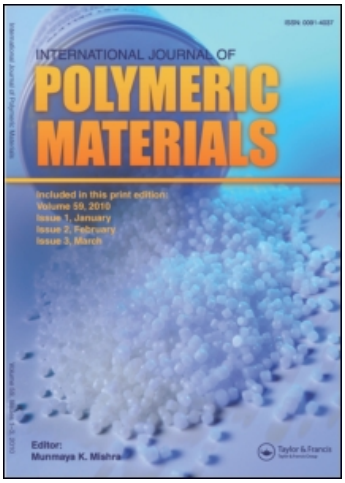

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Application of Minimax Method for Calculation of Viscoelastic Material Functions and Relaxation Spectra of Polymer Melts and Solutions

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Many publications were devoted to the problem of finding methods for calculating the distribution function of relaxation time spectra $H(\tau)$ for viscoelastic media. Direct calculations of this function on the basis of known relations of the linear theory of viscoelasticity connected with the solution of Fredholm integral equations of the first kind involve serious difficulties. At the same time, numerical approaches to determining the function $H(\tau)$ based on the use of experimentally determined material functions were proposed in a number of recent publications. Since the accuracy of calculating the functions depends directly on the confidence of determining the primary experimental data that generally always contain errors of a statistical nature, a number of authors employ smoothing numerical methods of determining the material functions, or ones that fail to react to the appearance of rough errors. These methods include methods of regularization and maximum of entropy. However, they have a number of serious shortcomings limiting the possibilities of their successful use.

In the present work, we propose to employ a different numerical method for these purposes, namely, the minimax technique. In our opinion, it is more accurate, rapid, and universal. We consider a scheme of constructing an algorithm, give examples of solving test problems showing how the algorithm functions in various extreme hypothetic situations. The results of the numerical calculations of the function $H(\tau)$ for a real object, viz. polybutadiene are based on experiments run in a rotary viscometer Rheotron of the firm Brabender.

KEY WORDS Relaxation times, viscoelastic media, distribution of relaxation times, numerical methods, data treatment, outlying values, polybutadiene.

INTRODUCTION

The viscoelastic reaction (behavior) of a system to deformation is a widely known experimental fact. From a physical viewpoint, such behavior is generally explained either by the existence of an internal structure and/or by the heterogeneous structure of the material. It features the most diverse systems, namely, polymers (at temperatures above the glass transition), composites based on polymers, hybrid composites, fluid systems of the type of highly structurized petroleums, suspensions, etc.

Unlike Hookian bodies or Newtonian liquids, the problem of describing the prop-

erties of such systems within a broad range of variation of the magnitudes and laws of deformation, the rates (or frequencies) of deformation, and other parameters generally consists in determining the time dependences of the mechanical characteristics, i.e. the material functions reflecting the viscoelastic mechanism of the behavior of these systems. In terms of moduli and viscosities and within the framework of a linear approximation (conditions not depending on the deformation amplitude), these characteristics can include the relaxation modulus $G(t)$, where t is the time, or the dynamic storage $G'(\omega)$ and loss $G''(\omega)$ moduli, where ω is the angular frequency of deformation. The storage and loss moduli are the real and imaginary components of the complex dynamic modulus $G^* = G' + iG''$.

The time dependences of G can be obtained quite simply from experiments involving stress relaxation wherein the dynamics of the change in the modulus is studied after the action of deformation is stopped. The values of $G'(\omega)$ and $G''(\omega)$ are determined for conditions of the periodic action of deformation set by the law $\gamma = \gamma_0 e^{i\omega t}$, where γ_0 is the deformation amplitude.

From the standpoints of a model approach, the ability of a viscoelastic body to resist a mechanical load and react thereto adequately is determined by a very important characteristic of a system, the relaxation time τ_i. As indicated in Reference 1, the relaxation time is determined by the ratio of the elastic and viscous (dissipative) properties of a material and in the simplest case can be introduced as

$$\tau_i = \eta_i / G_i$$

where η_i are the viscous and G_i the elastic components.

Such a model approach is simplified for real viscoelastic media that generally have a rather complicated internal structure. It is quite natural to introduce a distribution function of the relaxation time such as the relaxation spectrum $H(\tau)$. Experiments revealed[1,2] that for a broad class of materials (e.g. polymer solutions and melts, polymer blends, polymer-based composites), the range in the variation of the relaxation times may form many decimal orders of magnitude. The mechanical reaction of viscoelastic media to deformation is determined exactly by the features of this spectrum. Depending on the parameters of the external action (the laws of deformation, the rates or frequencies of deformation, temperatures, etc.), these media may reveal the properties of fluid, rubbery, leathery, or glassy bodies.

Establishment of the form of the function $H(\tau)$ is an important theoretical and practical task. It is used for constructing physically substantiated theories (phenomenological or molecular) of the viscoelastic behavior of such systems, as well as for predicting the properties of specific materials.

By the linear theory of viscoelasticity, the material functions $G(t)$, $G'(\omega)$, and $G''(\omega)$, and also the relaxation spectrum of the system $H(\tau)$, where τ is the relaxation time, are related by the following expressions[1]:

$$G(t) = G_e + \int_{-\infty}^{\infty} H(\tau) e^{-t/\tau} \, d \ln \tau, \quad t \in (-\infty, \infty); \tag{1}$$

$$G'(\omega) = G_e + \int_{-\infty}^{\infty} H(\tau)e^{-t/\tau}\, d \ln \tau, \quad t \in (-\infty, \infty); \tag{2}$$

$$G''(\omega) = G_e + \int_{-\infty}^{\infty} [\omega^2\tau^2/(1 + \omega^2\tau^2)]H(\tau)\, d \ln \tau, \quad \omega \in (-\infty, \infty); \tag{3}$$

$$G''(\omega) - iG'(\omega) = \omega \int_{-\infty}^{\infty} G'(t)e^{-i\omega t}\, dt, \quad \omega \in (-\infty, \infty). \tag{4}$$

The constant G_e added in expressions (1) and (2) considers the contribution of the discrete component into the spectrum for viscoelastic solids at $\tau \to \infty$. For viscoelastic liquids and uncrosslinked polymers above the glass transition temperature $G_e = 0$.

It can be seen from expressions (1)–(4) that from the theoretical viewpoint the determination of at least one of the functions $G(t)$, $G'(\omega)$, $G''(\omega)$, and $H(\tau)$ indicated above allows one to calculate the others. In practice, however, these calculations associated with integration of expressions (1)–(4) involve considerable mathematical difficulties, and consequently the obtaining of an exact solution is problematic.

From an experimental viewpoint, the possibility of determining the functions $G(t)$, $G'(\omega)$, and $G''(\omega)$ within broad ranges of t or ω depends on the features of the instruments employed. Quite often we succeed in establishing the form of a material function only within relatively narrow ranges of times or frequencies that do not overlap mutually. (The restrictions generally concern either relatively high values of t (or low ones of ω), or relatively low t's (or high ω's).)

Since direct experimental appraisals of the relaxation spectrum $H(\tau)$ are impossible we must rely on calculations based on material functions (see expressions (1)–(4), and also References 1–3).

Since the direct calculation of the function $H(\tau)$ is associated with the confidence of the experimental determination of the relations $G(t)$, $G'(\omega)$, and $G''(\omega)$, we shall briefly analyze below the possible experimental errors in determining the material functions we are interested in.

EXPERIMENTAL ERRORS AND APPROACHES TO THEIR SIMULATION

Experimental results always contain errors, chiefly of a statistical nature. They are explained by the influence of parameters not controlled during measurements. It is exactly the errors of a statistical nature that can tell considerably on the authenticity and correctness of interpretation of the results. Statistical errors are usually simulated by independent random quantities from the Gaussian distribution:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left\{-\frac{(x - m)^2}{2\sigma^2}\right\}, \quad x \in (-\infty, \infty),$$

where σ^2 and m are the dispersion and mean respectively and are considered to be known.

