs. (13) and (14) should be non-negative. Functions, kernels, and constants are specified in Table 1.

The calculation of a spectrum from a measured function Y_i is an inverse problem, which can be found frequently in rheology. Inverse problems may have different complexity. So the Volterra integral relating $G(t)$ and $J(t)$ may be solved easily while the integral transforms of the spectra are not easy to handle (Malkin, 1990).

Algorithm

Before describing the proposed algorithm, which was first published in short at the XIth International Conference on Rheology (Kaschta, 1992), we briefly discuss some methods to determine spectra, which

Table 1. Kernel functions, additional constants and time functions in Eqs. (13) and (14)

Viscoelastic function $Y_i(z)$	Kernel $K_i(z, \tau)$	$C_{i,-1}$	$C_{i,0}$	$C_{i,1}$
$J(t)$	$1 - \exp(-t/\tau)$	0	J_0	$1/\eta_0$
$J'(\omega)$	$1/(1 + \omega^2\tau^2)$	0	J_0	0
$J''(\omega)$	$\omega\tau/(1 + \omega^2\tau^2)$	$1/\eta_0$	0	0
$G(t)$	$\exp(-t/\tau)$	0	G_∞	0
$G'(\omega)$	$\omega^2\tau^2/(1 + \omega^2\tau^2)$	0	G_∞	0
$G''(\omega)$	$\omega\tau/(1 + \omega^2\tau^2)$	0	0	0

have been published in literature. The problem to be solved is the following: We have a set of M measured data points $f_1, f_2, \ldots, f_M$ of a function f (in this special case the creep compliance) at the observation points (here the creep times) $t_1, t_2, \ldots t_M$.

$$f(t_m) \equiv J(t_m) = J_0 + \sum_{k=1}^{N} J_k \cdot [1 - e^{-t_m/\tau_k}] + \frac{t_m}{\eta_0}$$

$$\text{for} \quad m = 1, 2, \ldots, M . \tag{15}$$

The theory supplies an explicit mathematical expression for the function f (Eq. (15)) containing $2N + 2$ parameters $a_0, a_1, \ldots, a_{2N+1}$, viz.

$$a_0 = J_0, \ a_1 = J_1, \ a_2 = J_2, \ \ldots, a_N = J_N$$

$$a_{N+1} = \tau_1, \ a_{N+2} = \tau_2, \ldots, a_{2N} = \tau_N, a_{2N+1} = 1/\eta_0 . \tag{16}$$

We are looking for mathematical or numerical tools to determine the unknown $2N + 2$ parameters, which fit the experimental response best. The number of parameters in Eq. (15) is $2N + 2$. The number of retardation times, N, is open to choice. In general, $2N + 2$ is chosen to be significantly smaller than the number of measuring points M.

Usually creep curves, plotted in a log-log plot, show a transition step attributable to the molecular process, which is to be described. If the experimental window is wide enough the transition will start with a horizontal plateau and end up with either another horizontal plateau (in the case of no flow) or with a straight line of slope unity (in the case of flow). Under this condition it will be possible to determine all parameters of Eq. (15) including a_0 and a_{2N+1}. In most cases, however, the complete information will not be available. If the first horizontal plateau is unknown, a_0 has to be set to zero before the evaluation of the other parameters can be started. If no region of slope unity is accessible, a_{2N+1} has to be set to zero.

In most cases the system defined by Eqs. (15) and (16) will be overdetermined. A measure for the quality of the description of the data by the set of the $2N + 2$ parameters has to be established. A measure which is often used is the mean square error F

$$F = \sum_{i=1}^{M} [f(t_i) - f_i]^2 . \tag{17}$$

F is considered to be a function of the parameters $a_0, a_1, \ldots, a_{2N+1}$ and has to be minimized with respect to these parameters. This is leading to the conditions $\partial F / \partial a_i = 0$ for $i = 0, 1, \ldots, 2N + 1$. If f is a linear function of the a_i's the evaluation of these conditions yield a set of linear equations, which can be solved using numerical techniques for matrix inversion. If f is non-linear, as in the case of Eq. (8), a non-linear regression technique has to be used.

Most methods proposed so far, linearize the problem by predetermining (prescribing) those parameters, which make the problem non-linear, viz. the parameters $a_{N+1}, a_{N+2}, \ldots, a_{2N}$. After this step, the remaining problem of determining $a_0, a_1, \ldots, a_N, a_{2N+1}$ is linear and may be easily solved; however, there is no guarantee that the obtained parameter values are positive. This has to be established by an appropriate procedure.

The first method published for this purpose was the collocation method. In this approach, the values of the parameters $a_{N+1}, a_{N+2}, \ldots, a_{2N}$ are predetermined and the number of the remaining parameters is chosen equal to the number of data points, viz. $N + 2 = M$ (or $N + 1 = M$, or $N = M$, depending on the accessibility of the beginning plateau and/or the flow region). Therefore, the system is no longer overdetermined and all data points used are exactly reproduced by the theoretical curve.

The observation points t_m are frequently chosen to be logarithmically equidistant. It was Schapery (Schapery, 1962), who chose the retardation times proportional to the position of the logarithmically equidistant observation times

$$\tau_k = a \cdot t_k = a \cdot t_1 \cdot c^{k-1} \quad \text{for} \quad k = 1, 2, \ldots, N , \tag{18}$$

a and c being constant. Now a set of N ($N + 1$ or $N + 2$) linear equations is obtained, which can be solved exactly. The main problem with the collocation method is that it only works successfully if the complete set of data is used for the collocation procedure and if the spacing of the collocation points is neither too large nor too close. If one of these conditions is

violated, negative retardation strengths are obtained. The result of the collocation method naturally depends on the choice of the number of data points, their location, and on the value of the proportionality factor a.

