Modified Maximum Entropy Method and Its Application to Creep Data

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ABSTRACT: In addition to the regularization method the maximum entropy method is also a tool to solve ill-posed problems such as the determination of relaxation or retardation spectra from rheological measurements. Here we modify the maximum entropy method to make it more reliable. We demonstrate the method by testing it with synthetic data and by applying it to realistic creep data.

1. Introduction

The determination of the relaxation spectrum from the measurements of the dynamic moduli $G'(\omega)$ and $G''(\omega)$ is a particular example where an integral equation of the first kind must be solved. This task belongs to the class of inverse problems, which are known to be ill-posed.[1] In general, there is a linear relationship between a measurable quantity $G(\omega)$ and a distribution function $h(\tau)$ of the form

$$G(\omega) = \int_{-\infty}^{\infty} \mathrm{d} \ln \tau \, K(\omega,\tau) \, h(\tau) \tag{1.1}$$

where the kernel function, $K(\omega,\tau)$, is known from the theory. There will be noisy observations, g_i^σ, of the quantity $G(\omega)$ at ω_i, $i = 1, ..., N$, so that we may assume

$$g_i^\sigma = G(\omega_i)\,(1 + \sigma_0\eta_i) \equiv G(\omega_i) + \sigma_i \tag{1.2}$$

where η_i is a standard Gaussian random number and σ_0 may be called the relative error and σ_i the absolute error.

The determination of the function $h(\tau)$ from these observations $\{g_i^\sigma, i = 1, ..., N\}$ cannot be done with the help of the naive linear regression method by choosing $h(\tau)$ so that the discrepancy

$$\chi^2 = \sum_{i=1}^{N} \frac{1}{\sigma_i^2}[g_i^\sigma - \int_{-\infty}^{\infty} \mathrm{d} \ln \tau \, K(\omega_i,\tau) \, h(\tau)]^2 \tag{1.3}$$

is minimized. Such a solution would not depend smoothly on the data g_i^σ, $i = 1, ..., N$. Practically, if one approximates the integral by

$$\int_{-\infty}^{\infty} \mathrm{d} \ln \tau \, K(\omega_i,\tau) \, h(\tau) = \sum_{\alpha=1}^{M} K_{i\alpha} h_\alpha \tag{1.4}$$

where τ_α, $\alpha = 1, ..., M$, may be some set of well-chosen points, $K_{i\alpha}$ are the elements of the corresponding matrix and $h_\alpha = h(\tau_\alpha)$, it turns out that small changes in the data (well within the experimental errors) will largely change the solution h_α. This indicates that a solution obtained by linear regression is not reliable and more sophisticated tools must be applied.

The breakdown of the naive linear regression method has been elaborated, e.g., in ref 2, where a more sophisticated tool, the regularization method, has been applied to the determination of the relaxation spectrum from the data of the dynamic moduli $G'(\omega)$ and $G''(\omega)$ in polymer rheology. This regularization method is also used in a widespread program package CONTIN elaborated by Provencher.[3] The difficult point in this method is always the choice of the regularization parameter. In ref 4 a new method for this choise was introduced, which proved to be much more robust and reliable than earlier ones.

There is another method for treating such ill-posed problems, the maximum entropy method. This approach has already been widely used, e.g., in image processing,[5] in quasielastic light scattering,[6] and in the determination of particle size distribution from SANS data.[7]

The maximum entropy method makes use of the fact that for any distribution $h(\tau)$ (which is a positive semidefinite quantity) one may define the entropy

$$S[h] = -\int_{-\infty}^{\infty} \mathrm{d} \ln \tau \, h(\tau) \ln [h(\tau)/h_0(\tau)] \tag{1.5}$$

where $h_0(\tau)$ is some prior distribution, which represents the prior knowledge about the distribution before any measurements are made. We will set in the following $h_0(\tau) = h_0 =$ constant. If there is no further information, we would of course assume $h(\tau)$ to be equal to $h_0(\tau)$. This is exactly what we get if we maximize $S[h]$.

In our case, we know a little bit more about the distribution function, namely, that it should be compatible with the observations.

Let us denote as the overall discrepancy between the observations g_i^σ and the expected values of these based on the distribution function (where each individual discrepancy is weighted by the measurement error)

$$D(\tilde{g}^\sigma,h) = \sum_{i=1}^{N} \frac{1}{\sigma_i^2}[g_i^\sigma - \int_{-\infty}^{\infty} \mathrm{d} \ln \tau \, K(\omega_i,\tau) \, h(\tau)]^2 \tag{1.6}$$

One may require that this value should be equal to N. This ensures that in the mean each individual discrepancy is within the experimental error.

