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ORIGINAL CONTRIBUTION

Estimation of the relaxation spectrum from dynamic experiments using Bayesian analysis and a new regularization constraint

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Abstract The relaxation spectrum is estimated from dynamic experiments using Bayesian analysis and a new regularization constraint. In the Bayesian framework, a probability can be calculated for each estimate of the spectrum. This offers several advantages; (1) an optimal estimate of the relaxation spectrum may be calculated as the mean of a large number of estimates, and (2) reliable errors for the optimal estimate can be provided using the deviation of all estimates from the mean. Furthermore, the Bayesian approach (3) gives an estimate of the overall noise level of the experiment, which is usually an important but unknown parameter for the calculation of relaxation spectra from dynamic experiments by indirect methods (determining the regularization parameter), and finally, (4) the information content in a given set of experimental data can be quantified. The validity of the Bayesian approach is demonstrated using simulated data.

Keywords Rheology · Relaxation spectrum · Bayesian analysis

Introduction

The response of a linear viscoelastic material to strain excitation is given completely by the relaxation spectrum. For a stress excitation, the analogue is the retardation spectrum. The two spectra are related in a simple manner, and in principle, they contain identical information (e.g., Ferry 1980; Tschoegl 1989). However, for practical reasons, strain excitation is the more frequently used for dynamic experiments. Over the last couple of decades, many different methods have been tested for estimation of the relaxation spectrum from dynamic experiments. A complication for the estimation is that this inverse problem is underdetermined and ill conditioned; due to noise and truncation of the experimental data, many relaxation spectra may fit the experimental data adequately, and small errors in the data may lead to large changes in the estimated spectrum.

The mathematical difficulties can be overcome by regularization. However, a serious problem for regularization methods is that the overall noise level of the experiment is usually not known a priori. Especially when the information content of the data is small (as is frequently the case for viscoelastic measurements), it may be difficult to balance the weight of the data correctly against the weight of the regularization constraint. This may also lead to problems for calculation of the error of the estimated function. Another important complication is that the (subjective) choice of the regularization functional naturally influences the result—and often in a non-transparent manner.

The use of regularization methods in rheology has been studied by, e.g., Honerkamp and Weese (1989, 1990, 1993) who estimated the relaxation spectrum giving preferences to smoother solutions. In the absence of prior information about the shape of the relaxation spectrum, smooth solutions should be preferred over solutions containing more structural features. The smoothness of estimated spectrum was determined by

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the noise level of the data, the assumption of higher noise levels leading to smoother estimates.

Elster and Honerkamp (1991) applied the maximum entropy method to the estimation of relaxation as well as retardation spectra. Elster and Honerkamp (1991) used a slightly modified criterion for estimation of the noise level of the experiment as well as the conventional uniform prior in the regularizing expression for the entropy. However, the uniform prior and the maximum entropy method is known to lead to artificial peaks in the final estimate, which is due to the fact that the prior information is not expressed correctly by using the uniform prior (a uniform distribution is not a likely outcome of the experiment). An example of this is given below.

To avoid artificial peaks in the estimate, Emri and Tschoegl (1993) developed a filtering algorithm leaving out a part of the experimental data, which was assumed to be less relevant for estimation of a particular part of the relaxation spectrum. The algorithm was demonstrated to work well for exponential kernels as well as the Lorentzian kernels relevant for dynamic experiments (Tschoegl and Emri 1993).

The general-purpose program CONTIN, written by Provencher (1982a,b) for inverting noisy linear algebraic and integral equations by means of inverse Laplace transform, was modified and tested for estimation of the relaxation spectrum by Mead (1994) combining the Tikhonov regularization with moment constraints. The addition of the moments constraints had the advantage that the regularization parameter was less important than in the method of Honerkamp and Weese. Mao et al. (2001) used CONTIN in a similar manner for the estimation of the retardation spectrum from creep data. This was similar to the original and much tested application of CONTIN to photon correlation spectroscopy that ensured the reliability of the approach for this purpose.

Recently, Jensen (2002) applied Monte Carlo methods for the estimation of the relaxation spectrum. Monte Carlo methods are known to be computationally demanding and time consuming, frequently requiring more than 10^6 function evaluations to obtain the global optimum, but Jensen demonstrated using simulated annealing, that it was possible to obtain good agreement between experimental data and fit within reasonable CPU times, i.e., on the order of 1 min.

In the present manuscript, elements from several of the abovementioned regularization methods are included in a Bayesian framework. Furthermore, regularization by a new constraint is compared to the conventional smoothness constraint as well as to the maximum entropy method. The Bayesian method ascribes a probability to each estimate of the relaxation spectrum. The probabilities make it possible to calculate an average spectrum from the set of all spectra having non-negligible probabilities. The set of spectra with their associated probabilities also provides reliable error bars for the estimated (average) relaxation spectrum. The Bayesian method gives a probability distribution for the regularizing parameter (or Lagrange multiplier) that determines the relative weight of the data and the prior information—i.e., belief that the spectrum of interest is smooth, etc. This probability distribution gives an estimate of the overall noise level of the data as well as an error estimate of this number. Finally, the method leads to a logical and transparent calculation of the information content in a given data set. These points are demonstrated below using simulated data.

Theory

The relaxation spectrum

Dynamic experiments are usually analyzed in terms of a generalized Maxwell model consisting of an infinite number of springs and dashpots connected in parallel (Ferry 1980). A relaxation time τ is associated with each spring/dashpot-element from $\tau_i = \eta_i / E_i$, where η_i is the viscosity of dashpot i and E_i is the dynamic modulus of spring i. Writing ω for the angular frequency, the connection between the relaxation spectrum $H(\tau)$ and the measured storage and loss moduli, G' and G'' respectively, is given by two Fredholm integral equations (Tschoegl 1989)

$$G'(\omega) = G_0 + \int_0^\infty H(\tau) \frac{\omega^2\tau^2}{1+\omega^2\tau^2} \frac{\mathrm{d}\tau}{\tau} \tag{1}$$

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

For a viscoelastic liquid, the residual modulus $G_0 = 0$, and for a viscoelastic solid, $G_0 \neq 0$.

