SOME ASPECTS OF DISCRETE RELAXATION TIME SPECTRA AS OBTAINED FROM DYNAMIC MODULI DATA

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Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.

The problem of finding a relaxation time spectrum best fitting dynamic moduli data in the least-squares sense is shown to be well-posed and to yield a discrete spectrum, provided the data cannot be fitted exactly, i.e., without any deviation of data and calculated values. Properties of the resulting spectrum are discussed. Examples of discrete spectra obtained from simulated literature data and experimental literature data on polymers are given. The problem of smoothing discrete spectra when continuous ones are expected is discussed. A detailed study of an integral transform inversion under the non-negativity constraint is given in Appendix.

During last decades, relaxation phenomena have attracted an increasing interest in polymer chemistry and physics. To study the relaxation behaviour of polymers, mechanical properties have been used frequently. Among mechanical data, those of dynamic moduli seem most suitable for this study. To obtain a relaxation time spectrum $H(\tau)$ from dynamic moduli data, the following equations[1] should be solved

$$G'(\omega) = \int_0^\infty \frac{H(\tau)}{\tau} \frac{\omega^2\tau^2}{1+\omega^2\tau^2} \, \mathrm{d}\tau \qquad (1a)$$

$$G''(\omega) = \int_0^\infty \frac{H(\tau)}{\tau} \frac{\omega\tau}{1+\omega^2\tau^2} \, \mathrm{d}\tau \ , \qquad (1b)$$

where G' is the storage modulus, G'' the loss modulus, ω the experimental frequency, and τ the relaxation time. The solution $H(\tau)$ should be non-negative over the whole integration interval (the so called non-negativity constraint). Sometimes, a complex modulus G^* is introduced and Eqs (*1a*) and (*1b*) then read

$$G^*(\omega) = G'(\omega) + \mathrm{i}G''(\omega) = \mathrm{i}\omega \int_0^\infty \frac{H(\tau)}{1 + \mathrm{i}\omega\tau}\, \mathrm{d}\tau \ , \qquad (2)$$

where i is the imaginary unit. The integral kernel in Eq. (*1a*) is Lorentz function in the variable $1/\omega$ (and also in $1/\tau$) and the kernel in Eq. (*1b*) is the dispersion component of Lorentz function. Therefore, I call either of the integral transformations (*1*) and (*2*) Lorentz transformation.

Gross[2] gave a simple form of solutions $H(\tau)$ of Eqs (*1*) when either the storage modulus $G'(\omega)$ or the loss modulus $G''(\omega)$ is given by a function of ω, analytical in terms of the theory of the functions of the complex variable. However, serious difficulties are met in using his result: the experimental G' and G'' values are available in a tabular form and their conversion to empirical functions may lead to negative values and/or an improper marginal behaviour of $H(\tau)$.

The standard method of treating experimental data is the least-squares method. However, solving Eqs (*1*) involves an integral transform inversion which is known to be ill-posed (ill-conditioned). Tikhonov[3] developed a regularization method to treat this difficulty and his method was used for analysis of dynamic moduli data[4,5]. An elaborated computer program for such an analysis named CONTIN was developed by Provencher[6,7] and has been widely used in analyses of dynamic light scattering (DLS) data. A more thorough testing of CONTIN program as used to the Laplace transform inversion[8] showed it to be sensitive to a proper choice of the regularizor. Moreover, it turned out that singularities (δ-functions, i.e., discrete modes, or edges of histogram bins) disturbed the result, producing splitting of wide bands, and that CONTIN had a pronounced tendency to replace asymmetric smooth bands by symmetric ones with shoulders or side bands on the slower decrease side.

Baumgaertel and Winter[9] sought a relaxation time spectrum in the discrete form

$$G'(\omega_i) = \sum_{j=1}^{r} g_j \frac{\omega_i^2 \tau_j^2}{1 + \omega_i^2 \tau_j^2} \qquad (3a)$$

$$G''(\omega_i) = \sum_{j=1}^{r} g_j \frac{\omega_i \tau_j}{1 + \omega_i^2 \tau_j^2} \qquad (3b)$$

using a small number r of distinct relaxation modes τ_j with positive relaxation strengths g_j as a compromise between a good fit of data and an ill-posedness. The problem of a discrete representation of an inverted integral transform under the non-negativity constraint was studied extensively in a related problem of Laplace transform. It was shown[10,11] that there exists a best least-squares solution with a finite number of modes, which is unique when it does not fit the transform data exactly (i.e., without any devi-

ation of data and calculated values). I will call this solution a complete discrete spectrum (CDS). This solution was shown to be better in the least-squares sense than any continuous solution and any mixed discrete-continuous solution[12]. Later on, the result that the least-squares solution to an integral transform inversion is of a discrete form with a finite number of modes, unless data are fitted exactly, was generalized for a wide class of integral kernels to which Lorentz kernel of Eqs (*1*) belongs (see Appendix in ref.[13]); this class is further extended in the present paper (see Appendix, Theorem 5). CDSs for simulated, with a noise added, Laplace transforms of model continuous relaxation spectra[12] showed relaxation modes more or less regularly spaced and their envelopes in a rough agreement with the model spectra. Spacing was usually about a half decade and the actual positions of the modes depended on the actual form of the noise added. This is in line with the finding[14] that some of experimental data pursued in ref.[9] are compatible with continuous relaxation time spectra as well. It may be sometimes difficult to decide whether two or three close discrete modes are necessarily individuals or their envelope may represent a continuous spectrum compatible with the data as well.