If we now maximize the entropy subject to the discrepancy constraint

$$D(\tilde{g}^\sigma,h) = N \tag{1.7}$$

then the solution $h(\tau)$ will differ from $h_0(\tau)$ by incorporating the information of the data. Hence, finding the distribution function with maximum entropy will lead to a solution that resembles most truly the information that one has and does not introduce more structure into the solution. A detailed search procedure for this version of the maximum entropy method was given by Skilling and Bryan.[8]

In this paper, we point out that this procedure must fail in some cases when $N > M$ and we give an improved version that is more robust. It is essentially the imposed constraint that is discussed and modified so that even with unrepresentative data a reliable solution is obtained. This

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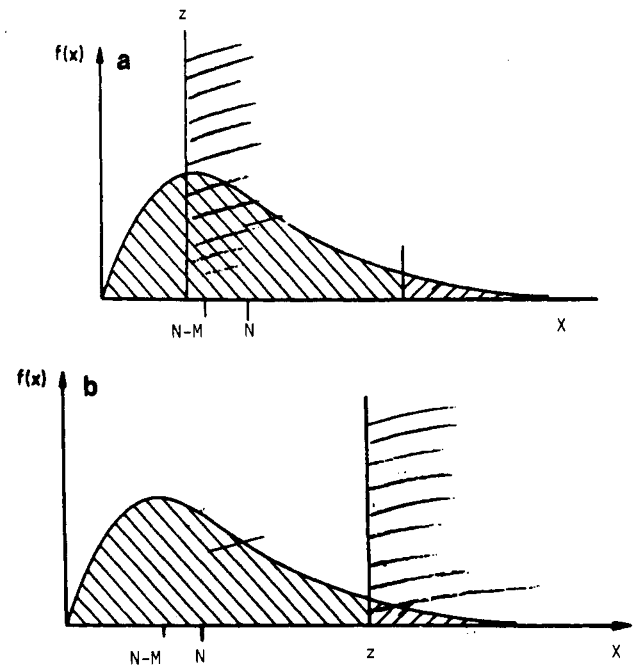

Figure 1. Density function of a χ^2 distributed random variable z with $N - M$ degrees of freedom. z is a realization of Z, and $D(\vec{g}^\sigma,\vec{h})$ can only lie right of z. Hence, in Figure 1b the usual discrepancy condition $D(\vec{g}^\sigma,\vec{h}) = N$ cannot be fulfilled.

is done in section 2, whereas in section 3 the superiority of the new version is demonstrated and applications are discussed.

2. Improved Discrepancy Constraint

In order to discuss the discrepancy constraint more deeply, let us introduce the discrepancy as a random variable

$$D(\vec{G},\vec{h}) = \sum_{i=1}^{N} \frac{1}{\sigma_i^2}(G_i - \sum_{\alpha=1}^{M} K_{i\alpha}h_\alpha)^2 \tag{2.1}$$

where $\vec{G} = (G_1, ..., G_N)$ is a random vector whose components G_i are random variables with $\langle G_i \rangle = G(\omega_i)$ and variance Var $(G_i) = \sigma_i^2$. g_i^σ is a realization of G_i. M was introduced as the number of gridpoints in τ and may be regarded as given in the following. If we define

$$Z = \min_h [D(\vec{G},\vec{h})] \tag{2.2}$$

then Z is a random variable that is χ^2 distributed with $N - M$ degrees of freedom. For a random variable with such a distribution, we have

$$\langle Z \rangle = N - M \tag{2.3}$$

A realization of Z, which we may call z, is exactly what we get, if for a realization of $\vec{G}$, namely, for the data g_i^σ, $i = 1, ..., N$, we apply the naive linear regression method.

Hence, for any vector $\vec{h} = (h_1, ..., h_M)$, we have

$$\langle D(\vec{G},\vec{h}) \rangle \geq \langle Z \rangle = N - M \tag{2.4}$$

and

$$D(\vec{g}^\sigma,\vec{h}) \geq z \tag{2.5}$$

How large the quantity

$$z = \min_h D(\vec{g}^\sigma,\vec{h}) \tag{2.6}$$

will be depends on the data. With some probability, z may lie in a region less than N; with some probability, z may be larger than N (see Figure 1a,b). Because of inequality (2.5), there will be no solution to the maximization of the entropy subject to the constraint

$$D(\vec{g}^\sigma,\vec{h}) = N \tag{2.7}$$

if the data are such that $z = \min_h D(\vec{g}^\sigma,\vec{h})$ is larger than N.