Having measured the moduli G'_m and G''_m at M frequencies $(\omega_1, \omega_2, \ldots \omega_M)$, Eqs. 1 and 2 take the discrete form:

$$G'_m(\omega_i) = G_0 + \int_0^\infty H(\tau) \frac{\omega_i^2\tau^2}{1+\omega_i^2\tau^2} \frac{\mathrm{d}\tau}{\tau} + e'_i \tag{3}$$

$$G''_m(\omega_i) = \int_0^\infty H(\tau) \frac{\omega_i\tau}{1+\omega_i^2\tau^2} \frac{\mathrm{d}\tau}{\tau} + e''_i \tag{4}$$

where e'_i and e''_i denote the experimental noise at the frequency ω_i.

Relation between time and frequency domains. As the experimental data are truncated at $\omega_{\min}$ and $\omega_{\max}$, limitations exist for the range $[\tau_{\min}; \tau_{\max}]$ where $H(\tau)$ can be estimated reliably. Often, it is assumed that an experiment done for frequencies in the interval $[\omega_{\min}; \omega_{\max}]$ will give information about relaxation times in the corresponding reciprocal interval $[\omega_{\max}^{-1}; \omega_{\min}^{-1}]$. However, as shown by Davies and Anderssen (1997), measurements done in the frequency range mentioned above only determines the relaxation spectrum in the interval $[e^{\pi/2}\omega_{\max}^{-1}; e^{-\pi/2}\omega_{\min}^{-1}] \approx [5\omega_{\max}^{-1}; 0.2\omega_{\min}^{-1}]$. Hence, for estimation of the relaxation spectrum by indirect methods, the frequency range of the measurements has to be at least 1.4 decades larger than the range of the relaxation times. However, the correlation between points in the relaxation spectrum imposed by, e.g., a smoothness constraint may increase the "effective" range over which the spectrum can be estimated, but outside the theoretical limitations, the estimated relaxation spectrum is mainly determined by the regularization constraint.

Regularization

A general method for the treatment of underdetermined problems was described by Tikhonov and Arsenin (1977). A function of interest H is estimated by minimizing a new functional written as a weighted sum of the chi-square χ^2 and a regularization functional S:

$$\alpha S(H) + \chi^2(H) \tag{5}$$

The χ^2 is defined in the conventional manner, i.e., for measurements at M frequencies

$$\chi^2(H) = \sum_{i=1}^{M} \frac{(G'_{\mathrm{m}}(\omega_i) - G'(\omega_i))^2}{\sigma'^2_i} + \sum_{i=1}^{M} \frac{(G''_{\mathrm{m}}(\omega_i) - G''(\omega_i))^2}{\sigma''^2_i} \tag{6}$$

where—leaving out primes—$G_{\mathrm{m}}(\omega_i)$ is the measured modulus, $G(\omega_i)$ is the calculated modulus, and σ_i is the standard deviation of the Gaussian noise, all at data point i. As G is related to H through Eqs. 1 and 2, χ^2 depends upon H.

By minimizing Eq. 5, a solution will be found that fits the data adequately as expressed by the χ^2, while simultaneously minimizing the additional constraint from the regularization functional S. Hence, the regularization parameter α determines the relative weight of the constraint from the data and regularization functional. Each estimate of α will correspond to an estimate of the noise level of the experiment as Eq. 5 is minimized.

Estimation of errors for $H(\tau)$ directly from Eq. 5 may lead to erroneous results (Honerkamp and Weese 1989) especially for cases where the regularizing parameter α is large (Hansen and Wilkins 1994). This is due to the fact that large values of α may dominate the Hessian of the regularizing functional that will lead to error estimates that are too small.

Choice of regularization functional. For the choice of regularization functional, several forms for S exist. The most frequently used regularization functional is $S = \int H''(\tau)^2 \, \mathrm{d} \ln \tau$, which gives preference to smooth functions $H(\tau)$. As the measurements often cover several orders of magnitude in frequency, a logarithmic scale is used for the corresponding relaxation time, i.e., $\tau_{i+1}/\tau_i = \text{const}$. Assuming $H(\tau_{\min}) = H(\tau_{\max}) = 0$, this regularization expression takes the discrete form

$$S(H) = \sum_{j=2}^{N-1} \left(H_j - \frac{(H_{j-1} + H_{j+1})}{2} \right)^2 + \frac{1}{2} H_1^2 + \frac{1}{2} H_N^2 \tag{7}$$

Omitting the terms H_1 or H_N will allow the endpoints of the estimate to vary freely, only constraining H_1 or H_N by the values of their neighboring points.

For regularization by the maximum entropy method (Elster and Honerkamp 1991; Skilling 1988), $S = \int [H(\tau) \ln(H(\tau)/m(\tau)) - H(\tau) + m(\tau)] \, d \ln \tau$, which (again on a log scale) takes the discrete form

$$S(H) = \sum_{j=1}^{N} H_j \ln \left(H_j / m_j \right) - H_j + m_j \tag{8}$$

where $(m_1, ..., m_N)$ is a prior estimate of $(H_1, ..., H_N)$. Using this method will bias the estimate toward the prior, (i.e., for the case of no constraints from the experimental data, minimizing Eq. 5 will lead to $H = m$).