The subject of this paper is to discuss some aspects of discrete relaxation time spectra in more detail, including the posedness of the problem of finding the best least-squares spectrum, and to show examples of these spectra obtained from literature dynamic moduli data[5,15]. Since the problem of inverting an integral transform under the non-negativity constraint is frequently met in polymer chemistry and physics, its detailed treatment is given in Appendix.

THEORETICAL

In Appendix, an exact representation of a set of n pairs of dynamic moduli data at distinct frequencies ω_i ($2n$ items total) by a discrete spectrum, (*3a*) and (*3b*), of r modes with distinct relaxation times τ_j and positive amplitudes g_j, when the feasible τ set is a single closed interval, is shown to be unique if and only if $r + s < 2n$, where s is the number of τ_j's inside the feasible τ interval. Further, it is shown that the least-squares solution of a discrete spectrum (CDS) for a data set not representable exactly is unique with $r + s < 2n$ and that the problem of its finding is well-posed from a mathematical point of view (according to ref.[3], p. 16). A bit more complicated result is obtained when the feasible τ set consists of several closed intervals and/or contains isolated τ point(s) (see Appendix, Theorem 4). The mathematical well-posedness established seems optimistic; however, when the actual relaxation time spectrum is continuous, uncertainties in peak positions produced by data errors are comparable to peak spacing. Then, the fact that the τ_j positions are adjusted is not essential and their values are of no use for a practician. In the Laplace transform inversion, a grid equidistant in log τ was used instead by Pike and Ostrowsky[16]; a subjective choice of the grid origin was avoided by shifting the grid by a fraction of the spacing interval several times and taking the average of the results obtained. A proper selection of grid spacing is critical: if too dense,

an artifact structure may be obtained in the result, if not dense enough, the data fit may be bad. Spacing comparable to that in CDS can be recommended. However, when an isolated very narrow band or a discrete mode appears in the actual spectrum together with a broad band in another τ region, it may happen that no suitable spacing exists: either the very narrow band gets too broad or the broad band acquires an artifact structure. The adjusted τ_j positions are of practical use when the actual spectrum is discrete with spacing less dense than spacing typical of CDS of continuous distribution data with the noise level equal to that in the actual data. Even in this case, a spectrum consisting of narrow continuous bands, spread over the estimated uncertainties of the τ_j positions, may be compatible with the actual data as well.

A serious consequence of the well-posedness of a problem is that a stable algorithm for solving it exists. My long-time experience with obtaining CDS in the Laplace transform inversion showed that the double precision (16 significant digits) was sufficient in all cases with a single practically irrelevant exception[12] of data simulated with the noise level of 10^{-6}. The fact that stability worsens when approaching data which can be fitted exactly is not surprising since the region of ill-posedness is approached at that. Another convergence worsening was observed when accidental close doublets in CDS were found.

CDS is suitable for testing the consistency of data since no spectrum with a better agreement with the data (in the least-squares sense) exists. When CDS residuals (the deviations from data values) are nonrandom, it follows that either the data are subject to some systematic errors or the experiment follows Eqs (*1*) (e.g., due to a nonlinearity of the viscoelastic behaviour) with the only accuracy comparable to the systematic deviations revealed. In both cases the statistical tests discussed below may become unreliable.

CDS is also suitable as a reference in considering whether another relaxation time spectrum (e.g. a continuous spectrum) is still compatible with data. CONTIN uses the Fisher test for this purpose and calls it Probability 1 to Reject[6]. This test works well in many cases; however, being global, sometimes it allows deviations in a τ region greater than statistically acceptable on account of lower deviations in other τ regions. An alternative, Probability 2 to Reject[6], justifies a full compatibility with data, but usually leaves much of the result unsmoothed. In using CDS as a reference, two degrees of freedom should be counted for every mode with a freely adjustable τ_j and one degree for that with a τ_j fixed in the boundary of the feasible τ set (e.g. at zero or infinity). In the Fisher test, the discrete spectrum with lowest standard deviation may be more suitable for a reference than CDS, since the standard deviation, serious for this test, seems better estimated with the former spectrum than with CDS. However, no such simple method of recognizing the former spectrum seems to exist as exists[10] for CDS. The former spectrum may contain one or a few modes less than CDS (especially when CDS contains a mode with a very low relaxation strength or a doublet of close relaxation

modes) and/or may differ from CDS by fixing a relaxation time τ_j at a close τ in the boundary of the feasible τ set (e.g. zero or infinity). When the Fisher test seems insufficient, an inspection of residuals may be used. A way of quantifying such an approach is to smooth data to some "best" values representable by Eqs (*3*) and on statistical grounds to estimate limits in which each of the "best" values may vary. The maximum of the ratio of the deviation of the calculated value from the "best" value to the allowed variation from the "best" value is a measure of the compatibility of a spectrum with data; when it does not exceed unity, the spectrum is surely compatible with data provided the above limits (spanning the so called confidence intervals[17]) are estimated correctly. I will call such an approach an IR test and the above measure of the compatibility an IR (inconfidence ratio) value.