The so-called multidata method (Cost and Becker, 1970) uses all M data points $(M \gg N)$ available to determine the $N(N+1, N+2)$ parameters. The system is now overdetermined and the condition (17) is used to fit the $N(N+1, N+2)$ parameters. Apart from the possibility of the occurrence of negative retardation strengths, there is another serious error involved in this procedure, which is often overlooked. The course of the measured creep compliance of polymers generally shows a very large change with creep time (usually orders of magnitude). Therefore, the assumption underlying Eq. (17) viz. that the same experimental error is connected with small and large values of the compliance is not justified.

Baumgärtel and Winter (Baumgärtel and Winter, 1989) published a method to evaluate discrete relaxation spectra calculated simultaneously from $G'(\omega)$ and $G''(\omega)$-data, which also uses an iterative multidata method. Instead of condition (17) the relative error of both $G'(\omega)$ and $G''(\omega)$ is used. The algorithm starts with an empirical choice of the number of modes per decade between 1 and 2. The number of modes, which is normally too large, is reduced by the program by merging or eliminating unnecessary modes. One criterion for this process is the occurrence of negative relaxation strengths.

The group of Honerkamp (Elster et al. 1991, Elster and Honerkamp, 1991) proposed two different methods to overcome the ill-posedness of the problem. They start with prescribing logarithmically equidistant values for the retardation times. For minimizing the error, they use a condition for the relative error similar to the expression K to be given later in Eq. (25). In order to avoid the occurrence of negative retardation strengths, an additional term is added to the relative error condition. In the case of Tikhonov's regularization method (Elster et al., 1991), this is the regularization parameter times a function of the spectrum to be determined. In the case of the maximum entropy method (Elster and Honerkamp, 1991), the additional term is an expression similar to the definition of the entropy in statistical thermodynamics.

Emri and Tschoegl (Emri and Tschoegl, 1993) recently published an algorithm for the determination of discrete relaxation spectra from $G(t)$, which makes use of a special feature of the kernel function in the spectral representation of the viscoelastic response

function. They conclude that a mode located at τ only contributes significantly in a time interval between $0.34 * \tau$ and $1.67 * \tau$ to the response function because of the exponential decay of the kernel of $G(t)$. Therefore, they only use the data at observation times t_m in that surrounding of τ for the calculation of the relaxation strength corresponding to the relaxation time t.

The method proposed by one of us (Kaschta, 1991), is an iterative multidata method. We start with the assumption that the measuring times are logarithmically equidistant, viz.

$$t_i = t_1 \cdot c^{i-1} \quad \text{for} \quad i = 1, 2, \ldots M \ . \tag{19}$$

This corresponds to the selection of data points in our automatic creep technique, in which case c equals 2 (Kaschta 1991). The assumption (19) is not crucial for the success of the method. The algorithm will work equally well in the case of measuring times, which are distributed in an irregular manner on the logarithmic time axis.

The retardation times are prescribed as logarithmically equidistant, too, but with a wider spacing than the measuring times:

$$\tau_i = \tau_1 \cdot b^{i-1} \quad \text{for} \quad i = 1, 2, \ldots N \tag{20}$$

with $b > c$.

It is clear that the time window of the experimental data $[t_1, t_M]$ limits the time window in which the spectrum is determinable. Therefore, we expect

$$\tau_1 \geq t_1 \quad \text{and} \quad t_N \leq t_M \ . \tag{21}$$

However, contributions to the spectrum can only be found in those regions where neither J_0 nor η_0 carry the main information of the creep compliance. In those cases in which either J_0 or η_0 or both contribute significantly to the creep compliance, the time window of the retardation times $[\tau_1, \tau_N]$ might be significantly smaller than the time window for the measuring times.

In order to decide whether the terms J_0 and/or t/η_0 are to be considered in the description of an experimentally determined creep function the latter should be inspected in double logarithmic representation. Only if the experimental curve shows a significant horizontal regime at the short time tail of the experimental data does the term J_0 have to be included in the algorithm; its value will be determined automatically by the procedure described later. The

viscosity term has to be included only if the experimental curve significantly shows a straight region of double-logarithmic slope unity. The viscosity η_0 will then be determined automatically also.

After this decision, we start with a choice for the first retardation time τ_1

$$\tau_1 = a \cdot t_1 \ , \tag{22}$$

with a somewhat smaller but near to unity.

If J_0 does not contribute significantly to the data, the method proposed will automatically determine an optimum value for a (near to unity). If there is a significant contribution of J_0 to the data, but no viscous contribution, the proposed method will automatically shift a to larger values until an optimum value for a is obtained, which produces only positive values for the retardation strengths and minimizes the error. Further, the value of J_0 will result from the method. In this and the former case, however, one has to ensure that τ_N does not exceed t_M significantly. For this purpose the additional condition

$$N = \text{Integer} \left[\frac{\log\left(\tau_{max}/\tau_1\right)}{\log\left(b\right)} \right] \tag{23}$$

is used. τ_{max} is set equal to t_M. Condition (23) together with (20) limits the number of modes and problems with ill-posedness are avoided.

In the case in which t/η_0 contributes significantly to the data, τ_{max} will be smaller than t_M. An estimate for τ_{max} is obtained by determination of η_0 and inspection of the difference $J(t) - t/\eta_0$. If this difference is smaller than 10% of $J(t)$, the corresponding value of t is defined as τ_{max}. In this case it will not be possible to determine those contributions of the retardation spectrum to the creep compliance which are masked by the flow term (e.g., the modes of the entanglement transition).

Those contributions may be calculated if, instead of the creep compliance, the recoverable compliance $J_R(t)$

$$J_R(t) = J_0 + \sum_{k=1}^{N} J_k \cdot [1 - e^{-t/\tau_k}] \tag{24}$$

has been determined experimentally. In these cases the number of the longest retardation time might be further limited by the occurrence of negative values of the corresponding retardation strength. In the procedure the longest retardation time has to be skipped until only positive retardation strengths remain.