As noted in Steenstrup and Hansen (1994) for $H \approx m$, a second order Taylor approximation of the entropy constraint Eq. 8 gives

$$S(H) \approx \sum_{j=1}^{N} \left[\left(H_j - m_j \right)^2 / 2 m_j \right] \tag{9}$$

From this equation, it can be seen that, using a prior $m_j = (H_{j+1} + H_{j-1})/2$, the maximum entropy constraint corresponds to the smoothness constraint Eq. 7 in a new metric defined by the denominator $2m_j$ in Eq. 9. Using this metric will combine the positivity constraint of Eq. 8 with the smoothness constraint of Eq. 7. For estimation of relaxation spectra, this particular constraint has some appealing qualities as will be demonstrated below.

Bayesian analysis

Estimation of α. Various principles for estimation of the regularization parameter α (which is equivalent to estimation of the overall noise level of the experiment) may be found in the literature. Honerkamp and Weese (1990) demonstrated that the features of the estimated relaxation spectrum were quite sensitive to the choice of regularization parameter. Using a Bayesian approach as described in MacKay (1992), the (posterior) probability P for the regularization parameter α can be calculated according to

$$P(\alpha) = \left(\left(\frac{1}{2}\right)^N (N+1)\right)^{1/2} \frac{\exp(-\alpha S - \chi^2/2)}{\det^{1/2}(\mathbf{A}+\mathbf{B})} \qquad (10)$$

using the regularization from Eqs. 5 and 7, writing $\mathbf{A} = \nabla\nabla S$ and $\mathbf{B} = \nabla\nabla\chi^2/2$. In Eq. 10, both matrices as well as $(-\alpha S - \chi^2/2)$ have to be evaluated at the point $(H_1, ..., H_N)$ where $(-\alpha S - \chi^2/2)$ takes its maximum value (for details see also Hansen 2000 and Vestergaard and Hansen 2006).

By Eq. 10, a probability is ascribed to each estimate of α (corresponding to a specific noise level of the experimental data). For each α, the best estimate $H_\alpha(\tau)$ is given by the minimum of Eq. 5, and the average $\langle H_\alpha(\tau)\rangle$ is calculated from all these solutions ($\langle\cdot\rangle$ denoting average over α). Using this method, no choice of a single value for the regularization parameter is necessary. For the examples shown below, the values of α that have non-negligible probabilities were found within one or two decades (see, e.g., Fig. 6), but all values of α were used in the calculation of the average. Calculation of $H_\alpha(\tau)$ for several hundreds values of α only requires a few seconds of CPU time. Typically, 200 different solutions of $H_\alpha(\tau)$ corresponding to 200 different values of α were used for each of the examples shown below. Increasing this number by diminishing the difference between two consecutive α's and/or extending the limits for α did not influence the final estimate. The variance for $H(\tau)$ can be determined from $\langle[\langle H_\alpha(\tau)\rangle - H_\alpha(\tau)]^2\rangle$ by using all the calculated solutions with their respective probabilities.

A further advantage of the Bayesian selection of the regularization parameter is that it is easily generalized to two noise levels for the same data set, which may be relevant to viscoelastic measurements, as the overall noise level for the storage modulus often differs from the overall noise level of the loss modulus. This will increase the necessary CPU time, but a calculation may still be done in less than 1 min with the present algorithm, which may be optimized further if necessary.

Information in the data—quantification. As a measure of the information content in the data, the "number of good parameters" N_g (e.g., Gull 1989) has been suggested from regularization by the maximum entropy method:

$$N_g = \sum_{j=1}^{N} \frac{\lambda_j}{\alpha + \lambda_j} \qquad (11)$$

Here, λ_j are the eigenvalues of $\mathbf{B}$ and α is the Lagrange multiplier of Eq. 5. By this equation, N_g "counts" the number of eigenvalues of $\mathbf{B}$, which is large compared to the Lagrange multiplier α, balancing the information in the data (eigenvalues for $\mathbf{B}$) against the weight of the regularizing functional or prior (eigenvalues for $\alpha\mathbf{A}$). For entropy regularization $\mathbf{A} = \mathbf{I}$, where $\mathbf{I}$ is the unity matrix. Hence Eq. 11 gives the number of directions in parameter space, which is determined well for the given noise level. For the general case—using other forms of regularization than maximum entropy—the denominator of Eq. 11 has to be replaced by the eigenvalues of the matrix $\alpha\mathbf{A} + \mathbf{B}$ (see, e.g., MacKay 1992). Overfitting the data will reduce the Lagrange multiplier α and increase N_g, whereas underfitting the data will have the opposite effect.

As the amount of new information in a given data set is dependent upon the prior knowledge, the number of good parameters in a given data set is dependent upon the regularization functional that expresses the prior knowledge. Mathematically, the information (entropy) is measured relative to a prior as given by Eq. 8—Changing the prior will change the information content of a given data set. As such, N_g is a relative number.

It should be noted that estimating N_g good parameters from the data corresponds to reducing the number of degrees of freedom for the χ^2 by N_g, which is similar to the conventional reduction of the number of degrees of freedom for the χ^2 by the number of fitting parameters. Fitting the "true" information in the data invariably leads to fitting of some of the noise as well (see MacKay 1992). Writing the reduced χ_r^2 for M data points leads to

$$\chi_r^2 = \frac{M}{M + N_g} \qquad (12)$$

For a recent overview paper on Bayesian inference in physics, see, e.g., Dose (2003).