In using CDS or another good discrete representation of a continuous spectrum to calculate further properties, correct results may be expected only when this calculation spreads the spectrum at least as much as Lorentz transformation does. Hence, relaxation modulus[9] $G(t)$, creep compliance[9] $J(t)$, and dynamic compliances $J'(\omega)$ and $J''(\omega)$ obtained in this way may be expected to be correct within the level of experimental errors in the dynamic moduli $G'(\omega)$ and $G''(\omega)$, whereas retardation spectrum[9] $L(\tau)$ obtained in this way may be continuous as well. An example of a similar approach in correcting GPC chromatograms for longitudinal spreading may be found in ref.[18].

For finding discrete relaxation time spectra with a given number of modes best in the least-squares sense, including CDS, I wrote a computer program similar to that previously described[12]. CDS may have some relaxation modes out of the region of data, i.e., with relaxation times τ_j much below $1/\omega_{max}$ and/or much above $1/\omega_{min}$, where ω_{min} and ω_{max} are the minimum and maximum data frequencies, respectively. The relaxation strength g_j of such a long relaxation mode represents the cumulative relaxation strength (i.e. $\int H(\tau)\tau^{-1}\,d\tau$) of all long modes including the static mode strength, if any; these modes cannot be resolved due to the lack of data in this region. Whether the numerical method tends to shift long modes to the static mode or vice versa depends on data errors in $G''(\omega)$ for lowest ω's. Such a short relaxation mode behaves similarly with the difference that the product $g_j\tau_j$ of its relaxation strength and relaxation time now represents the cumulative value of this product (i.e. $\int H(\tau)\,d\tau$) for all short modes and a tendency to shift these modes to zero relaxation time depends on data errors in $G'(\omega)$ for largest ω's. The zero relaxation time is unacceptable on physical grounds. However, when τ_j of a mode converges to zero, I keep it, since a restriction to a minimum τ is always ambiguous and anyway such a mode does not represent an actual relaxation time, but only the cumulative $g_j\tau_j$ value.

RESULTS AND DISCUSSION

For data simulated by Honerkamp and Weese[5], CDS, identical to the discrete spectrum with lowest standard deviation, is shown in Fig. 1 together with the model spectrum.

An agreement of the envelope of the CDS peaks with the model spectrum is apparent. The very weak mode at $\tau = 165$ represents the weak margin of the model spectrum just below $\tau = 100$. For its suppressing, the number of modes should be lowered to as little as four with a standard deviation increase greater than 20%, far beyond the limit statistically allowed. The sensitivity of the Lorentz transform inversion in the long-time region is governed by the data accuracy in the low ω region, in which both G' and G'' are

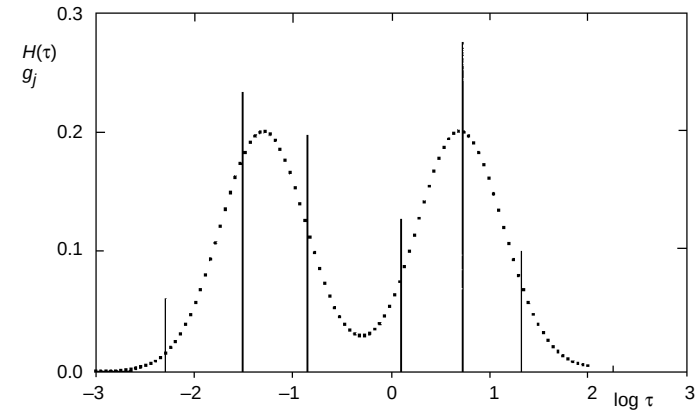

FIG. 1
The relaxation time spectrum obtained by the least-squares method (the complete discrete spectrum – CDS) from simulated data[5]. ■ Model distribution; vertical lines: CDS

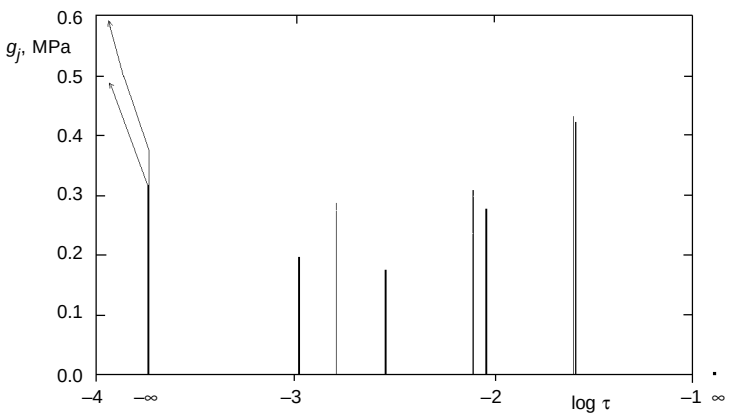

FIG. 2
Discrete relaxation time (τ in s) spectra calculated from dynamic moduli data of a polybutadiene melt[5]. Thick vertical lines: CDS; thin vertical lines: the discrete spectrum with lowest standard deviation. (The modes the relaxation times of which converged to zero are shown at τ equal to one-fifth of the reciprocal highest experimental frequency and with an arrow attached to indicate that τ converged to zero.)

small. When data are of a comparable relative accuracy in G^* as usual, they allow resolving weak modes in the long-time region. When in another region of the spectrum such a weak mode occasionally appears, it is absorbed by adjacent modes when switching to the discrete spectrum with lowest standard deviation, which is caused by large G' values at not low ω.