It is not the constraint

$$D(\vec{g}^\sigma,\vec{h}) = N \tag{2.8}$$

but

$$\langle D(\vec{G},\vec{h}) \rangle = N \tag{2.9}$$

that should be imposed. This could be realized by requiring, instead of (1.7) or (2.8)

$$D(\vec{g}^\sigma,\vec{h}) = z + M \quad \text{(sum condition)} \tag{2.10a}$$

or

$$D(\vec{g}^\sigma,\vec{h}) = \frac{N}{N-M}z \quad \text{(quotient condition)} \tag{2.10b}$$

which are realizations of

$$D(\vec{G},\vec{h}) = Z + M \tag{2.11a}$$

and

$$D(\vec{G},\vec{h}) = \frac{N}{N-M}Z \tag{2.11b}$$

respectively, and because of $\langle Z \rangle = N - M$ in both cases, the condition (2.9) is respected.

Hence, by using the sum or the quotient condition as constraint for the maximization of the entropy, we have to evaluate z for a given data set. This is easily done by applying the linear regression method, which gives

$$z = D(\vec{g}^\sigma,\vec{h}^*)$$

where

$$\vec{h}^* = (\mathbf{K}^t\mathbf{V}^{-1}\mathbf{K})^{-1}\mathbf{K}^t\mathbf{V}^{-1}\vec{g}^\sigma$$

and

$$V_{ij} = \delta_{ij}\sigma_i\sigma_j, \quad K^t_{ij} = K_{ji} \tag{2.12}$$

We close the section with three remarks.

(i) In the case where the evaluation of z in the above form leads to negative values of h_α^* for some α, this concept has to be changed. Because one knows that the relaxation spectrum must be positive semidefinite, one restricts the values of h_α^* to be nonnegative, e.g., replaces (2.12) by

$$z = \min_{\substack{\vec{h},\\ h_\alpha \geq 0}} D(\vec{g}^\sigma,\vec{h}) \tag{2.13}$$

An effective number of parameters, M_{eff}, is then defined through

$$M_{\text{eff}} = M - m \tag{2.14}$$

where m denotes the number of components h_α^* that are zero. We may thus write

$$z = \min_{\substack{\vec{h},\\ h_\alpha \geq 0}} D(\vec{g}^\sigma,\vec{h}) = D(\vec{g}^\sigma,\vec{h}) = \sum_{i=1}^{N} \frac{1}{\sigma_i^2}(g_i^\sigma - \sum_{\substack{\alpha=1\\ h_\alpha^* \neq 0}}^{M} K_{i\alpha}h_\alpha^*)^2 \tag{2.15}$$

where z is an unrestricted minimum of the M_{eff} parameters

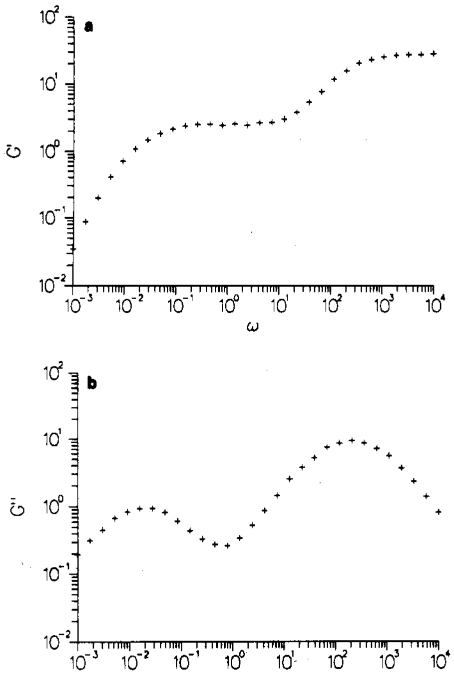

Figure 2. Generated dynamic moduli $G'(\omega)$ and $G''(\omega)$ according to (3.6) with the spectrum given in (3.1) and (3.2).

and therefore a realization of a random variable that is χ^2 distributed with $N - M_{\mathrm{eff}}$ degrees of freedom. Therefore, the quotient and sum condition are replaced by

$$D(\vec{g}^{\sigma},\vec{h}) = z + M_{\mathrm{eff}} \quad \text{(sum condition)} \tag{2.16a}$$

and

$$D(\vec{g}^{\sigma},\vec{h}) = \frac{N}{N - M_{\mathrm{eff}}} z \quad \text{(quotient condition)} \tag{2.16b}$$

respectively.

