

# A NUMERICAL METHOD FOR THE CALCULATION OF THE RELAXATION AND RETARDATION SPECTRA FROM THE LINEAR VISCOELASTIC MODULUS AND COMPLIANCE

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The possibility of using the numerical inversion of the Laplace transform, which determines the value of the inverse function from the value of the transform within a limited interval, in the calculations of the relaxation  $H(\tau)$  and retardation  $L(\tau)$  spectra has been discussed. The testing of this numerical method on the time dependence of the modulus  $G(t)$  and compliance  $J(t)$  expressed in terms of the modified power law using a computer with the word length of 8 bytes led to an approximative solution  $H^a(\tau)$  or  $L^a(\tau)$ , which was in accordance with the exact spectrum  $H^e(\tau)$  or  $L^e(\tau)$ , the average error being less than  $10^{-3}\%$  of their absolute values over the whole range of the times  $\tau$ . This means a marked improvement in the accuracy of determination of the  $H^a(\tau)$  or  $L^a(\tau)$  values compared to all the approximation methods used so far. Two simple expressions are also given which allow to calculate  $L^a(\tau)$  or  $H^a(\tau)$ , if the course of  $J(t)$  or  $G(t)$  is known. The expressions are suited for laboratory purposes and do not require the use of computers, the relative deviation in the spectrum being less than 5% over the whole range of the times used.

It follows from Boltzmann's principle of superposition that the linear viscoelastic shear behaviour of polymers is fully characterized by the knowledge of the modulus  $G(t)$  or compliance  $J(t)$  within the whole interval of the current time<sup>1</sup>  $t$ . However, from the viewpoint of linear irreversible thermodynamics it is more advantageous to characterize the viscoelastic behaviour in terms of a function of the relaxation or retardation times  $\tau$  which can be expressed easier than  $t$  in terms of molecular processes (that is, in terms of the internal degrees of freedom of a macromolecule) responsible for the viscoelastic behaviour<sup>2</sup>. The transition from the function  $G(t)$  or  $J(t)$  to the relaxation  $H(\tau)$  or retardation  $L(\tau)$  spectrum respectively is then given, in principle, by an integral Laplace operator which defines the transfer from the representation of the variable  $t$  to the representation of the variable  $\tau$ . The knowledge of the spectra enables any other viscoelastic function to be calculated, thus allowing to compare information obtained by different experimental techniques.

Since it is usually not possible to express analytically the measured function within the whole time range, an important rôle in the determination of the viscoelastic spectra is played, on the one hand, by the approximation methods<sup>1</sup>, and on the other, by the numerical methods of inver-

sion of the Laplace transform<sup>3</sup>. The use of numerical methods has shown that the solutions are very often unstable, owing to the high sensitivity of the inversion operator to the reasonable perturbations. For instance, the numerical method based on the solution of the inversion of Laplace operator using a system of linear equations led, in the case of a major number of equations, to solutions which oscillated between positive and negative values having no physical meaning. An additional requirement of minimalization of the curvature of the final solution led to an improvement of the method and to a stable solution for the relaxation spectrum; the retardation spectrum still oscillated, however<sup>4</sup>. An advantage of the approximation methods which allow to determine the values of the spectra using the time derivatives of the modulus or compliance consist in their simplicity; they are frequently employed in practice, but their accuracy is not high because of an accumulation of errors during numerical differentiation.

Lately, a numerical method of inversion of the Laplace transform has been suggested, which determines the value of the inversion function from the value of the transform within a limited interval of its definition region<sup>5,6</sup>. This paper is dealing in detail with the possibilities of using the inversion method described above for the calculations of the relaxation and retardation spectra in the main transition and rubberlike region.

#### Basic Relationships

If a linear viscoelastic material is subjected at a time  $t = 0$  to a constant strain  $\gamma_0$  or a constant stress  $\sigma_0$ , then for the resulting stress relaxation  $\sigma(t)$  or time dependence of deformation  $\gamma(t)$  we obtain, using Boltzmann's principle of superposition,

$$\sigma(t) = G(t) \gamma_0, \quad \gamma(t) = J(t) \sigma_0, \quad (1)$$

where  $G(t)$  is the modulus and  $J(t)$  is compliance. Viscoelastic spectra in the form most frequently used are then defined by<sup>1</sup>

$$G(t) = G_e + \int_{-\infty}^{+\infty} H(\tau) e^{-t/\tau} d \ln \tau, \quad (2a)$$

$$J(t) = J_0 + \int_{-\infty}^{+\infty} L(\tau) (1 - e^{-t/\tau}) d \ln \tau + t/\eta; \quad (2b)$$