There are several tests for verifying hypotheses for a normal (Gaussian) distribution.[4-6] One of them is the Kolmogorov-Smirnov test (see, for example, Reference 5). Another one, the W-test, was introduced by Shapiro and Wilk and was used in References 4 and 6. In the latter, the W-test was calculated by the expression

$$W = \frac{\left[\sum_{i=1}^{n} a_i \eta(i)\right]^2}{\sum_{i=1}^{n} [\eta(i) - \bar{\eta}]^2}, \tag{6}$$

where $\bar{\eta} = 1/n \sum_{i=1}^{n} \eta(i)$ is the sample mean, $\eta(1) \leq \eta(2) \leq \cdots \leq \eta(n)$ is the ordered sample, $a = (a_1, \ldots, a_n)^T = m^T V^{-1}[(m^T V^{-1})(V^{-1}m)]^{-1/2}$ is the vector of the parameters in (6), T is transposition, $m - (n \times l)$ is the mean vector, and $V - (n \times n)$ is the correlation matrix of the n-dimensional normal distribution.

However, when the tests indicated in References 4–6 are employed, we are always faced with an a priori indefinability with respect to the dispersion σ and mean m of this normal (Gaussian) distribution (see Equation (5)). This hinders the formulation of a process algorithm and its correct numerical realization. Moreover, the postulate of the correctness of the law of Gaussian distribution of errors was also questioned in several publications.[7]

If we presume that errors of a statistical nature always include freak values, the W-test in a number of cases may be unsuitable. Indeed, the appearance of a freak value in statistics $\{\eta(i)\}_{i=1}^{n}$ mainly determines the result of summation when calculating the sample mean $\bar{\eta}$. Moreover, the idefinability remains with respect to m and V. In this case, to obtain confident results according to experimental data, one must employ smoothing or a method that does not react to the appearance of rough errors. These methods include either the method of regularization[8,9] or the method of the maximum of entropy.[10]

It should be noted that the methods discussed in References 8–10 can according to Hadamard lead to incorrect solutions [?]. The solution $x \in X$ with respect to the data $y \in Y$ is considered by Hadamard [?] to be correct according provided that for any $y \in Y$ the solution $x = f(y) \in X$ exists, is unique and stable, i.e. $\rho_x(\tilde{x}, \bar{x}) \to 0$ when $\rho_y(\tilde{y}, \bar{y}) \to 0$. Here $\rho_x(\cdot)$ and $\rho_y(\cdot)$ are valuations of the X and Y functional spaces respectively, while $\tilde{x}$, $\tilde{y}$, and $\bar{x}$, $\bar{y}$ are approximate and unknown accurate values, respectively violation of one of the three conditions indicated above makes the problem incorrect.

Without refuting the usefulness of the methods of regularization and maximum of entropy employed, in particular, in References 4, 6, and 10 to calculate the relaxation spectra of selected viscoelastic media, we shall note that they have a number of serious shortcomings which can lead to incorrect results.

As applied to the problems of the present work, we prefer to use a different method of solving incorrectly formulated problems, namely, the minimax one.[11] Unlike the methods in References 6 and 8–10, the minimax method yields the best (optimal)

solution with the least favorable initial data. In addition, we shall consider the features of employing this method for calculating the function $H(\tau)$ using the values of material functions determined from rheological experiments.

MINIMAX METHOD. BRIEF DESCRIPTION OF ALGORITHM

From the standpoints of a numerical approach, the problem consists in calculating a function, e.g. $H(\tau)$, from experimental data containing outliers (freak values). We shall select the set of possible values of the loss modulus $\tilde{G}_i''$ as these data. The values were obtained in the range of frequencies, ω_i and contained the outliers $\xi(\omega_i)$, i.e.

$$\tilde{G}_i'' \equiv \bar{G}''(\omega_i) + \xi(\omega_i), \quad \text{when } i = 1, \ldots, N$$

When the outliers $\xi(\omega_i)$, $i = 1, \ldots, N$, are present, the problem of evaluating $H(\tau)$ is a priori indefinite with respect to the given $G''(\omega_i)$ and, consequently, requires additional a priori information. The latter can be introduced by the value set

$$\{\tilde{G}_i''\}: \frac{1}{N}\sum_{i=1}^{N} (\tilde{G}_i'' - \bar{G}_i'')^2 \leq \delta^2, \tag{7}$$

where $\{\bar{G}''\}_{i=1}^{N}$ are the unknown exact data, and $\delta \geq 0$ is a parameter of the error of the data.

With a view to the restrictions (7), the optimization problem acquires the form:

$$H^{\delta}(\tau) = \arg \min_{H} \max_{\tilde{G}''} (1/N) \sum_{i=1}^{N} \left[\tilde{G}_i'' - \int_{-\infty}^{\infty} \frac{w_i\tau}{1 + (w_i\tau)^2} H(\tau)\, d\tau \right]^2 \tag{8}$$

The use of (8) with the restrictions (7) guarantees the calculation of the approximation $H^{\delta}(\tau)$ converging to the unknown accurate solution $H(\tau)$ in a root-mean-square approach when $\delta \to 0$.

It should be noted that with the corresponding selection of the positive-negative Hilbert spaces, this convergence can be guaranteed in a uniform valuation with a certain degree of smoothness.[11]

The error parameter $\delta > 0$ in Equations (7), (8), is considered to be known a priori, as is in the method of regularization. Nevertheless, as in the methods of regularization and maximum entropy,[8-10] we may also obtain here a quite "poor" solution $H^{\delta}(\tau)$ if the values of the parameter $\delta > 0$ are set a priori by perturbations of the initial data not corresponding to the real values. This is why the error parameter $\delta > 0$ must be appraised by experimental results when employing methods of solving incorrectly posed problems.

For this purpose, let us consider a sequence of random values:

$$\tau_i = \tilde{G}_i'' - \int_{-\infty}^{\infty} \frac{\omega_i\tau}{1 + (\omega_i\tau)^2} H^{\delta}(\tau)\, d\tau, \quad i = 1, \ldots, N \tag{9}$$

where $H^{\delta}(\tau)$ is the solution of problem (7), (8) for a value of δ chosen arbitrarily beforehand. We shall adopt the following assumptions relative to the random values of r_i, $i = 1, \ldots, N$: the values $\{r_i\}$ are statistically independent and satisfy an ε-class of distribution functions[12]:

$$\phi = \{F_\varepsilon(x) = (1 - \varepsilon)F(x) + \varepsilon P(x), \quad \varepsilon \in [0, 1]\}, \tag{10}$$

where $F(\cdot)$ is the theoretically set distribution function, and $P(\cdot)$ is an unknown distribution function considering the presence of freak values.

The numerical parameter $\varepsilon \in [0, 1]$ can be interpreted as the probability of appearance of freak values in the experimental results. When $\varepsilon = 0$, we have the case of indefinability with respect to the parameters $F(x)$ or complete a priori definability (see, for example, Reference 6). When $\varepsilon = 1$, we have the case of nonparameteric a priori indefinitability wherein the distribution function $P(x)$ cannot be determined a priori. And, finally, the case $0 < \varepsilon < 1$ takes into account the parametrically-nonparametrically a priori indefinitability.

Let us assume that the ε-class of distribution functions (10) has symmetric densities $f_\varepsilon(x) = f_\varepsilon(-x)$ with the Fisher's asymptotic integral condition

$$I(f_x) = \int_{-\infty}^{\infty} (f'_\varepsilon/f_\varepsilon)^2 \, dF_x(x) < \infty, \quad \varepsilon \in [0, 1], \; I(f_x) < \infty$$

We consider the density $f(x)$ to be normal

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left\{-\frac{(x - m)^2}{2\sigma^2}, \quad x \in (-\infty, \infty)\right\}$$

with an a priori unknown mean m and dispersion σ^2. The latter characterizes the parametric indefinitability of the problem and is well consistent with practice. The density $p(x)$, $x \in (-\infty, \infty)$ is considered to be symmetric and unknown and takes into account the appearance of freak values for both large and small values of X (the requirement of symmetry). The latter reflects the nonparametric a priori indefiniteness of the problem. The quantity $\varepsilon \in [0, 1]$ in (10) determines the fraction of freak values in an infinite volume of data.