In our measurements, it is not the absolute experimental error, but the relative experimental error, which is approximately independent of creep time, respectively the order of magnitude of the compliance measured. We therefore use instead of Eq. (17) the following measure for the quality of the description of the data by the set of parameters:

$$K = \sum_{i=1}^{M} \left[\frac{f(t_i)}{f_i} - 1 \right]^2 \ . \tag{25}$$

Minimizing the sum of squares of relative errors K, with respect to the set of parameters to be determined $\{a_i\} = a_0, a_1, \ldots a_N, a_{2N+1}$, yields a set of linear equations for the calculation of those parameters.

In our method, after fixing the value of b, a starting value for a smaller than one is chosen and the set of parameters is calculated under the condition (23). Starting the algorithm, generally one or more of the parameters will be negative. Then a is substituted by a slightly larger value

$$a \rightarrow a \cdot (1 + \varepsilon) \ , \tag{26}$$

with small ε and the process is repeated, until all parameters become positive for the first time. Then the sum of squares of relative errors K is calculated. The substitution (26) is continued, which will yield another set of positive parameters with a different value for K. Continuing this process, a set of positive parameters $\{a_i\}_{opt}$ is found which minimizes the value of K. This set is used as the optimum description of the data.

The method is illustrated in Fig. 1, where the course of the sum of squares of relative errors, K, is shown as a function of the position of the first retardation time, τ_1, for the calculation of the spectrum from a synthetic creep curve (derived from a multi-box-spectrum defined later in Eq. (28)). Shown is the first window on the time axis for τ_1, which yields only positive retardation strengths. It extends from $1.8 \cdot 10^{-5}$ s to $2.04 \cdot 10^{-5}$ s. There is a distinct position for τ_1, which yields a minimum value for K.

There will exist another window for positive retardation strengths at higher τ_1-values, but the sum of squares K will be larger there.

Results and discussion

The application of this algorithm to experimental creep curves will be discussed in part two of this paper (Kaschta and Schwarzl, 1994). Here, we will test the
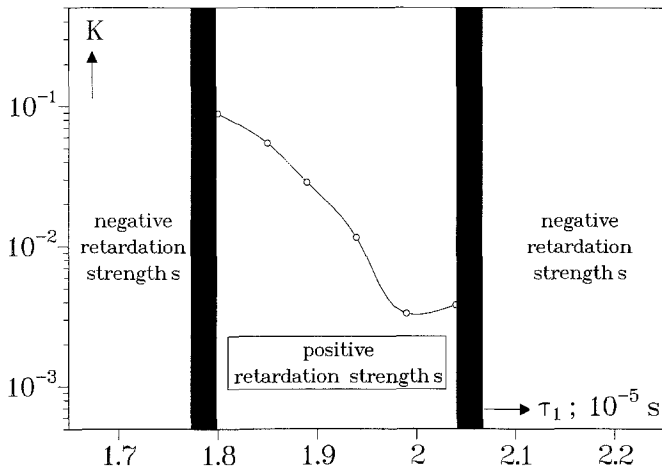
Fig. 1. Sum of squares of relative errors, K, for the calculation of the creep compliance from a set of logarithmically equidistant retardation times as a function of the shortest retardation time τ_1; regions of negative and positive retardation strengths are indicated

Fig. 2. Creep compliances as calculated from wedge and multi-box-spectra and recoverable compliance as calculated from wedge spectrum

algorithm on two continuous model spectra, which cover 10 decades of retardation time. The spectra and the additional parameters $J_0 = 10^{-9}\,\mathrm{Pa}^{-1}$ and $\eta_0 = 10^{12}\,\mathrm{Pas}$ have been chosen to describe approximately the master creep curves of amorphous uncrosslinked polymers in the glass-rubber transition region, followed by rubbery plateau and having a dominant viscous contribution at long creep times.

Two shapes for the logarithmic retardation spectrum were selected. The first consists of a wedge of constant slope one-half (Rouse-spectrum):

on the logarithmic time axis with $c = 2$ from 10^{-6} until 10^9 s. Only these points were used in order to recover the course of the underlying spectrum. Together with the creep compliances, the recoverable compliances $J_R(t)$ were calculated. The wedge spectrum shows a creep compliance with a single transition, a small rubbery plateau and the terminal region. The multi-box spectrum shows a creep compliance with three transitions, two of them being very close together.

Figure 3 shows the discrete spectra as calculated from the compliance by the proposed method with

$$L_w(\tau) = \begin{cases} 0 & \text{for } \tau < 10^{-4}\,\mathrm{s} \\ 10^{-8}\cdot\sqrt{\tau} & \text{for } 10^{-4}\,\mathrm{s} \le \tau < 10^6\,\mathrm{s} \\ 0 & \text{for } \tau \ge 10^6\,\mathrm{s}. \end{cases} \quad (27)$$

The other spectrum has a multi-box-shape:

$$L_{mb}(\tau) = \begin{cases} 0 & \text{for } \tau < 10^{-4}\,\mathrm{s} \\ 5\cdot 10^{-9} & \text{for } 10^{-4}\,\mathrm{s} \le \tau < 10^{-2}\,\mathrm{s} \\ 10^{-6} & \text{for } 10^{-2}\,\mathrm{s} \le \tau < 10^3\,\mathrm{s} \\ 10^{-5} & \text{for } 10^3\,\mathrm{s} \le \tau < 10^6\,\mathrm{s} \\ 0 & \text{for } \tau \ge 10^6\,\mathrm{s}. \end{cases} \quad (28)$$