CDS (heavy lines) and the discrete spectrum with lowest standard deviation (weak lines – one mode less) obtained from experimental data of a polybutadiene melt[5] are shown in Fig. 2. A very weak static mode (349 and 363 Pa) is present in both discrete spectra; its suppression again increases the standard deviation by almost 20%. This mode is well separated from the other part of the spectrum since $1/\omega_{min}$ is about 0.4 s. It is not necessarily quite static; however, its relaxation time certainly exceeds a few seconds. Zero relaxation time modes are shown at $\tau_0 = 0.2/\omega_{max}$; the $\tau \to 0$ limits of the τg product divided by τ_0 are shown on the ordinate and attached weak lines with arrows show the ratio increase when τ_0 is further lowered.

CDS and discrete spectra with lowest standard deviation for smoothed data of six molten polystyrene samples[15] are shown in Fig. 3. Again, a resolution of weak modes at the long-time margin of spectra is observed with no such effect in other regions. To study the effect of a data truncation, unmodified data[15] for polystyrene sample 5 for individual experimental temperatures with appropriate shift factors and their collection are used in Fig. 4. The fact that the mode at largest τ represents the collective strength of all long-time modes beyond the data region is traced.

Since interpretation of CDS or of the discrete spectrum with lowest standard deviation may sometimes be difficult, let me discuss some alternatives to this. Concerning Tikhonov regularization[3], serious artifact structures revealed sometimes in the Laplace transform inversion[8,19] are expected to persist in the Lorentz case, since Lorentz transform may be obtained by Fourier transformation of Laplace transform and through Fourier transformation, which is orthogonal, no information is lost. For example, one has to suspect that the side band at 0.001 s in Fig. 2*a* of ref.[5] is artifact due to the regularization method and an $H(\tau)$ similar to the power law one ($H(\tau) = a\tau^b$ for $\tau \le \tau_0$ and $H(\tau) = 0$ elsewhere) may be compatible with the experimental data as well; discrete spectra say nothing about this problem. Hence, a regularization method does not seem best for improving discrete spectra. However, as stated by Provencher[19], "at least as a stopgap measure it can still be useful". From methods not assuming a particular form of the spectrum, the peak-constraining method[13,19] (i.e., that restricting the number of maxima in the spectrum to a small number) seems most promising. It is able to resolve the above ambiguity in the interpretation of the spectrum[5] of the polybutadiene melt. A spectrum consisting of one band having a single maximum and of a very weak static mode is fully compatible[20] with the experimental data[5] (the IR value of 0.71). Suppressing the static mode yields[20] only a slight incompatibility at lowest ω (IR of 2.17), which may also be assigned to systematic errors in the experimental data or to a nonlinearity

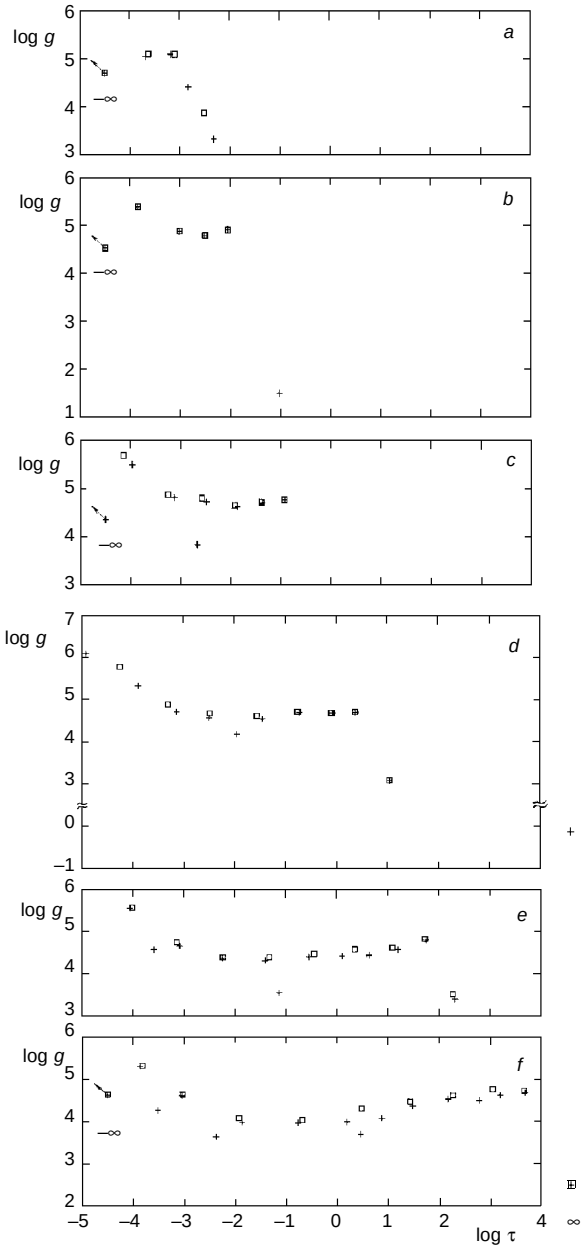

FIG. 3

Discrete relaxation time spectra (τ in s, *g* in Pa) calculated from dynamic moduli data of polystyrene melts, the smoothed set[15]. + CDS; ❒ the discrete spectrum with lowest standard deviation. (For additional explanation, see Fig. 2.) Polystyrene sample numbers in ref.[15]: *a* 1, *b* 2, *c* 3, *d* 4, *e* 5, *f* 6