(ii) The maximum entropy method with the quotient condition can also be applied if the constant relative (or absolute) error, σ_0, is unknown. This follows immediately from the fact that the quotient condition contains only the ratio of $D(\vec{g}^{\sigma},\vec{h})$ and z, which is independent of σ_0. Hence, we may set $\sigma_0 = 1$ in determining $\vec{h}$. One may then find an estimate of σ_0 by putting

$$\sigma_0^{\,2} = \frac{z}{N - M_{\mathrm{eff}}} \tag{2.17}$$

(iii) The maximum entropy method is also applicable if the relation between measurable quantity and spectrum reads, e.g.

$$J(t) = J_0 + J_1 t + \sum_{\alpha=1}^{M} l_\alpha (1 - e^{-t/\tau_\alpha}) \tag{2.18}$$

That means if there is a polynomial trend function with coefficients J_0, J_1, ... that also must be determined, then one may formulate the entropy as usual

$$S[\vec{l}] = -\sum_{\alpha=1}^{M} l_\alpha \ln\,[l_\alpha / l_0] \tag{2.19}$$

and the discrepancy as

$$D(J_i,\vec{l}) = \sum_{i=1}^{N} \frac{1}{\sigma_i^{\,2}} [J_i^{\sigma} - J_0 - J_1 t_i - \sum_{\alpha=1}^{M} l_\alpha (1 - e^{-t_i/\tau_\alpha})]^2 \tag{2.20}$$

An application of the method to such a case will be pointed out in the next section, where a retardation spectrum will be determined from creep measurements.

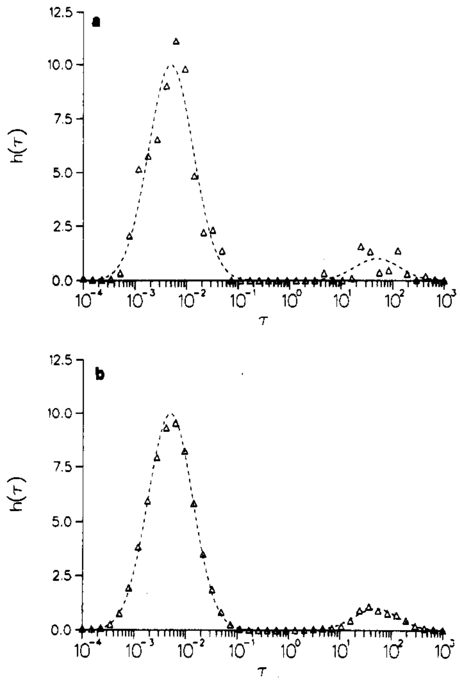

Figure 3. Dashed lines show the chosen model spectrum from (3.1) used to generate the data displayed in Figure 2, whereas the open triangles represent the reconstructions obtained by the discrepancy principle (Figure 3a) and the quotient condition (Figure 3b), respectively.

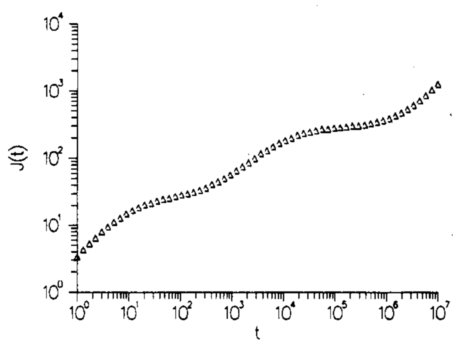

Figure 4. Synthetic creep data constructed according to (3.8) with a spectrum $\{l_\alpha,\ \alpha = 1, ..., 40\}$ generated as in (3.1) with parameters given in (3.7).