$L(\tau)$ is calculated in Pa^{-1} for τ in seconds. The creep compliances calculated by numerical integration of these spectra are shown in Fig. 2. Points were calculated at discrete creep times spaced equidistantly
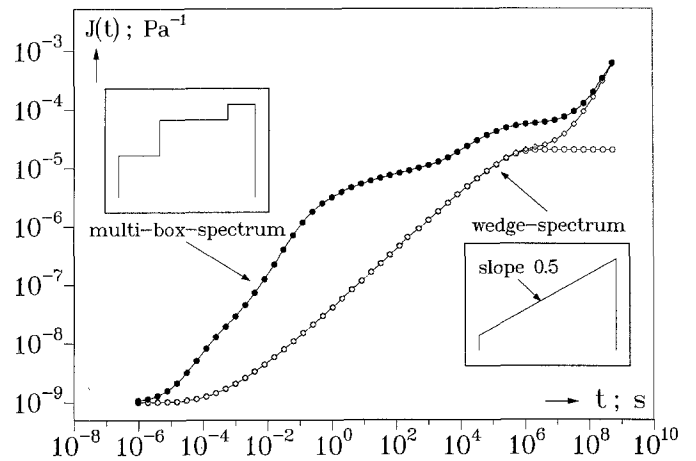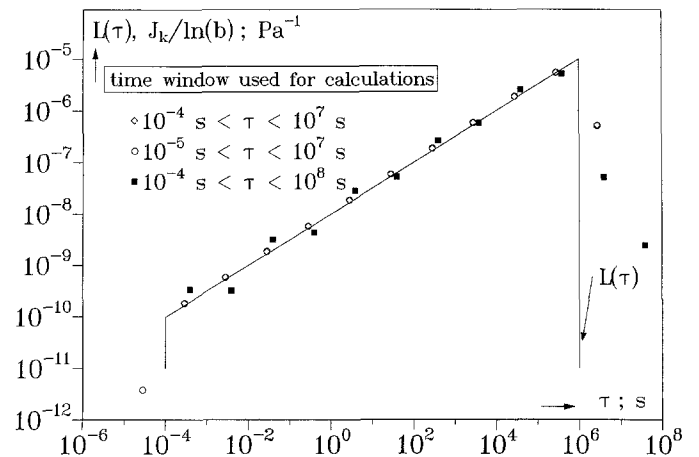
Fig. 3. Double-logarithmic plot of the normalized retardation strengths $J_k/\ln(b)$ vs retardation time calculated from the creep compliance data, derived from the wedge-spectrum, for fixed spacing ($b = 10$) and for three different retardation time windows

$b = 10$, together with the original wedge. To compare the values of the discrete spectrum with the continuous logarithmic input spectrum, the J_k values have been divided by the natural logarithm of the spacing b.

The figure shows the influence of the original time window, chosen for the calculation of retardation times. For all spectra calculated, the jump at the beginning and the drop at the end of the wedge are smeared out and cannot be recovered with the desired accuracy. It can be seen that one of the calculated spectra, viz. that with the window $[\tau_1, \tau_{max}] = [10^{-4}\,\text{s}, 10^8\,\text{s}]$ shows a significant waviness. This can be attributed to the calculation of modes located at retardation times more than one decade outside the long time boundary of the definition range of the input spectrum. The contribution of these modes has to be compensated by the others. On the other hand, if τ_{max} is chosen to be much too short (not shown in Fig. 3), we also find wavy behavior, because the last retardation strengths are forced to have too large values. Though the wavy spectrum shows only positive retardation strengths, it is connected with a relative large value for the sum of squares of the relative error, viz. $K = 2.27 \cdot 10^{-2}$.

If τ_{max} is chosen to be one decade smaller, the spectrum with the window $[10^{-4}\,\text{s}, 10^7\,\text{s}]$ describes the wedge very well, if the behavior at the edges is disregarded. It also yields a much smaller value for the sum of squares of relative errors, viz. $K = 1.36 \cdot 10^{-3}$. The description may be slighty improved if the starting value for τ_1 is chosen below the short time boundary of the definition range of the input spectrum. Therefore, the spectrum with the window $[10^{-5}\,\text{s}, 10^7\,\text{s}]$ describes the wedge equally well, with a slightly lower value for $K = 1.31 \cdot 10^{-3}$. Both non-wavy spectra coincide so well that they cannot be distinguished on the scale of Fig. 3 except for the first retardation strength.

Figure 4 shows the relative error of the creep compliances calculated from the spectra given in Fig. 3, when compared with the input data. It can be seen that waviness in the description of the spectrum is connected with a larger relative error in the reproduction of the original creep compliance. In the case of a wavy spectrum we find strong oscillations of the relative error on the order of 5% and more. For a non-wavy spectrum, we get relative errors in the order of 2% and less.

The influence of an additional viscous contribution on the calculation is shown in Table 2 for the wedge model creep compliance. The spectrum was calculated in two different ways. First, we have calculated the
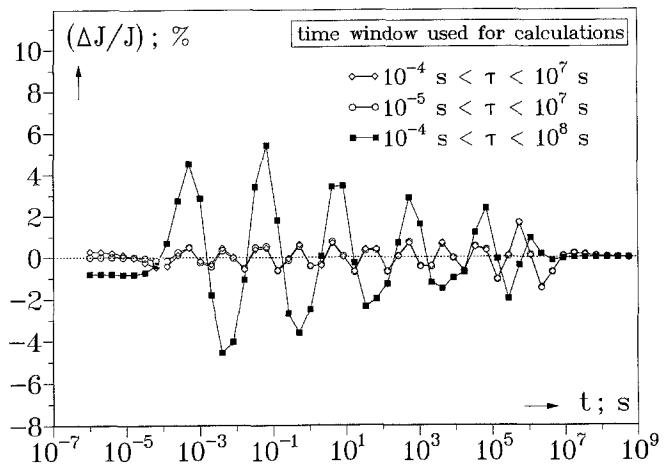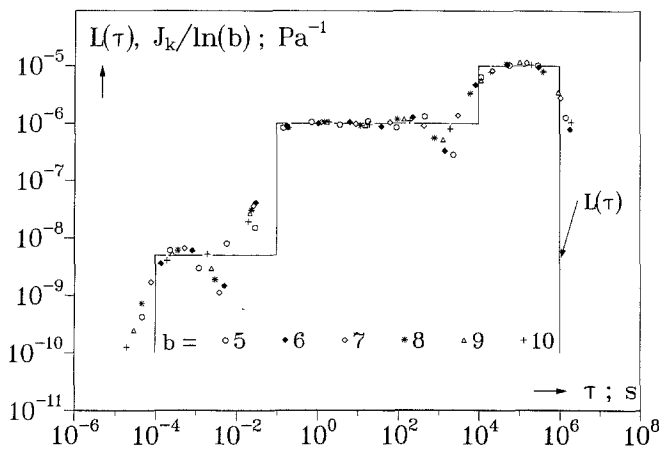