Consequently, it is necessary to appraise the parameters (m, σ) of a hypothetic normal distribution according to a finite sample of a fixed volume with parametric-nonparametric indefinability.

Let us introduce the minimax variation problem:

$$\begin{cases} (L^*, F^*) = \arg \min_{L \in G} \max_{F \in \phi} V^2(L, F), \\ V^2(L, F) = \left(\int_{-\infty}^{\infty} l^2(x) \, dF\right) \Big/ \left[c \left(\int_{-\infty}^{\infty} l'_s(x - s)|_{s=0} \, dF\right)^2\right] \end{cases} \tag{12}$$

for any $L \in G$ and $F \in \phi$. Here G is the set of convex functions $L(t)$, $t \in (-\infty, \infty)$ symmetric relative to the origin of coordinates and with continuous derivatives $l(t) = dL(t)/dt$, $t \in (-\infty, \infty)$ and such that for any $F \in \phi$ the inequalities

$$\int_{-\infty}^{\infty} l^2(x)\, dF < \infty, \quad (d/ds) \int_{-\infty}^{\infty} l(x - s)\, dF < \infty$$

are observed for any $S \in (-\infty, \infty)$.

Without reviewing the mathematical details, which treated in Reference 13, we shall give the final algorithm for appraising the parameters m and σ.

$$\begin{cases} \hat{m} = \dfrac{1}{N} \sum_{i=1}^{N} \varphi(r_i), \\ \hat{\sigma}^2 = \dfrac{1}{N} \sum_{i=1}^{N} \chi(r_i^c), \end{cases} \tag{13}$$

where $r_i^c = r_i - \hat{m}$ are centered random values.

The nonlinear without memory transforms $\varphi(\cdot)$ and $\chi(\cdot)$ minimize Fisher's asymptotic information for the distribution function that is the least favorable in the sense of (12) and has the following form:

$$\varphi(x) = \begin{cases} \hat{s} - K_m\hat{\sigma}, & x < \hat{s} - k_m\hat{\sigma}, \\ x, & \hat{s} - K_m\hat{\sigma} \le x \le \hat{s} + K_m\hat{\sigma}, \\ \hat{s} + K_m\hat{\sigma}, & x > \hat{s} + K_m\hat{\sigma}, \end{cases} \tag{14}$$

where $\hat{s} = \text{med}\{x_i\}_{i=1}^N$ is a sample median, and $\hat{\sigma} = \text{med}\{|x_i - \hat{s}|\}_{i=1}^N$ is the absolute median deviation.

Accordingly:

$$\chi(x) = \begin{cases} (\hat{\sigma}\ \text{Re}\sqrt{1 - k_\sigma})^2 - 1, & |x| < \sigma\ \text{Re}\sqrt{1 - K\sigma}) \\ x^2 - 1 & \hat{\sigma}\ (\text{Re}\sqrt{1 - K\sigma}) \le |x| \le \hat{\sigma}|\sqrt{1 + K\sigma}) \\ (\hat{\sigma}|\sqrt{1 + K_\sigma}|)^2 - 1, & |x| > \hat{\sigma}|\sqrt{1 + K\sigma}| \end{cases} \tag{15}$$

The parameters K_m and K_0 are consistent with the indefiniteness parameter ε with the aid of the relevant coupling equations:

$$\begin{aligned} &\int_{-K_m}^{K_m} \exp\{-x^2/2\}\, dx + (2/K_m)\exp\{-K^2/2\} = \sqrt{2\pi}/(1 - \varepsilon) \\ &\int_{\text{Re}\sqrt{1-K_\sigma}}^{\sqrt{1+K_\sigma}} \exp\{-x^2/2\}\, dx + [\text{Re}\sqrt{1 - K_\sigma}\exp\{-0.5\ \text{Re}\sqrt{1 - K_\sigma} \\ &\quad + |\sqrt{1 + K_\sigma}|\exp\{-0.5|\sqrt{1 + K_\sigma}|\}]/K_\sigma = \sqrt{2\pi}/[2(1 - \varepsilon)] \end{aligned} \tag{16}$$

Equations (16) have single solutions at $[0, \infty]$ for any $\varepsilon \in [0, 1]$. It should be noted that when $K_m \to \infty$ and $K_\sigma \to \infty$ the algorithm (12)–(16) coincides with the well known algorithm of maximum probability. When $K_m \to 0$ and $K_\sigma \to 0$, the algorithm (12)–(16) becomes nonparametric, the median remaining as an estimate of the mean, and the absolute median deviation as an estimate of the dispersion.

NUMERICAL REALIZATION OF THE ALGORITHM OF THE MINIMAX PROBLEM: SOLUTION OF INTEGRAL EQUATIONS OF THE FIRST KIND

As noted above, our task consists in obtaining an exact numerical solution of integral equations of the first kind [type (1–4)], or in a more general form:

$$u(t) = \int_a^b K(t, \tau)z(\tau)\, d\tau; \quad t \in [c, d]; \tag{17}$$

with approximately given initial data:

$$\tilde{K}[t, \tau], \tau \in [a, b], t \in [c, d], \tilde{u}(t), t \in [c, d]$$

such that

$$\int_a^b \int_c^d |\tilde{K}(t, \tau) - \bar{K}(t, \tau)|^2\, dt\, d\tau \le h^2, \int_c^d |\tilde{u}(t) - \bar{u}(t)|^2\, dt \le \delta^2$$

We shall seek the exact solution of Equation (17) in the form:

$$Z(t) = (1 - t^2)^2 + 0.5(\sin(\pi t))^4 + \cos(6.5\pi t), \quad t \in [-1, 1] \tag{18}$$

Analysis of function (18) reveals that it contains seven maxima and six minima in the region of determination. This allows us to analyze quite reliably each of the solutions obtained in a series of consecutive approximations to the exact solution. We shall select the following function as the exact description of the nucleus in Equation (17):

$$K(t, \tau) = \frac{1}{1 + 100(t - \tau)^2}, \quad t \in [-1, 1], \tau \in [-1, 1]. \tag{19}$$

Function (19) is characterized by the fact that the matrix $\{K(t_i, \tau_j)\}^{M,N}$ corresponding to it has an inverse, but which is poorly stipulated, because $\lambda_{max}/\lambda_{min} \gg 1$. Here λ_{max} and λ_{min} are its maximum and minimum eigenvalues, respectively.

An exact function of $\bar{U}(t)$ (Equation (17)) can be obtained by integrating it in view of (18) and (19). To simplify this task, let us assume that $h = 0$, the parameter $\delta > 0$ is unknown, while the approximate data are determined by the relation

$$\tilde{U}(t) = U(t) + \xi(t), \quad t \in [-1, 1]. \tag{20}$$

Here $\xi(t) \approx \{\xi(t_i)\}_{i=1}^{N}$ is a random function (an outlier in the experimental results) that is simulated by independent random numbers from two normals distributions and zero means and unknown dispersions by the relation:

$$\xi(t) = (1 - \zeta)\xi_1(t) + \zeta\xi_2(t), \quad t \in [-1, 1]. \tag{21}$$

In expression (21), ξ is a random number equal to 0 or 1, while $\xi_1(t)$ and $\xi_2(t)$ simulate the random noise and the outliers in the experimental results or due to interruptions in the operation of the instruments, respectively.