Results and discussion

For the purpose of comparing the regularizing functionals described above in combination with the

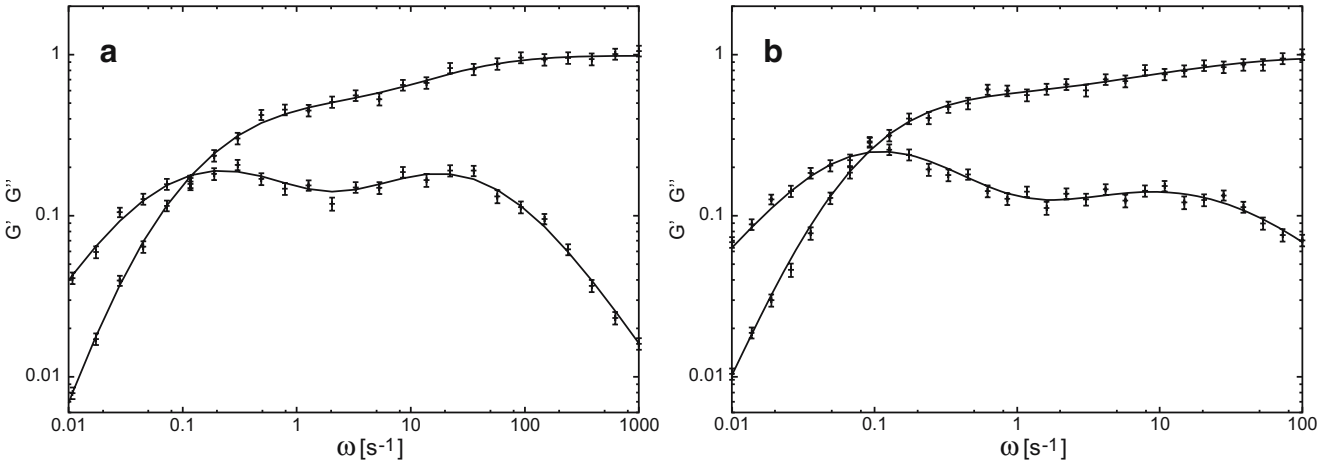


Fig. 1 **a** *Error bars* simulated data from example a added 8% Gaussian noise. *Full line* typical fit of data. **b** *Error bars* simulated data from example b added 8% Gaussian noise. *Full line* typical fit of data

Bayesian method to previous results for estimation of the relaxation function, examples similar to those of Honerkamp and Weese (1989, 1990) have been chosen. Two relaxation functions $H(\tau)$ have been used for the simulated data, one having two well-separated peaks of equal intensity and equal width and one having