here,  $G_e$  is the equilibrium value of the modulus for  $t \rightarrow \infty$ ,  $J_0$  is the instantaneous compliance value,  $\eta$  is viscosity (in the case of a crosslinked system  $\eta \rightarrow \infty$ ).  $H(\tau)$  or  $L(\tau)$  respectively are the logarithmic spectra of the relaxation or retardation times, and  $\tau$  is a variable (relaxation or retardation time). It also holds

$$\int_{-\infty}^{+\infty} H(\tau) d \ln \tau = G_0 - G_e, \quad \int_{-\infty}^{+\infty} L(\tau) d \ln \tau = J_e - J_0, \quad (3)$$

where  $G_0$  is the instantaneous (glassy) modulus and  $J_e$  is the equilibrium value of the viscoelastic part of the compliance.

The majority of the approximation methods originate in Post-Widder's formula<sup>7</sup>, which for the spectrum  $H(\tau)$  has the form

$$H(\tau) = \lim_{n \rightarrow \infty} \frac{(-1)^n}{(n-1)!} (n\tau)^n \left. \frac{d^n G(t)}{dt^n} \right|_{t=n\tau} \quad (4a)$$

and for the spectrum  $L(\tau)$ , the form

$$L(\tau) = \lim_{n \rightarrow \infty} \frac{(-1)^{n+1}}{(n-1)!} (n\tau)^n \left. \frac{d^n J(t)}{dt^n} \right|_{t=n\tau} \quad (4b)$$

Owing to the accumulation of errors during numerical differentiation of the experimental data, the second derivative is used at the utmost to estimate the limit, and the respective relationships are called Schwarzl-Staverman's approximations<sup>1,7</sup>.

#### Calculation of the Viscoelastic Spectra

Equation (2) can be rewritten in the form

$$G(t) - G_e = \int_0^\infty \frac{H(1/u)}{u} e^{-tu} du = \int_0^\infty \mathcal{H}^a(u) e^{-tu} du, \quad (5)$$

which represents Laplace transform in the usual form. The modified Gaver's method<sup>6</sup> leads to an approximative value of the inversion  $\mathcal{H}^a(u)$  from Eq. (5) in the form

$$\mathcal{H}^a(u) = \frac{\ln 2}{u} \sum_{i=1}^N V_i g \left( i \frac{\ln 2}{u} \right); \quad (6)$$

$N$  is a number characterizing the accuracy of approximation (the accuracy of the method increases with increasing  $N$ ),  $g[(\ln 2/u) i] = G[(\ln 2/u) i] - G_e$ , and the coefficients  $V_i$  are given by<sup>6</sup>

$$V_i = (-1)^{i+N/2} \sum_{k=[(i+1)/2]}^{\min(i, N/2)} \frac{k^{1+N/2} (2k)!}{(N/2 - k)! k! (k-1)! (i-k)! (2k-i)!} \quad (7)$$

It follows from Eq. (7) that  $N$  must be an even number and that the coefficients  $V_i$  depending on  $N$  are not affected by the course of the function  $g$ . Combining Eqs (5) and (6) gives for an approximative value of the relaxation spectrum  $H^a(\tau)$

$$H^a(\tau) = \ln 2 \sum_{i=1}^N V_i g(i\tau \ln 2). \quad (8)$$

It follows from Eq. (8) that to determine the spectrum in the point  $\tau$  it is necessary to know the values of the function  $g$  in the surroundings of the point  $t = \tau$ . This means that it is also necessary to know the equilibrium value  $G_e$  (in the case of crosslinked systems). However, in many cases the relaxation experiments are not carried out up to equilibrium. To determine  $H^a(\tau)$  it is then necessary either to use some extrapolation method<sup>8</sup> for the determination of  $G_e$ , or to apply the following procedure: On differentiating Eq. (2a) with respect to  $t$  it can be written

$$\frac{dG(t)}{dt} = \dot{G} = - \int_{-\infty}^{+\infty} \frac{H(\tau)}{\tau} e^{-t/\tau} d \ln \tau, \quad (9)$$

and by analogy with Eq. (8), the expression for the calculation of the spectrum acquires the form

$$H^a(\tau) = -\tau \ln 2 \sum_{i=1}^N V_i \dot{G}(i\tau \ln 2). \quad (10)$$

Comparing Eqs (2a) and (2b) and using Eqs (5) and (8), we obtain a similar expression for the calculation of the approximative value of the retardation spectrum  $L^a(\tau)$

$$L^a(\tau) = \ln 2 \sum_{i=1}^N V_i j(i\tau \ln 2), \quad (11)$$

where  $j(i\tau \ln 2) = J_e - J(i\tau \ln 2) + t/\eta$ . The constant  $J_e$  can be excluded by differentiating Eq. (2b) with respect to  $t$ , thus obtaining