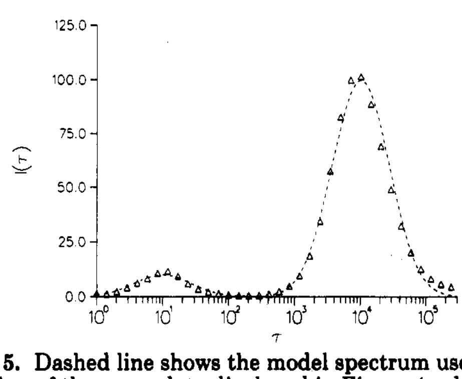

Figure 5. Dashed line shows the model spectrum used for the simulation of the creep data displayed in Figure 4, whereas the open triangles indicate the reconstructed spectrum.

3. Applications

In order to demonstrate the reliability and the robustness of the modified versions of the maximum entropy method, we apply the discrepancy method and the quotient method to some synthetic data of the dynamic moduli $G'(\omega)$ and

Table I

	by max entropy method		by linear regression	
T, °C	η_0	J_0^1	η_0	J_0^1
126	4.97×10^8	5.64×10^{-5}	$(5.01 \pm 0.13) \times 10^8$	$(5.78 \pm 0.38) \times 10^{-5}$
140	3.09×10^7	6.79×10^{-5}	$(3.12 \pm 0.03) \times 10^7$	$(7.43 \pm 0.60) \times 10^{-5}$
150	5.92×10^6	7.53×10^{-5}	$(6.00 \pm 0.07) \times 10^6$	$(8.37 \pm 0.85) \times 10^{-5}$
170	5.61×10^5	1.03×10^{-4}	$(5.68 \pm 0.06) \times 10^5$	$(1.12 \pm 0.12) \times 10^{-4}$

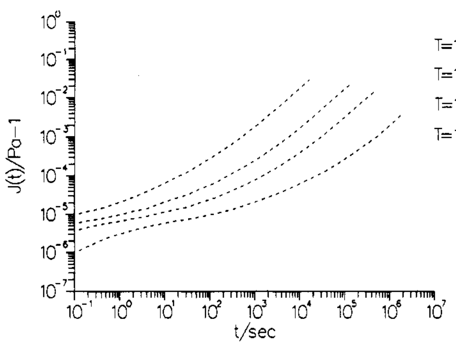

Figure 6. Creep measurements at technical polystyrol for various temperatures; data obtained from Schwarzl.[9]

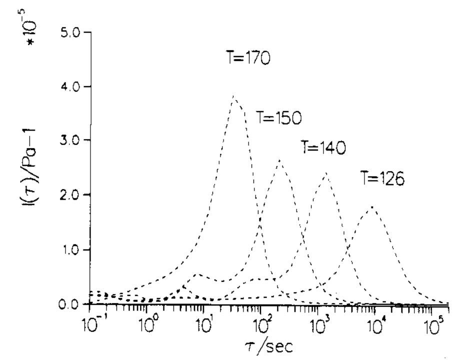

Figure 7. Evaluated retardation spectra of the data shown in Figure 6.

$G''(\omega)$. For the generation of the data, we choose a spectrum

$$h_\alpha = h_0[Ae^{-[\ln(\tau_\alpha/\tau_1)]^2/2\sigma_1^2} + Be^{-[\ln(\tau_\alpha/\tau_2)]^2/2\sigma_2^2}] \quad (3.1)$$

with

$$\tau_\alpha = \tau_a(\tau_b/\tau_a)^{(\alpha-1)/(M-1)}, \quad \alpha = 1, ..., M \quad (3.2)$$

and

$$\tau_a = 10^{-4}, \quad \tau_b = 10^3, \quad M = 40, \quad A = 10, \quad B = 1$$

$$\tau_1 = 5 \times 10^{-3}, \quad \tau_2 = 5 \times 10^1, \quad \sigma_1 = \sigma_2 = 1$$

so that the spectrum has two peaks at $\tau = 5 \times 10^{-3}$ and $\tau = 5 \times 10^1$ with width 1.