Fig. 4. Relative deviations between input compliance and compliances calculated from the spectra in Fig. 3

Table 2. Discrete wedge spectrum calculated from $J_R(t)$ and $J(t)$

From recoverable compliance		From creep compliance	
τ_k, s	J_k, Pa^{-1}	τ_k, s	J_k, Pa^{-1}
$2.81 \cdot 10^{-4}$	$4.27 \cdot 10^{-10}$	$2.77 \cdot 10^{-4}$	$4.16 \cdot 10^{-10}$
$2.81 \cdot 10^{-3}$	$1.36 \cdot 10^{-9}$	$2.77 \cdot 10^{-3}$	$1.38 \cdot 10^{-9}$
$2.81 \cdot 10^{-2}$	$4.31 \cdot 10^{-9}$	$2.77 \cdot 10^{-2}$	$4.21 \cdot 10^{-9}$
$2.81 \cdot 10^{-1}$	$1.37 \cdot 10^{-9}$	$2.77 \cdot 10^{-1}$	$1.37 \cdot 10^{-8}$
$2.81 \cdot 10^{0}$	$4.31 \cdot 10^{-8}$	$2.77 \cdot 10^{0}$	$4.23 \cdot 10^{-8}$
$2.81 \cdot 10^{1}$	$1.36 \cdot 10^{-7}$	$2.77 \cdot 10^{1}$	$1.36 \cdot 10^{-7}$
$2.81 \cdot 10^{2}$	$4.31 \cdot 10^{-7}$	$2.77 \cdot 10^{2}$	$4.25 \cdot 10^{-7}$
$2.81 \cdot 10^{3}$	$1.36 \cdot 10^{-6}$	$2.77 \cdot 10^{3}$	$1.36 \cdot 10^{-6}$
$2.81 \cdot 10^{4}$	$4.35 \cdot 10^{-6}$	$2.77 \cdot 10^{4}$	$4.29 \cdot 10^{-6}$
$2.81 \cdot 10^{5}$	$1.26 \cdot 10^{-5}$	$2.77 \cdot 10^{5}{}^{5}$	$1.26 \cdot 10^{-5}$
$2.81 \cdot 10^{6}$	$1.16 \cdot 10^{-6}$	$2.77 \cdot 10^{6}$	$1.27 \cdot 10^{-6}$
$J_0 = 9.9973 \cdot 10^{-10}\,\text{Pa}^{-1}$		$J_0 = 9.9997 \cdot 10^{-10}\,\text{Pa}^{-1}$	
$\eta_0 = $ not calculated		$\eta_0 = 1.0002 \cdot 10^{12}\,\text{Pas}$	

spectrum and the value for the instantaneous compliance J_0 from the recoverable compliance $J_R(t)$. Secondly, the spectrum, the steady-state viscosity η_0 and J_0 were calculated from the creep compliance $J(t)$. Both calculations have been performed for the same values of τ_1 and τ_{max} and with the same spacing $b = 10$.

As can be seen from Table 2, there is no significant difference between the calculated values for the spectrum lines except for the last line, where the intensities differ by about 10%. The instantaneous compliance is reproduced by up to three significant digits in both cases. When the spectrum is calculated from the creep compliance, the value for the viscosity is obtained with an accuracy of 0.1%.

If the calculated spectral intensities divided by $\ln(b)$ are compared with the values of $L(\tau)$ a difference of 10% is found, the discrete values being higher.

Figures 5 and 6 show the influence of the choice of the spacing varying from $b = 5$ to $b = 10$ on the calculated spectrum for the multi-box spectrum. In Fig. 5 the calculated spectra are given, while in Fig. 6 the relative error is plotted. Regions of constant value in the spectrum are reproduced quite well, especially when they extend over more decades in time. The jumps in the multi-box-spectrum are again badly

reproduced. The region which is influenced by this smear out effect is greater for higher logarithmic jumps in the original spectrum. A region of instability of the calculated spectrum is found just before the jump and this instability is more pronounced when the spacing of the retardation times is decreased. These instabilities make an interpretation of the calculated spectra more complicated and therefore we propose, that for describing measured creep compliances with discrete retardation spectra, it is sufficient to calculate only one line per decade.

As shown in Fig. 6 for selected spacings, an increase of the number of lines per decade results in a smaller relative error in the reproduction of the input creep compliance. It may occur that the value of K increases when decreasing the spacing, as it is shown for the spacing $b = 7$. This is due to the higher values of the relative errors in the short time region which are produced by a somewhat too small value of the initial compliance J_0. The amplitudes of the error at longer times for this spacing are smaller than the amplitudes for $b = 10$.

All calculations presented up to now have been performed with synthetic and therefore error-free data. We will now show how the method works with noisy data, like those which are extracted from the experiment. To test the algorithm with noisy data, we impose some random noise on the creep compliance calculated from the wedge spectrum. This was done by multiplying the exact values $f(t_k)$ with the factor $(1 + \delta \cdot rnd(k))$, where δ is a measure for the relative experimental error and $rnd(k)$ is a random number between -1 and 1.