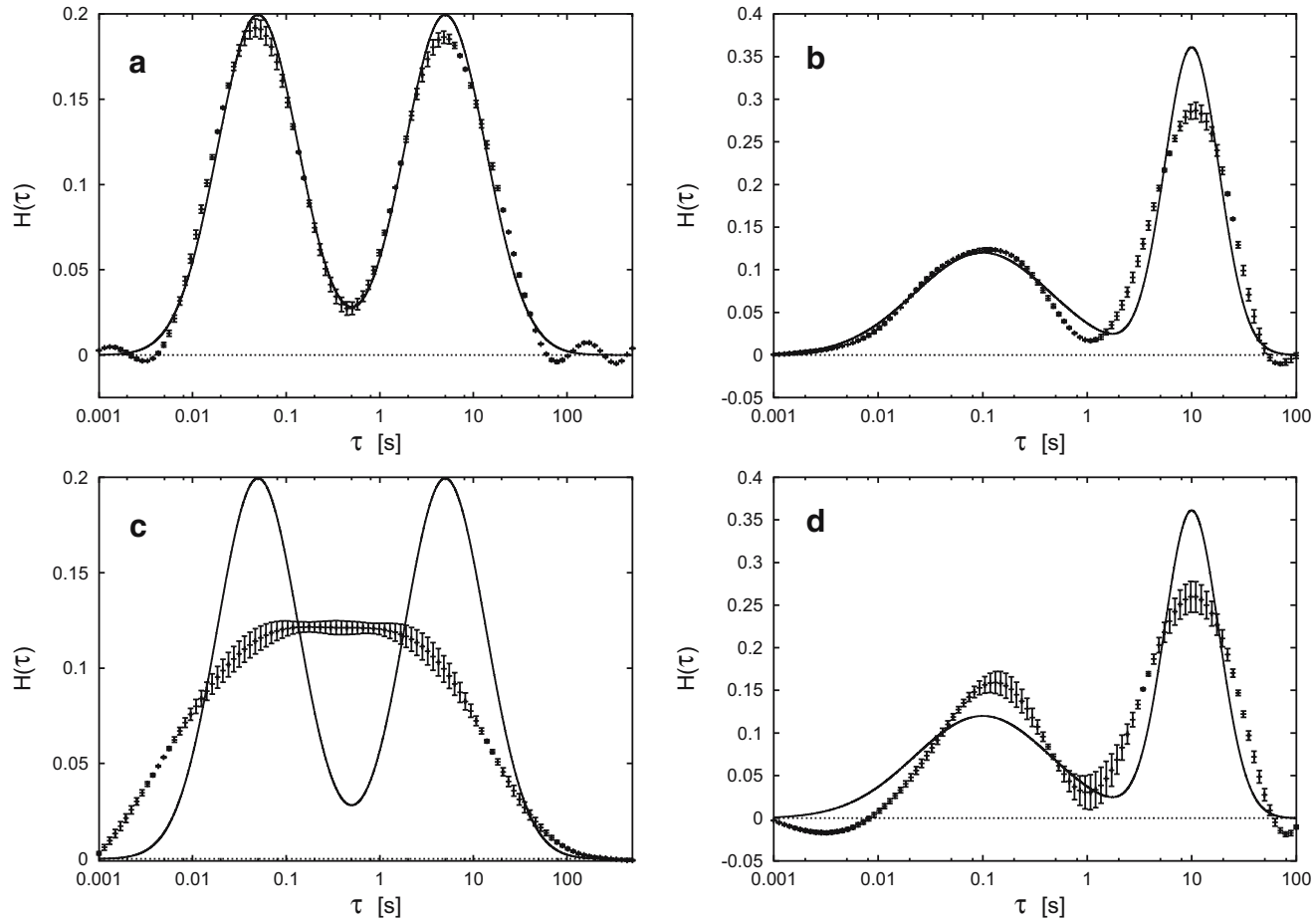


Fig. 2 **a** *Full line* original relaxation spectrum example a. *Error bars* estimated relaxation spectrum using smoothness constraint Eq. 7 and data with 4% noise. **b** *Full line* original relaxation spectrum example b. *Error bars* estimated relaxation spectrum using smoothness constraint Eq. 7 and data with 4% noise. **c** + **d** corresponding results for 24% noise

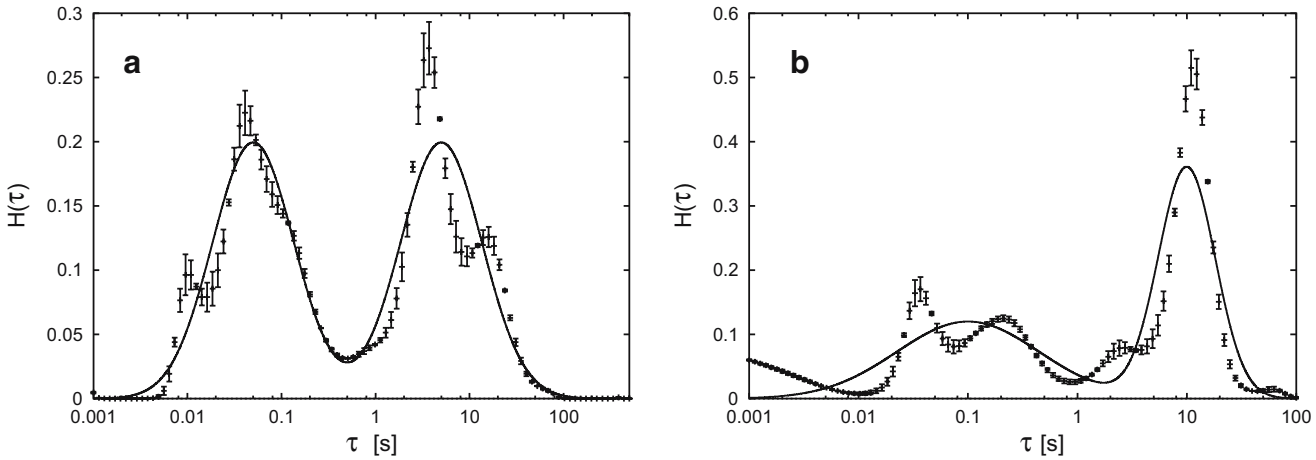


Fig. 3 **a** *Full line* original relaxation spectrum example a. *Error bars* estimated relaxation spectrum using entropy constraint Eq. 8 and 4% noise. **b** *Full line* original relaxation spectrum example b. *Error bars* estimated relaxation spectrum using entropy constraint Eq. 8 and 4% noise

two peaks of different intensities and different widths. These examples are referred to below as a and b, respectively, and the functions are shown in Fig. 2.

Furthermore, an example of a relaxation spectrum consisting of the superposition of two power laws was tested. This Baumgaertel–Schausberger–Winter (BSW) spectrum (Baumgaertel et al. 1990; Jackson et al. 1994) simulates the relaxation spectrum of a linear polymer, and the example chosen corresponds to polystyrene of molecular weight $1.0 \cdot 10^6$ (see Fig. 5). Further details about the mathematical form of the tested relaxation spectra can be found in Honerkamp and Weese (1990) and Baumgaertel et al. (1990).

From the original "true" relaxation functions, $H_{\text{true}}(\tau)$ storage and loss moduli $G'(\omega)$ and $G''(\omega)$ were calculated (Fig. 1), using $M = 30$ points for each modulus (corresponding to the examples of Honerkamp and Weese 1989, 1990) for examples $a + b$. Finally, for each data set, Gaussian noise of 1, 4, 8, 16, and 24% were added to $G'(\omega)$ and $G''(\omega)$ giving the noisy moduli $G'(\omega)_m$ and $G''(\omega)_m$ (Eqs. 3 and 4) from which a relaxation spectrum $H_{\text{est}}(\tau)$ was estimated by minimizing Eq. 5.