of the viscoelastic behaviour. The side band[5] at 0.001 s is unnecessary for a compatibility with the experiment anyway[20]. This method was shown to yield unattractive[13] or unaesthetic[19] histogram bin edges; however, it may serve[13] as a good tool for an estimate of a particular form of the spectrum with some parameters being refined later.

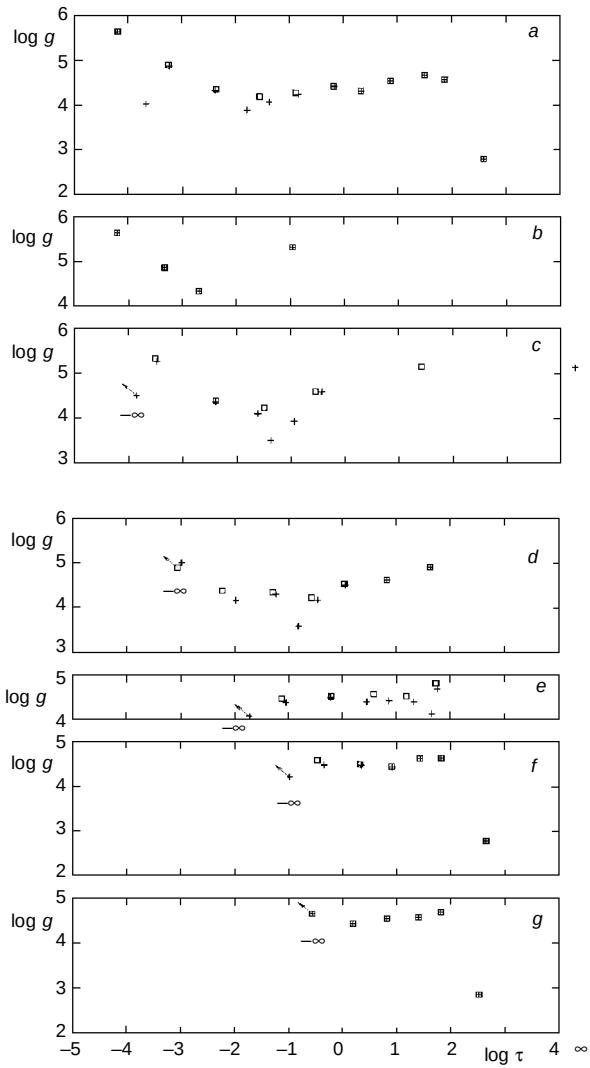

FIG. 4

Discrete relaxation time spectra (τ in s, *g* in Pa) calculated from dynamic moduli data of polystyrene sample 5, the unmodified set[15], with appropriate shift factors. + CDS; ❒ the discrete spectrum with lowest standard deviation. (For additional explanation, see Fig. 2.) *a* A collection of all experimental temperatures, *b* T = 150 °C, *c* T = 160 °C, *d* T = 180 °C, *e* T = 200 °C, *f* T = 220 °C, *g* T = 240 °C

A power law form is frequently used in analyzing dynamic moduli data (see e.g.[14]). The generalized exponential (GEX) distribution[21]

$$H(\tau) = |\, s \,| \, (\tau/\tau_0)^u \exp\left(-(\tau/\tau_0)^s\right)/\Gamma(u/s) \qquad (4)$$

is more flexible than that power law, since its position, width, and asymmetry may vary independently. It seems universal for unimodal structureless distributions[22] and as such most suitable for a description of relaxation spectra; a superposition of two or a few GEX functions may be used when one is insufficient. The GEX distribution was used in estimating the polydispersity index of narrow molecular-weight distributions from DLS data[23]. The power law form is a limiting case of GEX with the parameter *s* going to plus or minus infinity. Owing to its flexibility, GEX with a large *s* value can be expected to fix broadening of the power-law-form edge in the rubber-like region due to a polydispersity discussed in refs[24,14].

CONCLUSIONS

The problem of finding a relaxation time spectrum from dynamic moduli data by the least-squares method is well-posed and yields a discrete spectrum, provided that the data cannot be fitted exactly (i.e. without any deviation of data and calculated values) by any spectrum. When an actual spectrum is continuous, the envelope of the result roughly agrees with it, even though difficulties in interpreting results are often encountered. The result is suitable for considering the consistency of data and compatibility of another spectrum with the data. As an improvement to this approach, methods restricting the number of maxima in the spectrum or using a particular form of the spectrum with parameters adjusted should be preferred to penalizing methods, since the latter suffer from serious drawbacks.