Fig. 5. Double-logarithmic plot of the normalized retardation strengths $J_k/\ln(b)$ vs retardation time calculated from the creep compliance data, derived from the multi-box-spectrum, for different spacings of retardation times
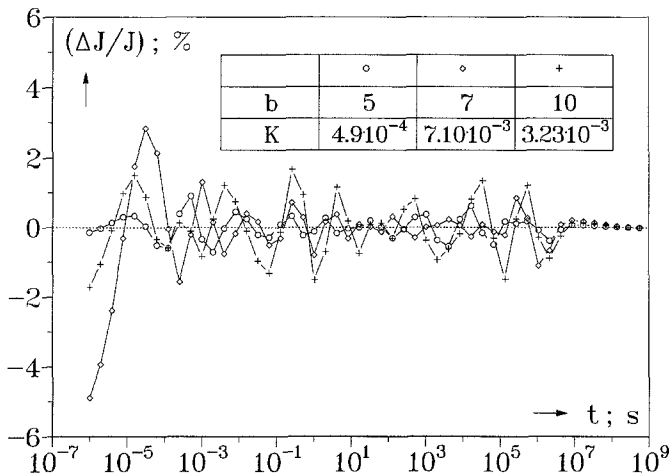

Fig. 6. Relative deviations between input compliance and compliances calculated from the spectra in Fig. 5 for selected values of b
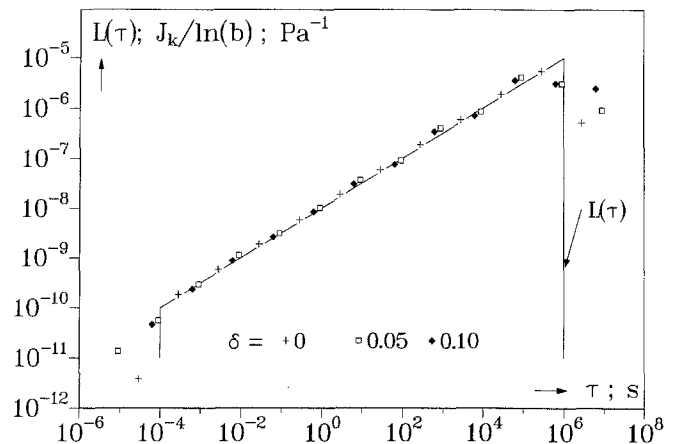

Fig. 7. Double-logarithmic plot of the normalized retardation strengths $J_k/\ln(b)$ vs retardation time as calculated from the noisy data for the creep compliance, for different values of δ
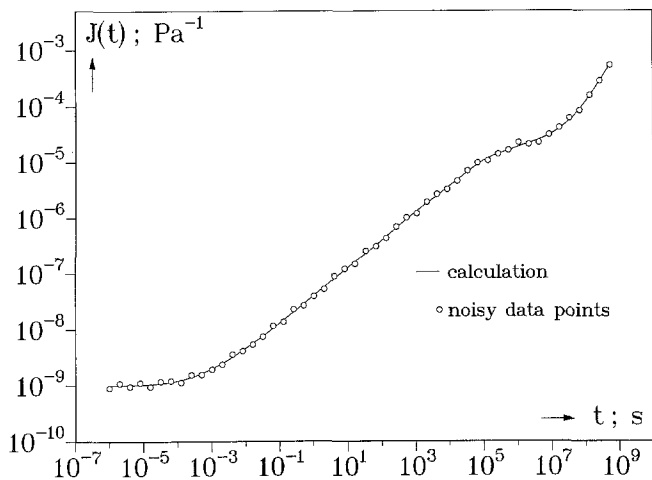
Fig. 8. Double-logarithmic plot of the data points of the creep compliance with 10% noise ($\delta = 0.1$), and the course of the creep compliance as calculated from the corresponding spectrum in Fig. 7

In Fig. 7 the resulting spectra from compliance data with $\delta = 0, 0.05, 0.1$ are compared. The superimposed noise results in a little higher waviness of the spectrum, especially in the long time region. The noise also influences the course of the spectra in the regions of the jump and of the drop.

In Fig. 8 we compare the creep compliance calculated from the spectrum derived from the 10% noise-data with the noisy input data for the creep compliance. The calculated line smoothes out the oscillations in the data points. The relative differences between the smooth recovered data and the noisy input data are shown in Fig. 9. The maximum relative deviation between smoothed and noisy input data is not larger than the amplitude of the noise we put in. This is also true for the viscosity, which was
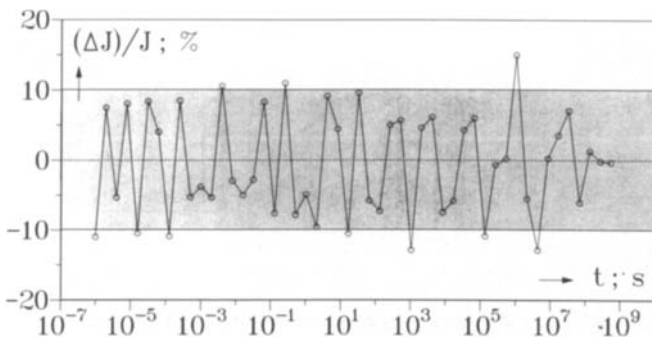

Fig. 9. Relative deviations between smooth compliance from spectrum and noisy input data

calculated to be $1.11 \cdot 10^{12}$ Pas (input value 10^{12} Pas). A value of $9.98 \cdot 10^{-10}$ Pa^{-1} was obtained for the glassy compliance (input value $J_0 = 10^{-9}$ Pa^{-1}).