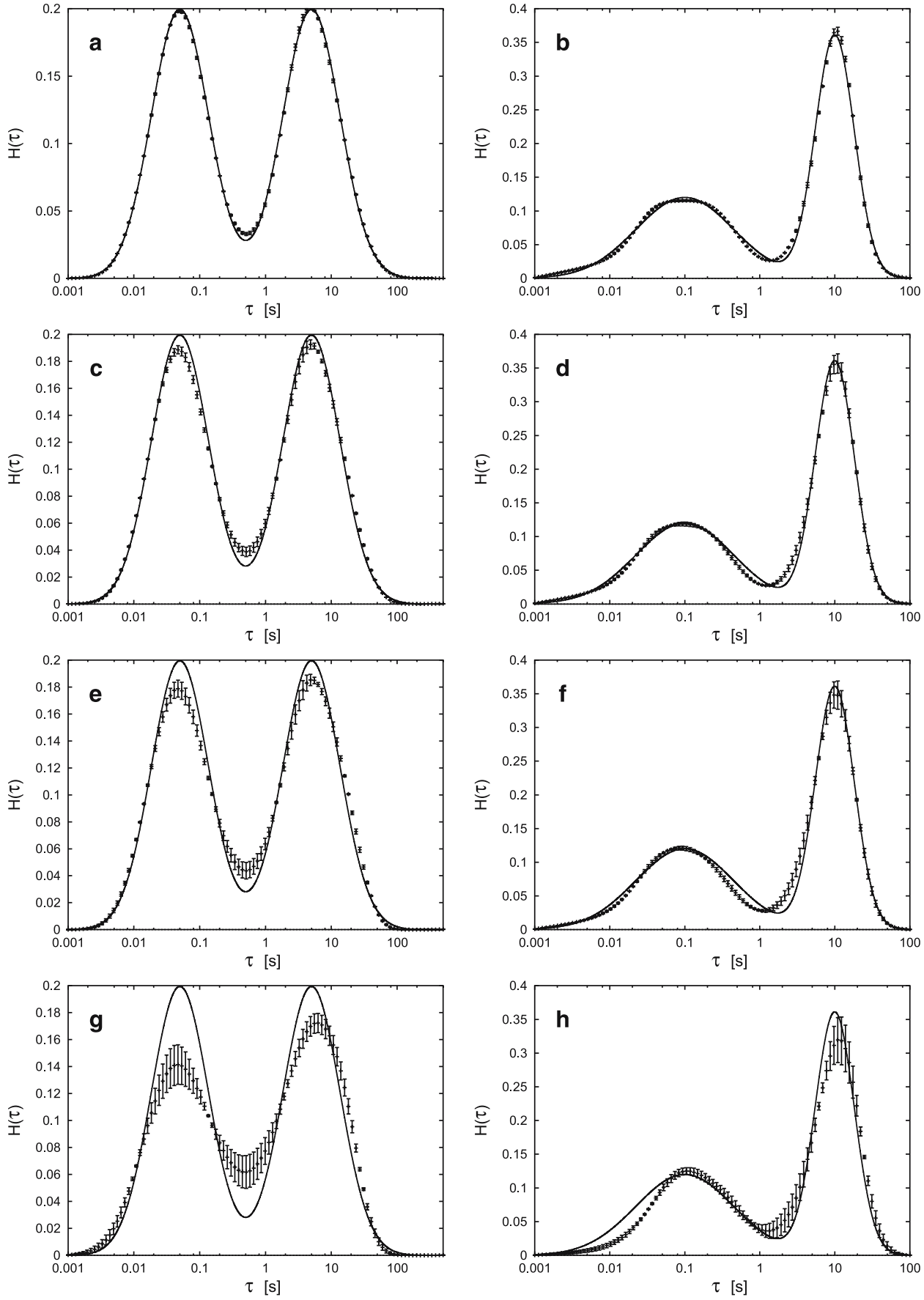
From the BSW relaxation spectrum, the corresponding moduli were calculated using $M = 50$ points for each modulus. The estimation of the BSW spectrum was tested for two noise levels: 2 and 10% in the same manner as the previous examples. The results are not sensitive to the number of points N used for estimation of $H(\tau)$ provided that N is chosen sufficiently large to account for the structure in the data (and of course provided that a stable algorithm is used). Above this number, an increase in N only increases the CPU time necessary for the calculations. For the examples given below, the number of points for estimation of the relaxation spectrum was $N = 100$. Variable spacing for τ may be used. The CPU time necessary for a complete calculation of a relaxation spectrum was about 5 s on a 2-GHz PC.

Honerkamp and Weese (1989, 1990) tested the regularization constraint $S(H) = \sum_{j=1}^{N} H_j^2$ as well as the conventional smoothness constraint Eq. 7 and found that the latter appeared to give slightly better results of the two. *Therefore*, only the smoothness constraint was tested below.

Results of the analysis using smoothness regularization (Eq. 7) are shown in Fig. 2. From the figures, it is evident that the missing positivity constraint may lead to nonphysical negative regions in the estimate. These estimates of $H(\tau)$ are in agreement with the results of Honerkamp and Weese (1989, 1990). Furthermore, it is seen that, for the highest noise level, the structure in example a is smeared out.

For maximum entropy regularization (Eq. 8), typical results of the analysis are shown in Fig. 3. A well-known artifact of this regularization method using a flat prior appears in the figures as oscillations ("line-splitting"). Furthermore, in Fig. 3b, it can be seen that the estimate is biased toward the (normalized) flat prior at low

Fig. 4 **a** *Full line* original relaxation spectrum example a. *Error bars* estimated relaxation spectrum using constraint Eq. 9 and 1% noise. **b** *Full line* original relaxation spectrum example b. *Error bars* estimated relaxation spectrum b using constraint Eq. 9 1% noise. **c** + **d** Corresponding results for 4% noise. **e** + **f** Corresponding results for 8% noise. **g** + **h** Corresponding results for 24% noise