APPENDIX

We deal with the integral equation

$$f(\omega) = \int_0^\infty K(\omega,\tau) g(\tau)\, \mathrm{d}\tau \qquad (A1)$$

for a non-negative function $g(\tau)$ when at n distinct ω_i values data values $f_i = f(\omega_i)$ are given. Setting $K_i(\tau) = K(\omega_i,\tau)$, we have

$$f_i = \int_0^\infty K_i(\tau) g(\tau)\, \mathrm{d}\tau \ , \quad i = 1, 2, \ldots, n \ . \qquad (A2)$$

We consider the feasible set, i.e., the set of all $\boldsymbol{F} \equiv (f_1, f_2, \ldots, f_n)$ vectors which may be represented by Eq. (*A2*). This set was considered[25] when $K_i(\tau)$ functions formed a T-system[25], i.e., on the interval $[0,\infty]$ were continuous and on any set of n distinct points from this interval were linearly independent. However, systems without T-property occasionally appear in practice (e.g., one datum of the storage modulus at ω_1 and one datum of the loss modulus at $\omega_2 < \omega_1/3$). Hence, a consideration of a more general case is desirable.

Let us start from a very general case assuming only that the integrals in Eq. (*A2*) exist in Lebesgue sense and are finite. When $K_i(\tau)$ functions are linearly dependent (save for a τ set of zero measure), one f_i may be calculated from the others and we may consider a problem with $n - 1$ values f_i. The feasible set is convex since with any $\boldsymbol{F}_1$ and $\boldsymbol{F}_2$ within the set and with $0 < \lambda < 1$ also $\lambda\boldsymbol{F}_1 + (1 - \lambda)\boldsymbol{F}_2$ is within the set. If the boundary of the feasible set contains a nonzero $\boldsymbol{F}_0$ and also $-\boldsymbol{F}_0$, then, due to the convexity, with every interior $\boldsymbol{F}$ and any λ also $\boldsymbol{F} + \lambda\boldsymbol{F}_0$ is interior and one of the f_i components may be omitted in considering whether a vector is interior. If not, a linear transformation bringing components of any feasible vector to non-negative values exists. The non-negativity of transformed $K_i(\tau)$ functions follows. We normalize the transformed $K_i(\tau)$ functions to the unity i-sum when the sum is nonzero and replace $g(\tau)$ by $g(\tau)\sum_{i=1}^{n} K_i(\tau)$. Integrals in Eq. (*A2*) exist if and only if the replaced $g(\tau)$ function is Lebesgue-integrable with a finite integral.

For considering the feasible set further, we assume that $K_i(\tau)$ are non-negative, linearly independent, and with an i-sum normalized to unity when the sum is nonzero (in fact, it is sufficient to assume that $K_i(\tau)$ are linearly independent and $\sum_{i=1}^{n} |K_i(\tau)|$, when nonzero, is positively downbound and upbound); $g(\tau)$ is assumed to be Lebesgue-integrable with a finite integral. According to the previous paragraph, no loss of generality yields.

Theorem 1. When no τ interval of a nonzero length exists on which, exempt a τ set of zero measure, $\sum_{i=1}^{n} K_i(\tau) > 0$ and $K_i(\tau)$ are linearly dependent (which is met, e.g., when $K_i(\tau)$, in addition to the overall linear independence, are analytical in terms of the theory of the functions of the complex variable), the feasible set is zero vector plus the interior of the set representable by

$$f_i = \sum_{j=1}^{r} u_{ij} g_j \ , \qquad i = 1, 2, \ldots, n \ , \tag{A3}$$

where g_j are positive, $\boldsymbol{U}_j \equiv (u_{ij}, u_{2j}, \ldots, u_{nj})$ nonzero, r finite, and in every neighbourhood of each of the $\boldsymbol{U}_j$ vectors, vectors $\{K_i(\tau)\} \equiv (K_1(\tau), K_2(\tau), \ldots, K_n(\tau))_1$ for a τ set of a nonzero measure exist. When such an interval exists, some of nonzero vectors in the boundary of the set representable by Eq. (*A3*) may also be feasible.

When $g(\tau) = 0$ holds outside the τ set for which $\{K_i(\tau)\}$ is within a neighbourhood small enough of a $\boldsymbol{U}_j$ and when $\int g(\tau)\,\mathrm{d}\tau = 1$, Eq. (*A2*) represents a vector arbitrarily close to $\boldsymbol{U}_j$. The set of $\{K_i(\tau)\}$ vectors (save for a τ set of zero measure) may be covered by a finite set of disjoint subsets of neighbourhoods small enough of some $\boldsymbol{U}_j$ vectors. Replacing in every above subset the $\{K_i(\tau)\}$ vector by the above $\boldsymbol{U}_j$ vector and integrating $g(\tau)$ over the subset yields an (*A3*) representation of a vector arbitrarily close to the vector represented by Eq. (*A2*). The coincidence of the interiors of the feasible set and of the set representable by Eq. (*A3*) follows by standard methods. When n linearly independent $\boldsymbol{U}_j$ vectors are found such that, taking any neighbourhood of any of these vectors, $\int g(\tau)\,\mathrm{d}\tau > 0$ holds when the integral is taken over the τ set where $\{K_i(\tau)\}$ is in the neighbourhood, Eq. (*A2*) represents an interior vector. When such $\boldsymbol{U}_j$ vectors cannot be found for a nonzero (on a τ set of a nonzero measure) $g(\tau)$ function, a τ interval of a nonzero length exists where, save for a τ set of zero measure, $\sum_{i=1}^{n} K_i(\tau) > 0$ and $K_i(\tau)$ are linearly dependent. The feasible set of the system $n = 2$, $K_1(\tau) = (\tau + 1 - |\tau - 1|)/4$, $K_2(\tau) = 1 - K_1(\tau)$ is an example where the boundary vectors $f_1 = f_2 \geq 0$ are feasible and the boundary vectors $f_1 = 0$, $f_2 > 0$ are unfeasible.