$$L^a(\tau) = \tau \ln 2 \sum_{i=1}^N V_i [\dot{J}(i\tau \ln 2) - 1/\eta], \quad (12)$$

where  $\dot{J} = dJ(t)/dt$ . A further differentiation of Eq. (2b) with respect to time  $t$  allows to remove also the constant  $\eta$  and to write the spectrum in the form

$$L^a(\tau) = -\tau^2 \ln 2 \sum_{i=1}^N V_i \ddot{J}(i\tau \ln 2), \quad (13)$$

where  $\ddot{J} = d^2J/dt^2$ .

## DISCUSSION

### *Application to the Case of the Relaxation Modulus*

To test the accuracy of the method, we chose the course of the modulus in the form

$$G(t) = G_e + (G_0 - G_e)(1 + t/k)^{-n}, \quad (14)$$

from which it is possible, by using the inversion of Laplace transform, to obtain an exact relaxation spectrum

$$H^e(\tau) = \frac{G_0 - G_e}{\Gamma(n)} \left(\frac{k}{\tau}\right)^n \exp(-k/\tau), \quad (15)$$

where  $\Gamma(n)$  is the  $\Gamma$ -function. The constants had the values  $G_0 = 10^{10}$  dyn/cm<sup>2</sup>,  $G_e = 10^6$  dyn/cm<sup>2</sup>,  $n = 0.5$  and  $k = 100$ , typical of the course of the modulus in the main transition region of the polymers. The results were computed using a Tesla-200 computer with the word length of 8 bytes, which allowed to calculate up to 17 valid figures. The relaxation spectrum was calculated in the region of the relaxation times  $10^1 \leq \tau \leq 10^{30}$ .

Theoretically, it can be expected that the higher the value of  $N$ , the greater the accuracy with which the spectra are determined. Since, however, the absolute values

of the coefficients  $V_i$  increase with increasing  $N$ , it can be expected as a consequence of the rounding-off errors that the overall accuracy of the method passes through a maximum at a given word length on the computer. To characterize the deviation of the approximation spectrum from an exact one (Eq. (15)), we chose the mean square deviation

$$\bar{\varepsilon} = \left[ \sum_{i=1}^M \varepsilon^2(\tau_i) \right]^{1/2} / M = \left\{ \sum_{i=1}^M [\log \{H^e(\tau_i) / H^a(\tau_i)\}]^2 \right\}^{1/2} / M, \quad (16)$$

while  $\log \tau_i$  was changing its value by 0.1 within the region  $1 \leq \log \tau_i \leq 30$ ; i.e.  $M = 291$ . The most accurate approximation was reached for  $N = 16$ , where  $\bar{\varepsilon} \approx 10^{-3}$ ; Schwarzl-Staverman's approximation method leads in the same region to  $\bar{\varepsilon} = 0.177$  (first approximation  $n = 1$ ) and  $\bar{\varepsilon} = 0.145$  (second approximation  $n = 2$ ), which are higher by two orders of magnitude. A detailed comparison of  $H^e(\tau)$

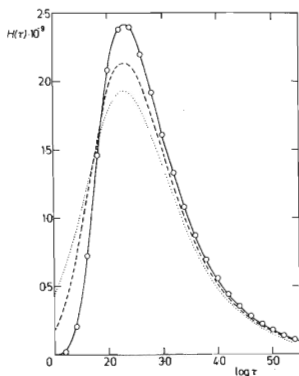


FIG. 1

Dependence of the Relaxation Spectrum  $H(\tau)$  (dyn cm $^{-2}$ ) on Time  $\tau$  (s)

..... Schwarzl-Staverman,  $n = 1$ ;  
 ----- Schwarzl-Staverman,  $n = 2$ ;  $\circ$  method used in this work,  $N = 16$ ; ——— exact spectrum, Eq. (15).

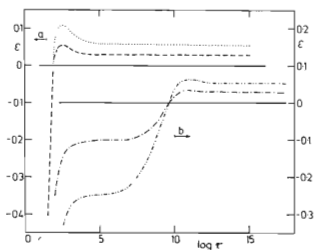


FIG. 2

Dependence of the Relative Deviation  $\varepsilon$  on Time  $\tau$  (s)

.....  $H(\tau)$ , Schwarzl-Staverman,  $n = 1$ ;  
 -----  $H(\tau)$ , Schwarzl-Staverman,  $n = 2$ ;  
 .....  $L(\tau)$ , Schwarzl-Staverman,  $n = 1$ ;  
 -----  $L(\tau)$ , Schwarzl-Staverman,  $n = 2$ ;  
 ——— method used in this work  $H(\tau)$  for  $N = 16$ ,  $L(\tau)$  for  $N = 14$ .