a
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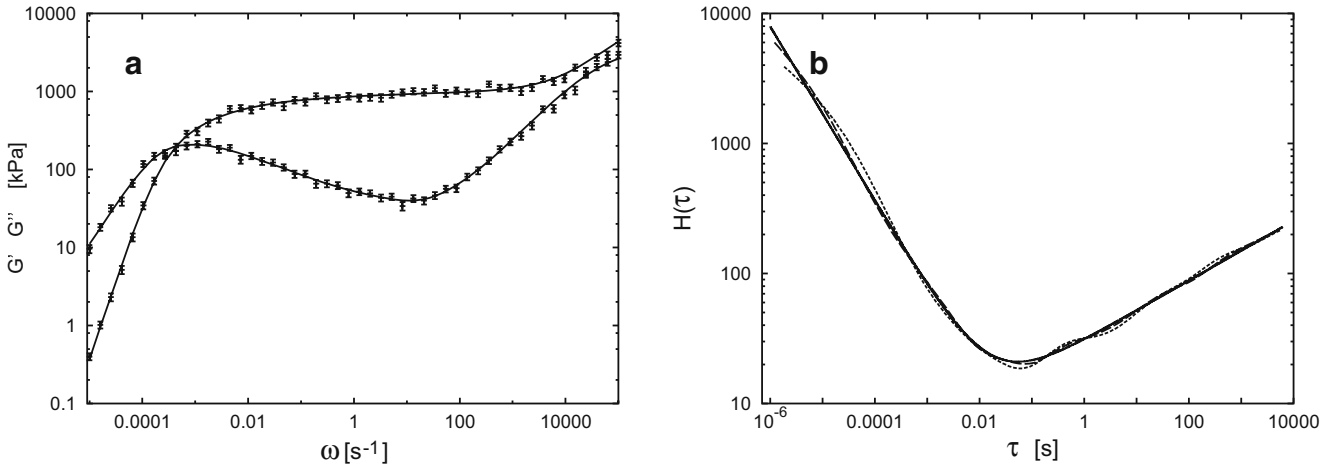

Fig. 5 **a** *Error bars* simulated data from BSW spectrum shown in **b** added 10% Gaussian noise. *Full line* fit of data. **b** *Full line* original relaxation spectrum. *Dashed line* estimated relaxation spectrum from data added 2% Gaussian noise. *Dotted line* estimated relaxation spectrum from data added 10% noise [corresponding to **a**]

relaxation times where the data do not impose strong constraints upon the estimate. According to the criteria mentioned in "The relaxation spectrum," the region $\tau < 0.01$ s is well outside the range of the data. Using a non-normalized flat prior of a lower numerical value will force the estimate toward zero at the low τ-values, but will also increase the line-splitting. Increasing α will reduce the oscillations, but will bias the estimate toward the flat prior and ignore relevant information in the data.

Using the entropy regularization (Eq. 9) with the prior $m_j = (H_{j+1} - H_{j-1})/2$ leads to the results shown in Fig. 4. By the positivity constraint, the negative estimates for $H(\tau)$ shown in Fig. 2 are avoided, and the smoothness constraint removes the oscillations of Fig. 3. The two peaks in example a using 24% noise are now resolved. This gives a clear indication that the positivity constraint (and the consequent reduction of hypothesis space) is important for the estimation of the relaxation function.

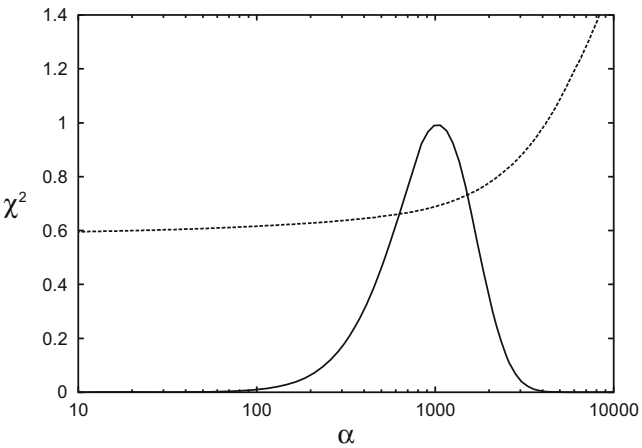

Fig. 6 *Full line* posterior probability for the Lagrange multiplier α calculated using Eq. 10. *Dotted line* χ^2 for fit calculated using Eq. 6

According to the criteria of Davies and Anderssen (1997), it should only be possible to estimate the relaxation spectrum reliably for τ in the range [0.005; 20] s for example a and in the range [0.05; 20] s for example b. The results shown in Fig. 4 demonstrate that the sensible regularization constraint combined with the fixed endpoints allow the estimation of the relaxation spectrum well outside the range of Davies and Anderssen (1997).

For each example and each noise level, the information in the data can be quantified using Eq. 11. Results are shown in Tables 1 and 2. The wider frequency range and extra structure in example a is reflected in the slightly larger N_g compared to example b. As the noise level of the simulated data is increased, N_g is decreased as should be expected. Quantification of the information content of experimental data may be relevant, e.g., to experimental design. As N_g can be calculated in real time while an experiment is done, N_g may be used to optimize the efficiency of experimental time. A sudden change in N_g could indicate deterioration of the sample that is also relevant information for the experimentalist.

Contrary to the first simulated examples, the BSW spectrum is not expected to have $H(\tau) = 0$ at the endpoints. Consequently, the constraint in Eq. 7 has to be changed. For the estimation of the BSW spectrum in Fig. 5, the endpoints of the estimate of $H(\tau)$ were allowed to vary freely, which was expressed through the prior given at the endpoints by $m_1 = m_2 \cdot m_3/m_4$ and $m_N = m_{N-1} \cdot m_{N-2}/m_{N-3}$.

Table 1 Results example a

%	N_g	$\langle\chi^2\rangle$	σ_{χ^2}	χ_r^2
1	8.36	0.824	0.036	0.861
4	5.85	0.863	0.045	0.902
8	4.73	0.873	0.046	0.921
16	3.34	0.911	0.058	0.944
24	2.16	0.947	0.053	0.964

The large dynamic range of the data and the truncation of the relaxation spectrum may lead to numerical problems that can be solved by reducing the step length (relaxation parameter) for the used algorithm at the cost of an increase in CPU time. Too large values of the step length resulted in local minima showing large oscillations in the solution. However, these solutions are characterized by a lower value for the evidence than the optimal solution found for the smaller step length. Honerkamp and Weese (1993) used a nonlinear regularization method for solving these numerical problems. The linear algorithm used for the present manuscript was not optimal for the large dynamical range, but it still gave satisfactory results.