Expression (21) is identical to (10) at a certain present value of $\varepsilon \in [0, 1]$. In view of (8), the task of optimization for Equation (17) becomes:

$$Z^{\delta}(t) = \arg \min_{Z \in W_2^1} \max_{\tilde{U} \in L_2} \left\{ \int_c^d \left[\tilde{U}(t) - \int_a^b K(t, \tau) Z(\tau)\, d\tau \right]^2 dt, \right. \tag{22}$$

where $\delta > 0$ is considered to be unknown.

We shall seek the approximation of Z_t^{δ} to $\bar{Z}_t$ in the valuation of functional space $W_2^1[-1, 1]$:

$$\|V\|_{W_2^1}^2 = \int_{-1}^{1} |V(t)|^2\, dt + \int_{-1}^{1} \left| \frac{dV(t)}{dt} \right|^2 dt.$$

We shall consider below some specific test examples illustrating the applicability, sensitivity, and features of the proposed algorithm.

NUMERICAL TEST CALCULATIONS

Test Problem No. 1

We shall investigate the sensitivity of the solution of (22) to an inaccuracy in setting the error parameter $\delta > 0$. We performed the calculations for various values of δ and σ^2. Their results are presented in Figures 1–4. In these and subsequent figures, the following notation is used:

M, N is the dimension of the matrix $\{K(t_i, \tau_j)\}$ corresponding to nucleus (19) of Equation (17); $\bar{Z}(t)$ is the exact solution of (18) (it is needed for illustrative comparison with the solution of (22)); $\tilde{U}(t) = \bar{U}(t) + \xi(t)$ is the right-hand side of (17) perturbed by an outlier and corresponding to the experimental results; $\zeta(t)$ is a random function corresponding to (21), and ε is an interruption breakdown parameter. The random quality in (21) was determined as follows:

θ is a random quantity from the sensor of random quantities on the segment [0, 1] with a uniform distribution; σ_0^2 and σ_{int}^2 are the dispersions of the random processes $\zeta_1(t)$ and $\zeta_2(t)$ in (21), respectively.

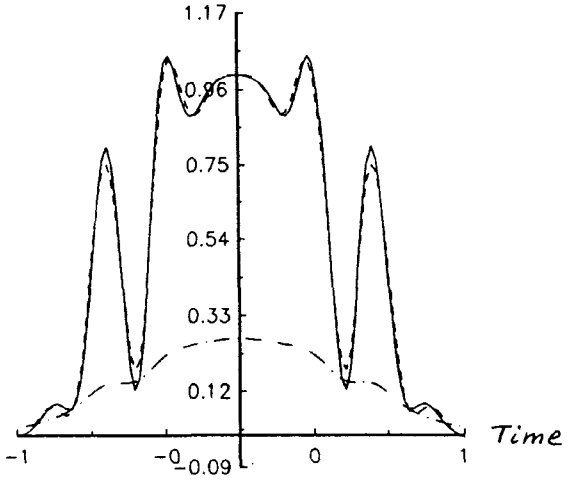

FIGURE 1 Influence of parameters and on solution by $M = N = 100$, $\delta = \sigma^2 = 10^{-5}$, $\varepsilon = h = 0.0$. —— $\bar{Z}(t)$, – – – $Z^{\delta}(t)$, —— · —— · —— $\tilde{U}(t)$.

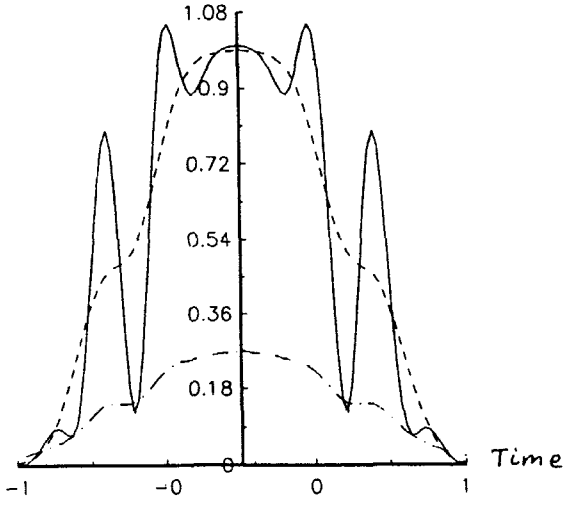

FIGURE 2 Influence of parameters δ and σ^2 on Z^{δ} solution by $M = N = 100$, $\sigma^2 = \delta = 10^{-3}$, $\varepsilon = h = 0.0$ (see Figure 1 for symbols).

Figures 1 and 2 give solutions of problem (22) with complete agreement of δ and σ_0^2 for $\varepsilon = 0$ (no interruption in the observations). We can see that when the dispersion of the outlier σ_0^2 is greater at $\sigma_{\text{int}}^2 = 0$, a smoother solution of (22) is obtained. When $\sigma_0^2 = \delta = 10^{-3}$ (Figure 2), all the extremes on $Z^0(t)$ are smooth.

Figures 3 and 4 give numerical experiments for the case when σ_0^2 does not correspond to the value of the parameter δ with $\sigma_{\text{int}}^2 = 0$. It can be seen (see Figure 3) that the difference between the parameters δ and σ_0^2 tolerated for normal functioning of algorithm (22) is about a decimal order of magnitude. If this difference is greater, solution (22) is excited by external noise (Figure 4).

The examples in Figures 1–4 reveal that a priori setting of the parameter $\delta > 0$

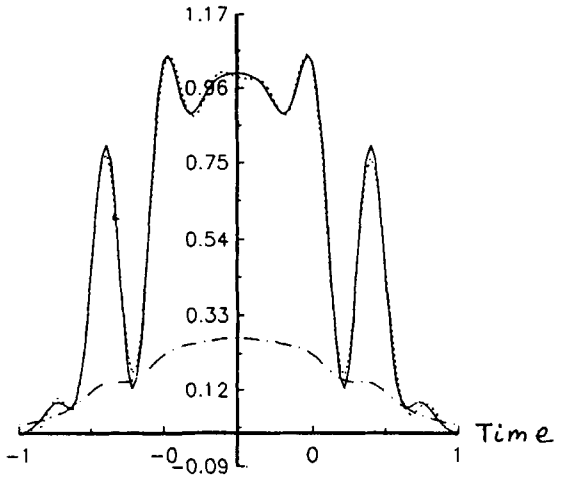

FIGURE 3 Influence of discrepancy of δ and σ^2 on Z^{δ}, $\delta = 10^{-5}$, $\sigma^2 = 10^{-4}$, $\varepsilon = h = 0.0$ (see Figure 1 for symbols).

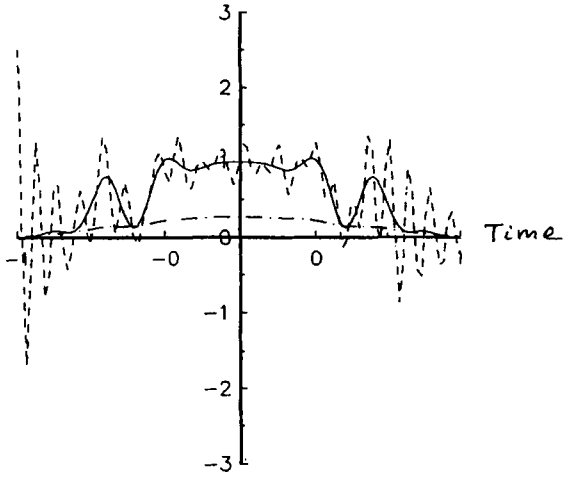

FIGURE 4 Influence of discrepancy of δ and σ^2. $M = N = 100$, $\delta = 10^{-5}$, $\sigma^2 = 10^{-3}$, $\varepsilon = h = 0.0$ (see Figure 1 for symbols).

may lead either to excessive smoothing of the solution or to its oscillation. It is therefore necessary to use the algorithm with appraisal of the parameter $\delta > 0$ using the same experimental data $\tilde{U}(t)$, $t \in [-1, 1]$.