After having derived the retardation spectrum from the creep compliance, it is possible to calculate storage and loss compliance by means of Eqs. (9) and (10). Therefore, the proposed method yields a way to convert measurable viscoelastic functions into each other.

This is illustrated in Fig. 10 for the creep compliance derived from the wedge distribution, where the original points for the creep compliance are plotted together with the storage and loss compliance and with the damping. The curves for $J'(\omega)$, $J''(\omega)$ (stipped curves) and tan δ (drawn line) were derived from the calculated retardation spectrum given in columns 3 and 4 of Table 2, not from the original given wedge. Of course if the method is used to convert measurable viscoelastic functions into each other, the window for the inverse circular frequency ($1/\omega$) of the calculated curves may not exceed the original window for the creep time, in which the data were given. Conversely, the window for the calculated functions has to be smaller, because of the truncation errors (unknown creep behavior outside the window).

A further check for the accuracy of calculated values for $J'(\omega)$ and $J''(\omega)$ may be obtained in the following way. One of us (Schwarzl, 1969) has derived numerical formulae for the direct conversion of creep compliance into storage and loss compliance, without the detour via the retardation spectrum. These formulae have the shape
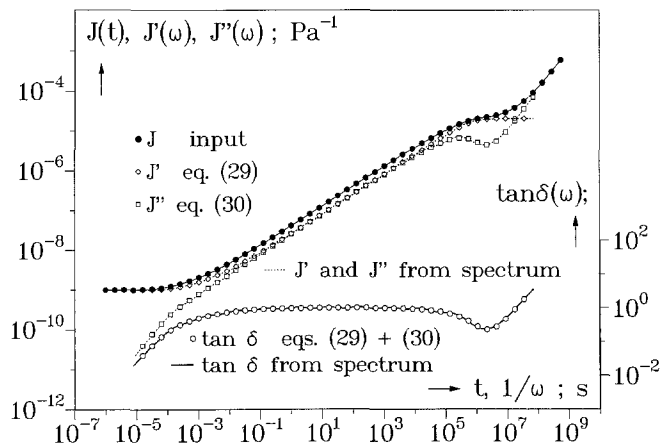

Fig. 10. Double-logarithmic plot of the creep compliance, storage and loss compliance calculated from the spectrum (cf. column 3 and 4 of Table 2 − lines −) and from approximation formulae Eqs. (29) and (30) (points) vs creep time t or vs reciprocal angular frequency

$$J'(\omega) = J(t) - a \cdot [J(32t) - J(16t)] - b \cdot [J(16t)$$
$$- J(8t)] - c \cdot [J(8t) - J(4t)] - d \cdot [J(4t)$$
$$- J(2t)] - e \cdot [J(2t - J(t)] - f \cdot [J(t)$$
$$- J(t/2)] - g \cdot [J(t/2) - J(t/4)] - h \cdot [J(t/4)$$
$$- J(t/8)] \quad \text{with} \quad \omega = 1/t \tag{29}$$

$$J''(\omega) = d \cdot [J(4t) - J(2t)] + e \cdot [J(2t) - J(t)]$$
$$+ f \cdot [J(t) - J(t/2)] + g \cdot [J(t/2) - J(t/4)]$$
$$+ h \cdot [J(t/4) - J(t/8)] + j \cdot [J(t/8) - J(t/16)]$$
$$+ k \cdot [J(t/16) - J(t/32)] + l \cdot (J(t/32) - J(t/64)]$$
$$+ n \cdot [J(t/64) - J(t/128)] + \ldots \quad \text{with} \quad \omega = 1/t ,$$
$$\tag{30}$$

where $a, b, \ldots n$ are numerical constants. These formulae were derived by approximating the kernel function in the spectral representation of storage and loss compliance (Eqs. (6, 7) using a linear combination of the kernel functions of the creep compliance $J(t)$ and of finite differences of the shape $J(2\alpha t) - J(\alpha t)$ with different values of $\alpha (\alpha > 0)$. As the expressions cited above are linear, each approximation for the kernel function will yield an approximation for the corresponding experimental function. The error in the approximation of the kernels may be calculated explicitly. As the logarithmic retardation spectrum $L(\tau)$ is assumed to be non-negative, the error in the approximated experimental function will be smaller or equal to the error in the approximation of the kernel. In this way error bounds for the approximation of the experimental functions are obtained. For approximations using a fixed number of difference terms the coefficients $a, b, \ldots, n$ have been determined to minimize the error bounds.

We used an approximation for $J'(\omega)$ with the coefficients $a = 0$, $b = 0$, $c = -0.099$, $d = 0.608$, $e = 0$, $f = 0.358$, $g = 0$, $h = 0$. This numerical conversion formula has bounds for the relative error between $\pm 7.5 \cdot \tan \delta \%$. The calculation was performed using the recoverable compliance $J_R(t)$ instead of $J(t)$. For the calculation of $J''(\omega)$ we used a formula with the coefficients $d = -0.505$, $e = 1.807$, $f = 0$, $g = 0.745$, $h = 0$, $j = 0.158$, all other constants in Eq. (30) are set to zero. This approximation has bounds for the relative error beetween $+ 1.1 \cdot [1 + 1/\tan \delta] \%$ and $- 1.3/\tan \delta \%$. This formula was applied to $J(t)$. The result of the direct numerical conversion is indicated by the open points in Fig. 10. Differences between

both methods of conversion do not show up on the given scale. The direct conversion shows the shortening of the window due to the truncation errors explicitely.

In the transition $J'(\omega)$ is smaller than $J(t)$. The shape of $J'(\omega)$ very much resembles the shape of $J(t)$, and the damping $\tan \delta$ shows a broad and flat maximum. This is due to the choice of the wedge distribution for the spectrum and does not correspond to the behavior of the characteristic functions found experimentally in the glass rubber transition of amorphous polymers. This will be shown later (Kaschta and Schwarzl, 1994).