Now, representations by Eq. (*A3*) are considered and the feasible set now means the set representable by Eq. (*A3*). The set of normalized (i.e., with $\sum_{i=1}^{n} f_i = 1$) feasible vectors is closed since the set of $\boldsymbol{U}_j$ vectors is closed and the $\boldsymbol{U}_j$ vectors are of the unity i-sums, i.e., we extend the feasible set with its boundary. A vector represented by Eq. (*A3*) with infinite r is also feasible since truncated r-sums are feasible and in every neighbourhood of the vector some of them exist.

Condition 1. Any n distinct $\boldsymbol{U}_j$ vectors are linearly independent.

Theorem 2. A feasible vector may be represented by Eq. (*A3*) with linearly independent $\boldsymbol{U}_j$ vectors that belong to the boundary of the feasible set. Representing an interior vector in this way, any $\boldsymbol{U}_j$ vector may be required to appear, and with the maximum possible g_j value, the representation is unique when Condition 1 is met. Representing a boundary vector in this way, then $r < n$, and the representation is unique when Condition 1 is met. Every boundary vector is feasible.

When a $\boldsymbol{U}_j$ in Eq. (*A3*) is interior, $\boldsymbol{F}$ is interior. For an interior $\boldsymbol{F}$ and a feasible $\boldsymbol{F}'$, the $\boldsymbol{F}'' = \boldsymbol{F} - a\boldsymbol{F}'$ vector, with the maximum a leaving $\boldsymbol{F}''$ feasible, is boundary. For linearly dependent $\boldsymbol{U}_j$'s in Eq. (*A3*), a dependence relation may be used to remove some of them

in such a way that a selected parent $\boldsymbol{U}_j$ is retained. When n linearly independent $\boldsymbol{U}_j$'s appear in Eq. (*A3*), $\boldsymbol{F}$ is interior. Under Condition 1, the average of two different representations of a vector by Eq. (*A3*) contains at least $n + 1$ distinct $\boldsymbol{U}_j$ vectors.

We confine the allowed τ_j values to a set of all or some of τ values for which $\{K_i(\tau)\}$ is nonzero; note that disabling a τ when $\{K_i(\tau)\}$ is nonzero, some $\boldsymbol{F}$ vectors yet feasible may become unfeasible. When the set of nonzero $\{K_i(\tau)\}$ vectors is closed, which is met when the τ set is closed (e.g., consists of distinct closed τ intervals and/or a finite number of isolated τ points) and $K_i(\tau)$ are continuous on it, we may set $u_{ij} = K_i(\tau_j)$. Equation (*A3*) then reads

$$f_i = \sum_{j=1}^{r} g_j K_i(\tau_j) , \qquad i = 1, 2, \ldots, n \tag{A4}$$

with positive g_j's and distinct τ_j's taken from a closed subset (the feasible τ set) of the τ set where $\{K_i(\tau)\}$ is nonzero. Condition 1 is restated as follows:

Condition 2. For any n distinct feasible τ_j's, $\{K_i(\tau_j)\}$ vectors are linearly independent.

Theorem 3. When Condition 2 holds and $K_i(\tau)$ are continuous on the feasible τ set, a vector $\boldsymbol{F}$ in the boundary of the feasible set is uniquely represented by Eq. (*A4*) with $r + s < n$, where s is the number of τ_j's representing $\boldsymbol{F}$ and being inside the feasible τ set (i.e., inside a τ interval belonging to this set).

Theorem 4. Suppose Condition 2 and the continuity of $K_i(\tau)$ hold on the whole interval $[\tau_{min},\tau_{max}]$, where τ_{min} and τ_{max} are the minimum and maximum feasible τ's, i.e., including unfeasible τ regions. Then an $\boldsymbol{F}$ is in the boundary of the feasible set if and only if it is represented by Eq. (*A4*) with $r + s + t < n$, where t is the number of clusters of adjacent τ_j's representing $\boldsymbol{F}$ that contain neither τ_{min} nor τ_{max} and contain an odd number of members; for s see Theorem 3. A cluster of adjacent τ's with a property is a set of τ's having the property and being in the boundary of the feasible τ set (e.g., at an endpoint of a feasible τ interval or at an isolated feasible τ point) so that all feasible τ's between the minimum τ and the maximum τ of the cluster belong to the cluster and no feasible τ with the property may be added without violating this; a cluster may also consist of a single τ. Note that $t = 0$ when the feasible τ set is a single closed interval.