Test Problem No. 2

We study the influence of the appraisal of the maximum likelihood $\hat{\delta}$ of the parameter $\delta > 0$ on the nature of the solution of (22).

A glance at Figure 5 clearly reveals that when the appraisal of the maximum likelihood is introduced, the renewed solution of $Z^{\delta}(t)$ is appreciably closer to the exact solution $Z(t)$ in a uniform valuation than the solution of $Z^{\delta_0}(t)$ from (22).

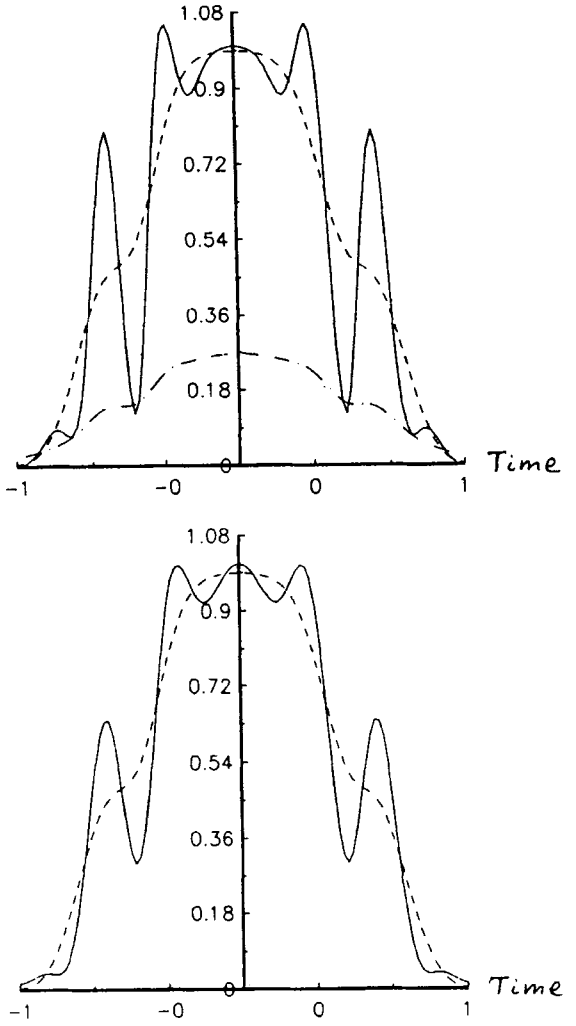

FIGURE 5 Maximum likelihood method—estimation of δ-parameter $M = N = 100$, $\sigma_0^2 = 10^{-5}$, $\sigma_{int}^2 = 0.0$, $\delta_0 = 10^{-3}$ δ = 0.4698 E-4 ε—$h = 0.0$. (a) —— $\tilde{Z}(t)$, ---- $Z^{\delta_0}(t)$, - · - · - · - · $\tilde{u}(t)$; (b) —— $Z^{\delta}(t)$, ---- $Z^{\delta_0}(t)$.

However, in this experiment (as in the preceding one), interruptions in the observations are absent.

According to (9), at a certain given value of $\delta_0 > 0$, a random process (mismatch signal) is calculated:

$$\Delta U(t) = \tilde{U}(t) - \int_{-1}^{1} K(t, \tau) Z^{\delta_0}(\tau)\, d\tau \tag{23}$$

The realization of this process is shown in Figure 6 by the symbol ΔU_t. The figure also shows the functions $\tilde{U}(t) = \bar{U}(t) + \xi(t)$ and

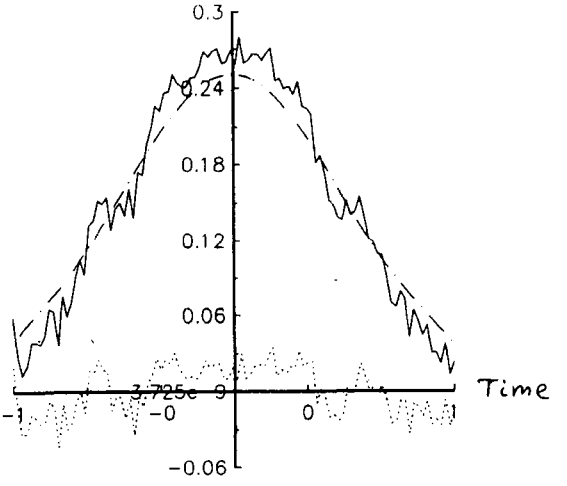

FIGURE 6 Maximum likelihood method—formation of mismath signal $\delta_0 = 10^{-2}$ (see Figure 5 for other parameters). —— $\bar{u}(t)$, ---- $\Delta u(t)$, – – – – $u^{\delta_0}(t)$.

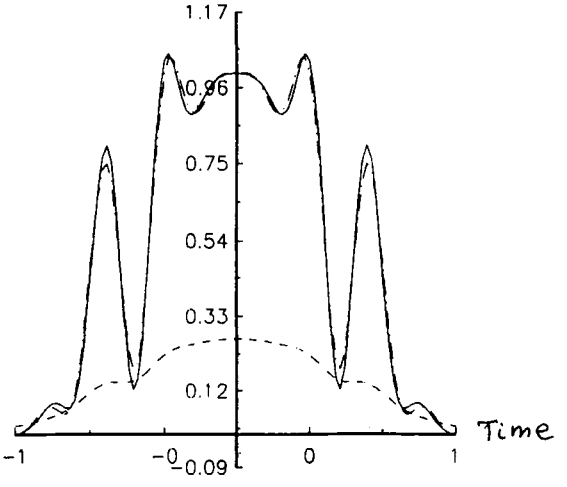

FIGURE 7 Influence of freak in an experiment $M = N = 100$, $\delta = \sigma_0^2 = 10^{-5}$, $\sigma_{int}^2 = 10^{-3}$, $\varepsilon = 0.4$, $h = 0.0$ (see Figure 1 for symbols).

$$U_t^{\delta_0} \equiv \int_{-1}^{1} K(t, \tau) Z^{\delta_0}(\tau)\, d\tau.$$

Test Problem No. 3

We study how interruptions in the experimental results affect the solution of (22) if we know the value of the error parameter $\delta > 0$ exactly, i.e. $\delta = \sigma_0^2$ (hypothetically, this case has a low probability), but there is no information on there being interruptions in the measurements. In the given case $\delta = \sigma_0^2$, and the outlier was simulated by (21) with various values of the parameter $\varepsilon \in [0, 1]$. We adopted "sparing

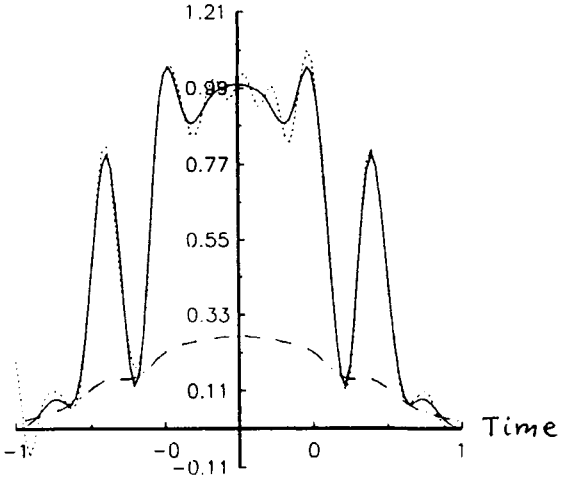

FIGURE 8 Influence of freak in an experiment $\varepsilon = 0.6$ (see Figure 7 for parameters and Figure 1 for symbols).