From this spectrum we computed

$$G'(\omega_i) = \sum_{\alpha=1}^{M} \frac{\omega_i^2\tau_\alpha^2}{1 + \omega_i^2\tau_\alpha^2} h_\alpha m_\alpha, \quad i = 1, ..., N \quad (3.3a)$$

$$G''(\omega_i) = \sum_{\alpha=1}^{M} \frac{\omega_i\tau_\alpha}{1 + \omega_i^2\tau_\alpha^2} h_\alpha m_\alpha \quad (3.3b)$$

with

$$\omega_i = \omega_a(\omega_b/\omega_a)^{(i-1)/(N-1)}, \quad i = 1, ..., N \quad (3.4)$$

$$m_\alpha = \ln(\tau_b/\tau_a)/(M-1) \quad (3.5)$$

$$\omega_a = 10^{-3}, \quad \omega_b = 10^4, \quad N = 30$$

and finally the synthetic data were obtained by

$$g_i'^\sigma = G'(\omega_i)\,(1 + \sigma_0 N(0,1)) \quad (3.6a)$$

$$g_i''^\sigma = G''(\omega_i)\,(1 + \sigma_0 N(0,1)) \quad (3.6b)$$

where $N(0,1)$ stands for a standard normally distributed random number and the relative error has been set equal to $\sigma_0 = 0.02$. We generated several realizations and took an unrepresentative one, i.e., one for which z from (2.12) is near N. These data are displayed in Figure 2.

Figure 3 shows the reconstruction of the spectrum with the discrepancy condition (constraint (1.7)) and the quotient condition (constraint (2.10b)). Whereas the traditional discrepancy condition fails to find the correct spectrum, the quotient condition leads to a good result. As an estimate for σ_0, we also obtain $\sigma_0 = 0.022$ in good agreement with $\sigma_0 = 0.02$.

Now we demonstrate the ability of the method to infer the retardation spectrum from creep data. We start with a spectrum of the same form as in (3.1) but now with parameters

$$\tau_a = 10^0, \quad \tau_b = 10^7, \quad \tau_1 = 10, \quad \tau_2 = 10^5$$

$$\sigma_1 = \sigma_2 = 1, \quad M = 40, \quad A = 1, \quad B = 10 \quad (3.7)$$

so that the spectrum has two peaks at $\tau = 10$ and $\tau = 10^5$ with width 1 and is calculated within the interval $(10^0, 10^6)$. With this spectrum l_α we generate creep data according to

$$J(t_i) = J(0) + \frac{1}{\eta_0}t_i + \sum_{\alpha=1}^{M} l_\alpha(1 - e^{-t_i/\tau_\alpha}), \quad i = 1, ..., N \quad (3.8a)$$

$$t_i = t_a\left(\frac{t_b}{t_a}\right)^{(i-1)/(N-1)}, \quad t_a = 10^0, t_b = 10^7 \quad (3.8b)$$

and we choose $J(0) = 0$ and $\eta_0 = 10^4$.

Figure 4 shows the synthetic data, where again an "experimental error" with relative strength $\sigma_0 = 0.02$ as in (1.2) has been introduced. Figure 5 shows the original spectrum and the reproduced one. The estimates for $J(0)$ and η_0 are

$$\hat{J}(0) = 10^{-10} \qquad \hat{\eta}_0 = 1.02 \times 10^4 \quad (3.9)$$

which are in good agreement with the exact ones. Also the spectrum is reproduced very well.

Finally we apply our method to realistic creep data of technical polystyrol[9] shown in Figure 6 for various temperatures T. The spectra we obtain are given in Figure

7. The corresponding estimates for η_0 and

$$J_0^1 = J(0) + \sum_{\alpha=1}^{M} l_\alpha \tag{3.10}$$

are given in Table I. These quantities could also be obtained by observing that $J(t)/t$ approaches a linear polynom of $1/t$ for $t \rightarrow \infty$:

$$J(t)/t \underset{1/t\rightarrow 0}{\rightarrow} \frac{1}{\eta_0} + [J(0) + \sum_{\alpha=1}^{M} l_\alpha]\frac{1}{t} + O\left(\frac{e^{-t/\tau}}{t}\right) \tag{3.11}$$

By linear regression we obtain the values for η_0 and J_0^1 also given in Table I, which are consistent with the estimates using the maximum entropy method.

One observes that the spectra are shifted according to the temperature–time superposition rule. Of course, each spectrum contains only the information of the whole spectrum restricted to a certain interval of retardation times.

4. Conclusions

We have shown that the maximum entropy method is a very general and efficient tool to infer distribution functions from experimental data, such as determining the relaxation spectrum from the dynamic moduli for polymer solutions. The method is modified in this paper to make it more robust and to allow applications to the case where the constant (relative) error is unknown. Also the determination of the retardation spectrum from creep data is possible. Our experience with the method is that it is very reliable. The comparison of the maximum entropy method with the regularization method also used by Provencher (CONTIN)[3] will be published elsewhere.

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