The (unknown) maximum relaxation time $\tau_{\max}$ for $H(\tau)$ may be estimated either through the value of the evidence for a given $\tau_{\max}$ or simply by choosing the $\tau_{\max}$ that minimizes the value of the constraint $S(H)$. Using a smoothness constraint minimizing $S(H)$ will give the solution with less oscillations, but for the examples tested, the difference between the two approaches was small.

Figure 5b shows the result of estimations of $H(\tau)$ using noise levels of 2 and 10%, respectively. For the example using 2% noise, the estimate is almost identical to the original spectrum. However, for the example using 10% noise, the estimate suffers from small oscillations. The relative difference between the original spectrum H_{true} and the estimate H_{est} given as $[(H_{\text{true}} - H_{\text{est}})/H_{\text{true}}]^2$ calculated for τ in the interval $[10^{-5}, 10^5]$s was 0.162 and 0.924%, respectively. The corresponding estimate of the noise level of the simulated data calculated from the estimated moduli was 2.09 and 10.6%, respectively, which agree well with the simulated noise levels.

Table 2 Results example b

%	N_g	$\langle\chi^2\rangle$	σ_{χ^2}	χ_r^2
1	7.13	0.887	0.034	0.881
4	5.02	0.951	0.043	0.916
8	3.99	0.964	0.043	0.934
16	2.89	0.968	0.042	0.952
24	2.26	0.968	0.043	0.962

As mentioned previously, the estimation of the overall noise level of the data is very important for correct estimation of the relaxation function. Honerkamp and Weese (1990) compared three different methods for determination of the regularization parameter α. They found that the self-consistence (SC) method that selects α by minimizing the deviation between H_{est} and H_{true} gave reliable results and was superior to the other methods tested. However, Monte Carlo simulations indicated a systematic overestimation of α for the SC method compared to the optimal value for α.

The Bayesian estimation of the noise level for the simulated data was tested using the posterior probability for the Lagrange multiplier α given by Eq. 10. The posterior probability $P(\alpha)$ leads to a corresponding distribution of χ^2 as shown in Fig. 6. Consequently for each simulation, an average (estimated) $\langle\chi^2\rangle$ can be calculated as well as an error estimate σ_{χ^2} of this average. For a single calculation of each noise level, $\langle\chi^2\rangle$ and σ_{χ^2} are given in Tables 1 and 2. These values can be compared to the "correct" values of the corresponding reduced χ_r^2 given by Eq. 12 also shown in Tables 1 and 2. As indicated by the examples in the tables, there is very good agreement between the estimated noise level $\langle\chi^2\rangle$ and the correct noise level χ_r^2.

For 20 different simulations of example a with 8% noise corresponding values of $\langle\chi^2\rangle$, σ_{χ^2}, and χ_r^2 (for comparison, all normalized to $\chi^2 = 1$ for the simulated data sets) are shown in Fig. 7. Calculating $(\chi_r^2 - \langle\chi^2\rangle)^2/\sigma_{\chi^2}^2$ for a large number of simulations for both examples and all noise levels give average values close

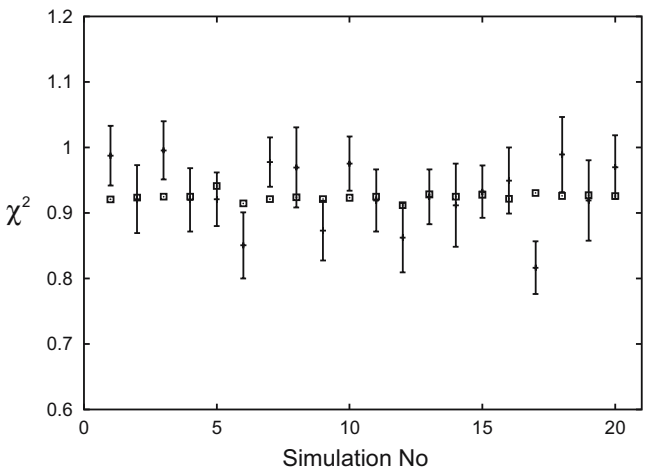

Fig. 7 *Error bars* estimated $\langle\chi^2\rangle$ for 20 simulations of example a using 8% noise and Eq. 9. *Boxes* χ_r^2 calculated using Eq. 12. For comparison, the simulated noise level for the examples in this figure was renormalized such that $\chi^2 = 1$

to 1. The good agreement between the theoretically predicted value and the estimated value of the noise level indicates that the Bayesian estimation of the overall noise level of the data is reliable and may give better results than the SC method, although more examples are needed to verify this.

Conclusion

Comparing the three methods of regularization gives a clear indication that a combination of the smoothness constraint and the maximum entropy metric will be appropriate for estimation of relaxation functions. Using this regularization in a Bayesian framework leads to (average) estimates that appear to be free of artifacts. Furthermore, the Bayesian method provides a large number of solutions with associated probabilities for each set of data, which makes it possible to calculate reliable errors for the average relaxation function. The overall noise level of an experiment may be estimated, including an error estimate of the noise level. An additional advantage of this method is that the user does not have to provide the program with any input parameters, which makes the method objective as well as easy to use. Finally, the information in a given set of experimental data may be quantified as a number of good (independent) parameters N_g that may be estimated from the data.

The Fortran source code used for the present manuscript is available from the author. The program calculates: (1) the optimal estimate of the relaxation function, (2) provided with error bars, as well as (3) an estimate of the overall noise level of the experiment. Finally, (4) the information content in the experimental data is calculated. No user input in the form of program parameters is required.

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