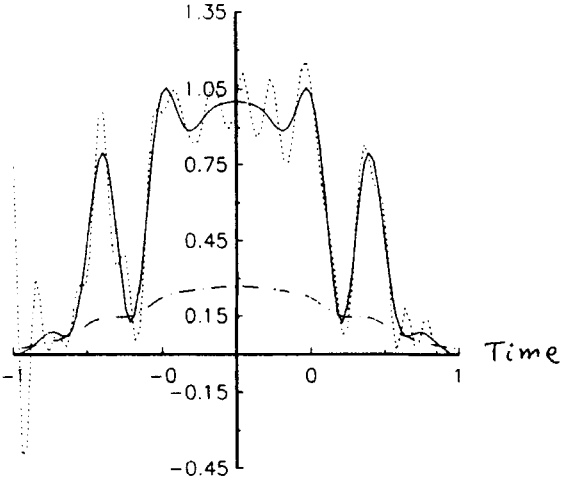

FIGURE 9 Influence of freak in an experiment $\varepsilon = 0.7$ (see Figure 7 for parameters and Figure 1 for symbols).

conditions'' of interruption in the experiment producing no avalance loss of stability. The random process determining the interruption was simulated from a Gaussian distribution with a zero mean and a dispersion close to the level of stability of the solution of (22).

Figures 7–9 show the loss of stability of the solution of (22) because of interruptions when ε varied from 0.4 to 0.8, ε—is present number of the outliers in the data, σ^2_{int}—is dispersion of the outliers.

The data of Figures 7–10 allow us to conclude that even if the exact value of the error parameter is known a priori, the occurrence of interruptions in an experiment will nevertheless result in oscillation of the solution of (22). But it is impossible to

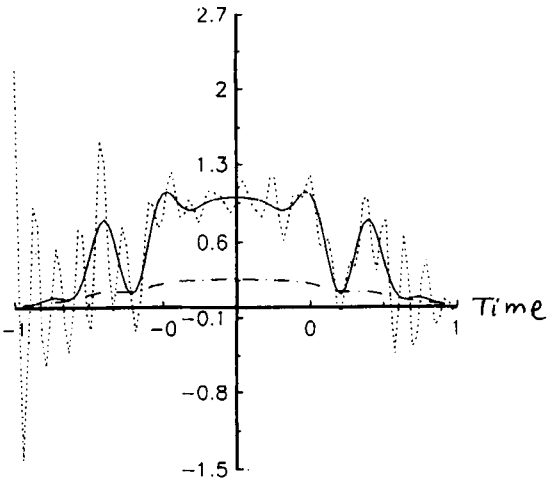

FIGURE 10 Influence of freak in an experiment $\varepsilon = 0.8$ (see Figure 7 for parameters and Figure 1 for symbols).

determine the occurrence of interruptions in an experiment a priori. This is why algorithm (22) must be supplemented with an additional mechanism for automatically detecting interruptions in observations and their correction.

Test Problem No. 4

We shall further analyze the influence of an interruption on the solution of (22) when appraising the error parameter $\delta > 0$ by the maximum likelihood method. In the given example, an outlier is no longer a steady normal random process and therefore the appraisal of the maximum likelihood of the parameter δ no longer corresponds to the true unknown value of this parameter.

The above examples No. 1 and 2 show that an increase in the value of the parameter $\delta > 0$ in comparison with the true one leads to smoothing out of the solution of (22). However, the same perturbations present in the values of the function $\tilde{U}(t)$, conversely, result in oscillation of the solution of (22). The question therefore arises as to what the solution of (22) will be in the general case, namely, smooth or oscillating.

Our results (Figure 11a, b) show that oscillation prevails, and the solution of $Z^0(t)$—(Figure 11b)—becomes oscillating. This does not correspond to the exact solution of $\bar{Z}(t)$. Consequently, in this case too the algorithm must be supplemented with an additional mechanism for automatically detecting interruptions in the data and their correction.

Test Problem No. 5

Let us now consider the action of the mechanism for automatically seeking and eliminating inhomogeneities in the data $\tilde{U}(t)$. The algorithm of operation of this

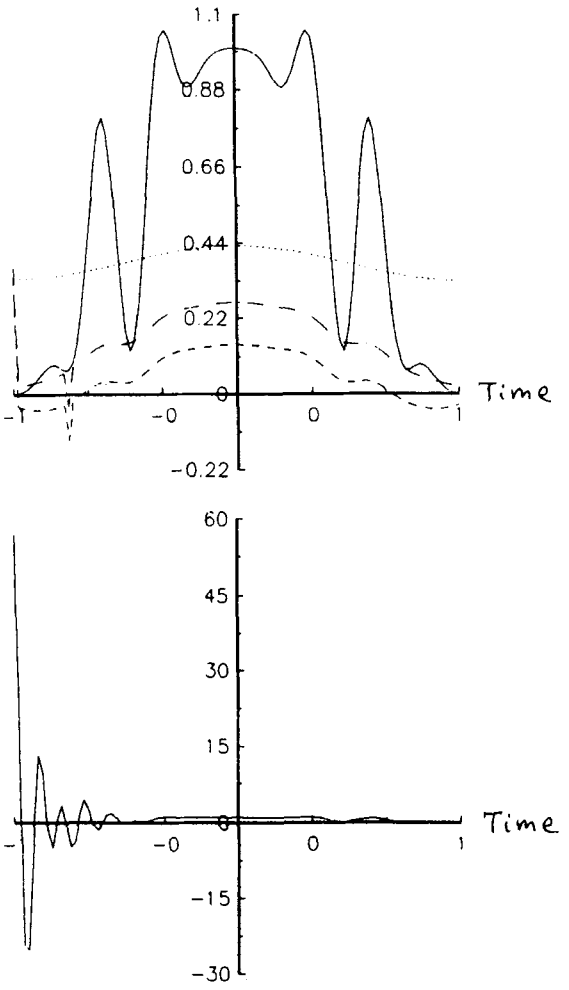

FIGURE 11 Influence of freak in an experiment on maximum likelihood estimation of δ-parameter $M = N = 100$, $\delta_0 = 0.1$, $\sigma_0^2 = 10^{-5}$, $\sigma_{im}^2 = 0.1$, $\varepsilon = 0.1$, $\hat{\delta} = 0.5762$ E-02, $h = 0.0$. (a) —— $\tilde{Z}(t)$, ---- $\Delta u(t)$, – – – – $\tilde{u}(t)$, · · · · $z^{\delta_0}(t)$; (b) —— $Z^{\hat{\delta}}(t)$.

mechanism was described above in expressions (12)–(16). It consists in the automatic construction of an adaptive nonlinear inertia-free converter that is optimal in the sense of (12). It makes the initial unsteady process steady, but never smooths it and, consequently, does not result in a loss of the high-frequency components of the initial data.

Figure 12a presents the initial data of the problem $\tilde{U}(t)$ in which, apart from the additive outlier, a freak value at the instant $t \approx -0.6$ can be seen quite clearly. This freak value "oscillated" the solution in Example 4.