Conditions of Theorem 4 mean that either $\{K_i(\tau)\}$ or a system obtained by an odd permutation of $K_i(\tau)$ functions is a T-system. When the feasible τ set is a single closed τ interval, Theorem 4 is given by Theorem 2.1 in Chap. II of ref.[25], and for a discrete feasible τ set, by Theorem 4.2 in Chap. VII of ref.[25]. The general validity of Theorem 4 and the validity of Theorem 3 may be shown by methods used[25] in the above two particular cases.

When data form an unfeasible $\boldsymbol{F}$ vector, we search a least-squares solution, i.e., a feasible vector $\boldsymbol{F}'$ which minimizes a norm of $\boldsymbol{F}' - \boldsymbol{F}$, the norm being a (weighted) sum of squared elements of $\boldsymbol{F}' - \boldsymbol{F}$ or a positively definite quadratic form of the elements

when a complete variance matrix of data is known or assumed. $\boldsymbol{F}'$, if it exists, is a boundary vector of the feasible set; due to the convexity, the boundary contains a single vector closest to $\boldsymbol{F}$ in the least-squares sense. Using Theorems 1–3 we obtain:

Theorem 5. Suppose, that on every τ interval of a nonzero length where $\sum_{i=1}^{n} K_i(\tau) > 0$ (save for a τ set of zero measure), the $K_i(\tau)$ functions are linearly independent even when any τ set of zero measure is exempt from the interval. Then assuming that the data vector is not exactly representable by Eq. (*A2*), no least-squares solution of Eq. (*A2*) exists among ordinary $g(\tau)$ functions except the solution $g(\tau) = 0$ for an unpractical case when among representable vectors zero vector is closest to the data vector (i.e., any least-squares solution is of a discrete form). A least-squares solution of Eq. (*A3*) always exists. A least-squares solution of Eq. (*A4*) exists when nonzero $\{K_i(\tau)\}$ vectors form a closed set. The solution of Eq. (*A3*) or (*A4*) is unique when Condition 1 or 2 holds and the data vector is not representable exactly.

Theorem 6. When a data vector cannot be represented exactly by Eq. (*A4*) and, on a closed feasible τ set, $K_i(\tau)$ functions are continuous and Condition 2 holds, the problem of finding a least-squares solution of Eq. (*A4*) is well-posed in terms of ref.[3], p. 16, provided a change in r is considered as continuous when realized by limiting some of g_j's to zero and/or some group(s) of τ_j's to common limit(s).

The existence and uniqueness are stated by Theorem 5. The transformation of an $\boldsymbol{F}$ outside the feasible set to closest $\boldsymbol{F}'$ in the boundary of the set is continuous since, due to the convexity, it cannot increase the norm of the difference of two outside vectors. Since the transformation to $\boldsymbol{F}'$ from such g_j's and τ_j's that yield an $\boldsymbol{F}'$ in the boundary of the feasible set is mutually unique by Theorem 3 and continuous when a change in r is considered as in Theorem 6, its inverse, the transformation from $\boldsymbol{F}'$ to (g_j,τ_j), is also continuous. Hence, the transformation from $\boldsymbol{F}$ to (g_j,τ_j), being composed of two continuous transformations, is continuous as well. This proves the stability.

With the Lorentz transform inversion, we consider n pairs of $G'(\omega_i)$ and $G''(\omega_i)$ data at a set of n distinct nonzero finite ω_i. For the respective determinant with $2n$ values of τ_j, we obtain

$$D = \left| \frac{\omega_i^2\tau_j^2}{1+\omega_i^2\tau_j^2}, \frac{\omega_i\tau_j}{1+\omega_i^2\tau_j^2} \right| =$$

$$= (-1)^n \prod_i \omega_i^3 \prod_{k>i} (\omega_k^2 - \omega_i^2)^2 \prod_j \tau_j \prod_{m>j} (\tau_m - \tau_j) / \prod_{i,j} (1+\omega_i^2\tau_j^2) \ , \qquad (A5)$$

where i, k run from 1 to n and j, m from 1 to $2n$ when forming the determinant and the products. We see that for a set of $2n$ nonzero distinct τ_j's, D is nonzero, justifying the

linear independence of the $\{K_i(\tau_j)\}$ vectors. A similar result is obtained when n data of only $G'(\omega)$ or only $G''(\omega)$ and n values τ_j are considered. When a τ_j converges to infinity, the respective determinant elements converge to (1,0) for every ω_i and D converges to a finite nonzero value when other τ_j's are distinct and nonzero. Since $K_i(0) = 0$ for every i, $\tau = 0$ cannot be feasible. To allow for this, we multiply the kernel with τ_0/τ for $\tau < \tau_0$, then τ_j's less than τ_0 are replaced by τ_0 in the product over j in Eq. (*A5*) and D is still nonzero; for $\tau_j < \tau_0$ we calculate $g_j\tau_j/\tau_0$ values instead of g_j values. With this modification, Theorems 1–6 are seen to hold for the Lorentz transform inversion, the feasible τ set being any closed subset of the closed interval $[0,\infty]$.

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