To demonstrate the difference in the result of the conversion using both methods the relative error between the result of the exact calculation of $J'(\omega)$ from the wedge spectrum and the conversion based on the derived retardation spectrum is plotted vs. inverse angular frequency by open symbols in Fig. 11. The relative error is found to fluctuate with an amplitude of about 4%. The corresponding relative error using the error bound formula (29) is shown to be smaller, but to be biased (filled symbols in Fig. 11). It has to be noted that the calculated error for the approximation is within the bounds derived theoretically.

The same is shown for the conversion of $J(t)$ to $J''(\omega)$ in Fig. 12. Again, the relative error of the conversion based on the calculated spectrum fluctuates around zero with an amplitude of about 5%, except for two points at short frequencies. The relative error
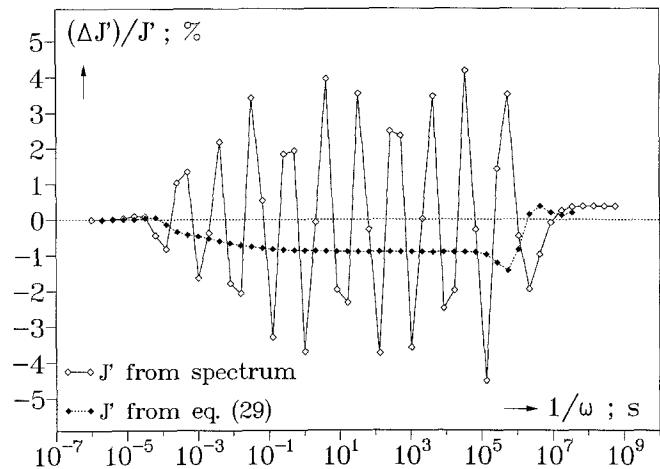

Fig. 11. Relative deviations between exact values for the storage compliance computed from the wedge spectrum and those calculated from a set of discrete retardation strengths (open symbols). Relative deviations between exact values for the storage compliance computed from the wedge spectrum and those calculated from an error bound numerical formula (29) (filled symbols)
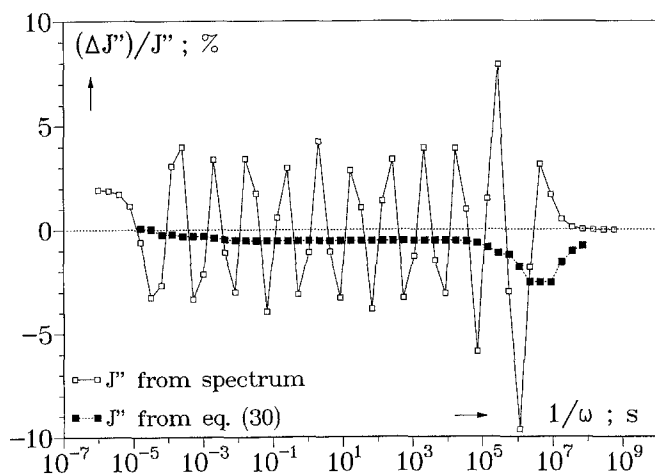
Fig. 12. Relative deviations between exact values for the loss compliance computed from the wedge spectrum and those calculated from a set of discrete retardation strengths (open symbols). Relative deviations between exact values for the loss compliance computed from the wedge spectrum and those calculated from an error bound numerical formula (30) (filled symbols)

of the conversion based on the error bound numerical formula (30) is smaller, but biased. The bump in the error at short frequencies can be attributed to the truncation error of the formula and again lies within the error bound. At these frequencies tan δ is rather low, which makes the error bound rather high.

Conclusions

Most methods (for example the IRIS program (Baumgärtel and Winter, 1989)) for the calculation of discrete spectra presented recently are used to analyze forced vibration experiments and thus yields relaxation spectra. We have presented an easy to use algorithm for the calculation of the retardation spectrum from creep and recovery data. The algorithm described always ends up with a set of positive retardation strengths having a logarithmically equidistant spacing of retardation times. The spectrum minimizes the relative error of description of the input data. About three logarithmically equidistant experimental points per decade (the logarithmic spacing of the measuring points is not essential for the success of the algorithm) are sufficient to calculate up to 1.5 spectrum lines per decade. This density of discrete lines is sufficient to describe the course of the spectrum $L(\tau)$ (Baumgärtel and Winter, 1992). For most applications it will be sufficient to calculate one spectrum line per decade. It was shown that even for this density of spectrum lines the input compliance is reproduced

well in all regions of consistency of polymeric materials.

From calculations with error-free data we found that the calculated spectrum nearly coincides with the course of the input spectrum, if the time window for the calculation is choosen correctly and if the input spectrum does not contain steep jumps or drops. Regions where the retardation spectrum is either constant or obeys a power law behavior are reproduced quite well. If the spectrum shows discontinuities, the algorithm is not able to recover the spectrum in the vicinity of these points. Regions of steep changes in the spectrum are smeared out and it was found that this effect is more severe when the logarithmic height of the jump is increased. Noisy data do not remarkably influence the performance of the algorithm. Quite to the contrary, it is possible to use the algorithm as a powerful smoothing tool, which supplies with the smoothing information about the course of the spectrum characterizing the material behavior.

The method can be used to convert creep data into storage and loss compliance. The error in this procedure is an approximation error which originates from the chosen finite number of spectral lines. The results for $J'(\omega)$ and for $J''(\omega)$ have been compared with those obtained by a different method which leads to a direct conversion of the creep function to the dynamic compliances without knowledge of the spectrum. The conversion using those error-bound numerical formulae leads to biased results. The errors in this procedure are truncation errors. They are within the limits derived for the corresponding formulae.

Both methods of conversion yield the same course for the dynamic compliances within the order of the experimental error. In our opinion this supports the quality of the spectrum determined from the creep data as well as the quality of the direct conversion.

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