In Figure 12b we can clearly see correction of the mismatch signal by the adaptive converter. Here ΔU_t is the mismatch signal without correction, ΔV_t is the same after correction. We can see that the adaptive converter automatically discovered a freak

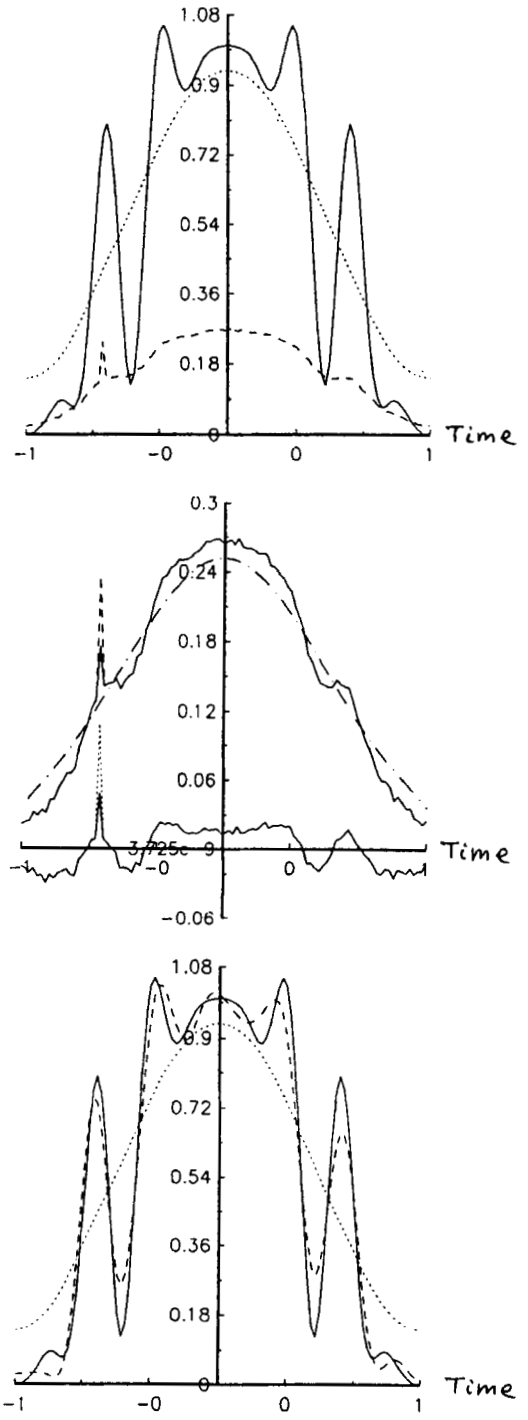

FIGURE 12 Correction of data by uninertia nonlinear converter $\delta_0 = 0.01$, $\hat{\delta} = 0.3986$ E-3 (for parameters see Figure 11). (a) —— $\bar{Z}(t)$, – – – $U(t)$, · · · · · $Z^{\delta_0}(t)$; (b) – – – $(\bar{t})$, —— $\tilde{U} = U^{\delta_0} + f(\Delta U) = f(t)$ (upper line), —— $\Delta V = f(\delta U) = f(t)$ (lower line); (c) —— $\bar{Z}(t)$, – – – $Z\hat{\delta}(t)$, · · · · $Z^{\delta_0}(t)$.

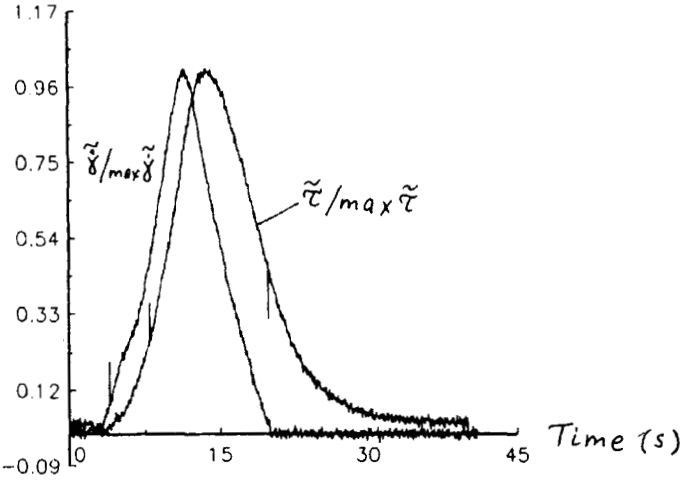

FIGURE 13 Experimental dependencies of $\dot{\gamma}(t)$ and $\tau(t)$ for polybutadiene (PB), $M = 8.3 \cdot 10^4$.

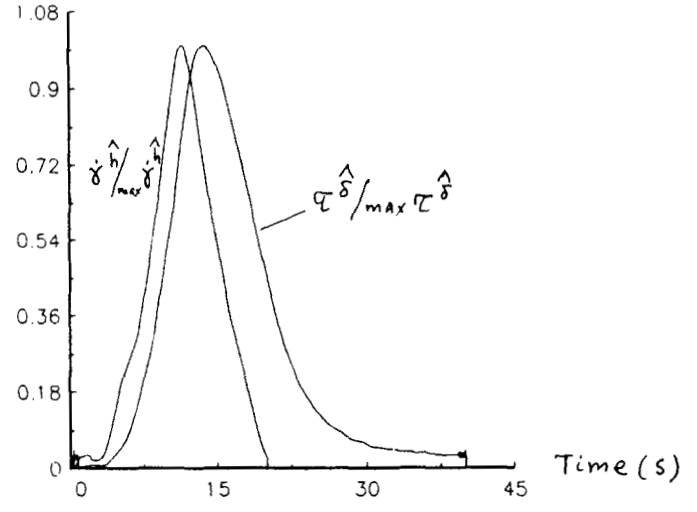

FIGURE 14 Dependencies of $\dot{\gamma}(t)$ and $\tau(t)$ for PB $M = 8.3 \cdot 10^4$ after processing with the algorithm (22).

value at the instant $t \approx -0.6$ and reduced this value to one converting the entire random process into a steady one.

The corrected initial data in Figure 12a are represented by the function $\tilde{\tilde{U}}(t)$. We can note the appreciable diminishing of the freak value on $\tilde{\tilde{U}}(t)$ in comparison with the initial data $\tilde{U}(t)$.

Figure 12c shows the modified solution of $Z^0(T)$ to be much closer to the exact solution of $\bar{Z}(t)$ in a uniform valuation than the initial solution of $Z^{\delta_0}(t)$.

Our numerical experiments suggest the following conclusions:

1. The a priori indefinability with respect to the parameters (h, δ) in problem (8) and (12) may substantially distort the solution being sought.

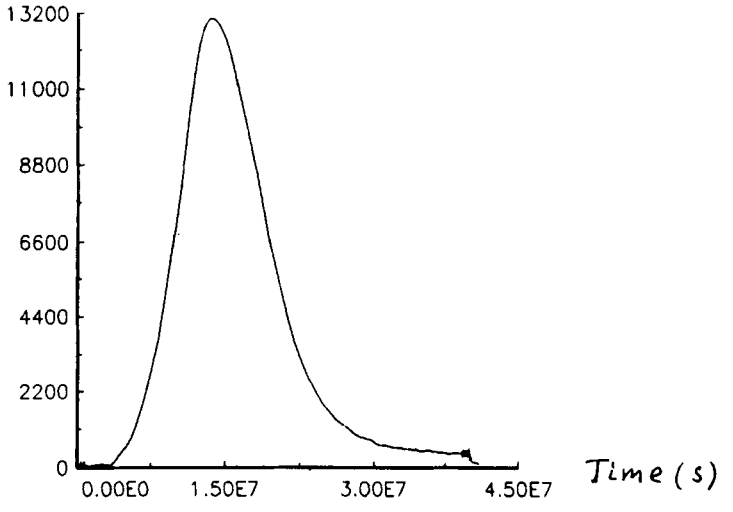

FIGURE 15 Dependence of stresses (*Pa*) vs. times (*s*) for PB, $M = 8.3 \cdot 10^4$, $N = M = 1024$.

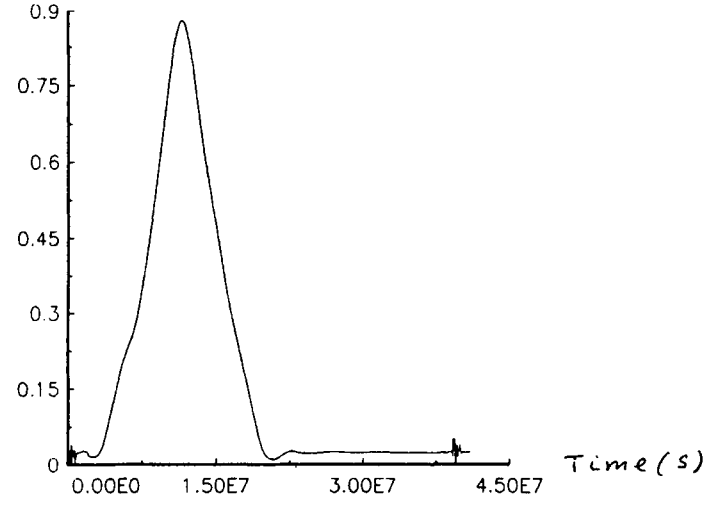

FIGURE 16 Dependence of deformation rate (s^{-1}) vs. time (*s*) for PB, $M = 8.3 \cdot 10^4$.

2. To improve the confidence of the solution, a statistical appraisal of the parameters (h, δ) according to the real experimental data must be used.

3. To appraise the parameters (h, δ), adaptive inertia-free nonlinear conversions must be employed. In the absence of anomalies (interruptions or deviations in the real distribution of outliers from the presumed Gaussian one) in the experimental results, these conversions automatically degenerate. However, when anomalies appear, the conversions automatically go into action and increase their role with a growing number of anomalous elements. In the limiting cases when information on distribution of outliers is absent, the algorithm becomes a nonparametric one.

USE OF THE MINIMAX METHOD IN SOLVING PRACTICAL PROBLEMS

Let us now consider an example of using the algorithm (22) proposed above for calculations of specific material functions of a real viscoelastic medium. It was convenient to choose polybutadiene (PB), a linear flexible-chain polymer as the material simulating such a medium. The rheological properties of this polymer were described many times in the literature (see, for example, Reference 2). Moreover, in Reference 14, the method of regularization was employed to calculate the function $H(\tau)$ for exactly this polymer.

We shall select the function of the relaxation modulus $G(t)$ (see Equation 1) as the material function being determined, i.e. calculated with the aid of the above algorithm. The experimental results obtained in a rotary viscometer "Rheotron" of the firm Brabender were the initial ones for the calculations. The experiments were run at different gradients of the rates of deformation $\dot{\gamma}$ and the values of the shear stress τ corresponding to them were determined.

Hence, the object of the numerical calculations was to calculate the material function $G(t)$ according to the preset function of the gradient of the deformation rate $\dot{\gamma}(t)$ and to the function of the shear stress determined experimentally.

Figure 13 presents the normalized experimental functions $\tilde{\dot{\gamma}}(t) = \dot{\gamma}(t) + \xi(t)$ and $\tilde{\tau}(t) = \tau(t) + \delta(t)$, where $\xi(t)$ and $\zeta(t)$ are random processes. The normalization of $\tilde{\dot{\gamma}}(t)/\max \tilde{\dot{\gamma}}(t)$ and $\tilde{\tau}(t)/\max \tau(t)$ was performed to visualize the outliers in the initial data. In the plots in Figure 13, we can see very clearly the anomalous freak values.

Figure 14 shows the same functions, but after processing with the described algorithm (22). Since the function $\tilde{\dot{\gamma}}(t)$ is set a priori, its mismatch signal was evaluated by the direct difference $\xi(t) = \tilde{\dot{\gamma}}(t) - \dot{\gamma}(t)$ and was processed by the above algorithm for seeking and eliminating anomalous freak values. Moreover, the operation of smoothing a random mismatch signal after eliminating the anomalous freak values was applied to the functions $\tilde{\dot{\gamma}}(t)$ and $\tilde{\tau}(t)$.

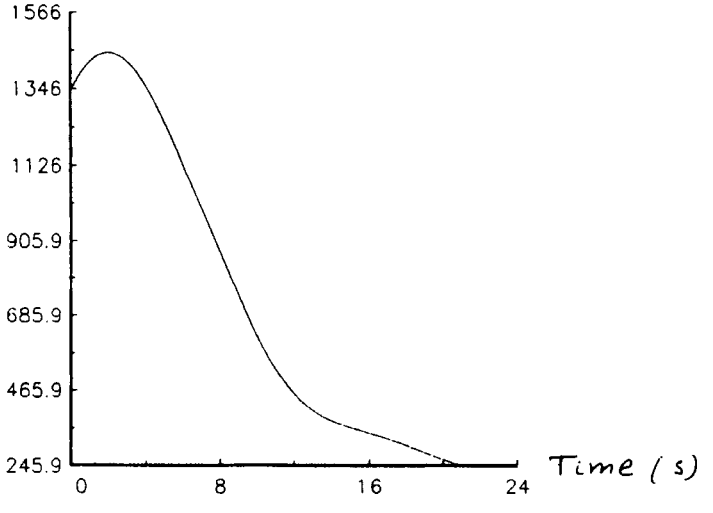

FIGURE 17 Dependence of relaxation modulus (*Pa*) vs. time for PB, $M = 8.3 \cdot 10^4$.

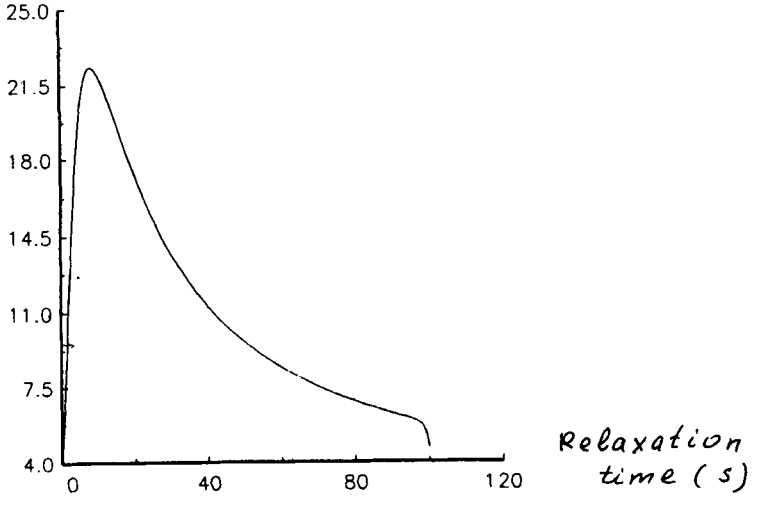

FIGURE 18 Relaxation time distribution spectra for PB, $M = 8.3 \cdot 10^4$, calculated according to data of Figure 17 and Equation (23).

Figures 15 and 16 present the nonnormalized functions $\dot{\gamma}^{\hat{h}}(t)$, $\tau^{\hat{\delta}}(t)$, respectively, used to find the function of the relaxation modulus $G^{\hat{\gamma}}(t)$, $\hat{\gamma} = (\hat{h}, \hat{\delta})$ according to the above algorithm (Figure 17).

The function $G(t)$ determines the initial data for calculating the relaxation spectrum of polybutadines (see Equation 1) with the aid of a linear intergral operator

$$G^{\hat{\gamma}}(t) = \int_0^{t'} \exp\{-t/\tau\} H(\tau)\, d\tau \tag{23}$$

The function $H(\tau)$ is shown in Figure 18. It should be noted that the calculation program (Figures 15–17) employs the rapid Fourier transform and can process arrays of a considerable size. The program for calculation of the relaxation spectrum according to the relaxation modulus $G(t)$, modulus of elasticity $G'(\omega)$ or loss modulus $G''(\omega)$ operates with an unsteady nucleus of the integral equation. This is why the algorithms of the rapid Fourier transform cannot be applied here, and the rapidity of program operation is based on the algorithm of rapid conversion of the initial matrix-nucleus to a tridiagonal form.

We noted above that $G(t)$, $G'(\omega)$, and $G''(\omega)$ are related by a pair of Fourier transforms. This is why applied programs can feed the functions $G'(\omega)$ and $G''(\omega)$ calculated by the functions $\tilde{\gamma}(t)$ and $\tilde{\tau}(t)$ into the output files of a computer.

Acknowledgment

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