and  $H^a(\tau)$  shows that the mean values of  $\bar{\varepsilon}$  over the whole interval are mainly affected by the magnitude of  $\varepsilon$  for low  $\tau_1$  values. For reasons of comparison, it can be pointed out that  $\varepsilon(\tau_1 = 10^5) \approx 10^{-6}$ , thus being lower by three orders of magnitude than mean values of  $\bar{\varepsilon}$ . The same value yielded by Schwarzl-Staverman's approximation is  $\varepsilon = 0.0526$  ( $n = 1$ ) and  $\varepsilon = 0.0269$  ( $n = 2$ ).

Fig. 1 shows a comparison of this method for the calculation of the relaxation spectrum (Eq. (8) and Eq. (10)) for  $N = 16$  with an exact spectrum (Eq. (15)) along with both approximations of Schwarzl-Staverman's method within a wide range of the relaxation times  $\tau$ . It can be seen that while Schwarzl-Staverman's method leads to a systematic average error of the absolute value of the relaxation spectrum of 13% or 7% ( $n = 1$  or  $n = 2$  respectively) in the region of the maximum and to its right, the method described above attains an accuracy higher than  $2 \cdot 10^{-4}\%$ , which means an agreement between  $H^c(\tau)$  and  $H^a(\tau)$  with an accuracy of 5 valid figures. Also in the region to the left of the maximum Eqs (8) and (10) help to improve the value of the relaxation spectrum (Fig. 1, 2).

### Application to the Case of Creep Compliance

The possibilities of the calculation of the retardation spectrum by using the method suggested above (Eq. (11)) were tested on the course of compliance in the form

$$J(t) = 1/G(t), \quad (17)$$

where the values of the constants determining the time dependence  $G(t)$  are the same as before, *i.e.* in the calculation of the relaxation spectrum. The equilibrium compliance is  $J_e = 1/G_e = 10^{-6}$  cm<sup>2</sup>/dyn and the viscosity  $\eta \rightarrow \infty$ . From Eq. (17) it can be written for the viscoelastic part of the compliance  $j(t)$

$$j(t) = K/(\sqrt{(t+k)+c}), \quad (18)$$

from which the following relationship for the retardation spectrum can be obtained

$$L^c(\tau) = Ke^{-k/\tau} \left[ \frac{1}{\sqrt{\pi\tau}} - \frac{c}{\tau} e^{-c^2/\tau} (1 - \operatorname{erf}(c/\sqrt{\tau})) \right]; \quad (19)$$

here,  $K = (G_0 - G_e) k^{0.5}/G_e^2$ ,  $c = K/G_e$ ,  $\operatorname{erf}(x) = (2/\sqrt{\pi}) \int_0^x \exp(-t^2) dt$  is the Laplace-Gauss integral. In the region of large values of  $x$  (short times  $\tau$ ), an asymptotic expansion can be used for  $\operatorname{erf}(x)$ , and Eq. (19) can be rewritten to become

$$L^c(\tau) = \frac{Ke^{-k/\tau}}{\sqrt{\pi\tau}} \left[ \frac{1}{(2c^2/\tau)} - \frac{1 \times 3}{(2c^2/\tau)^2} + \frac{1 \times 3 \times 5}{(2c^2/\tau)^3} - \dots \right]; \quad (20)$$

In the calculation of the spectrum  $L^c(\tau)$  by means of Eq. (19), the algorithm 304 from CACM was used to calculate  $\operatorname{erf}(x)$ ; this guarantees the accuracy of calcula-

tions for all the valid figures of the computer<sup>9</sup>. Owing to the rapid convergence of  $\text{erf}(x) \rightarrow 1$ , Eq. (19) could be used in the region  $\log \tau \geq 8.6$ . In the region of shorter times, Eq. (20) was used to calculate  $L'(\tau)$ , for which convergence of the series was ascertained in the region  $\log \tau \leq 8.2$ , and the summation of the series was calculated with an accuracy of 17 valid figures. Thus, combination of both equations, Eq. (20) and (19), made it possible to calculate an exact retardation spectrum  $L_e(\tau)$  over the whole region of the times  $\tau$ .

The  $\bar{\varepsilon}$  values (analogy of Eq. (16) for  $L(\tau)$ ) determined from the region  $2 \leq \log \tau_i \leq 20$  (the value of  $\log \tau_i$  was changing by 0.2, i.e.  $M = 91$ ) pass through a minimum depending on  $N$ , similarly to the case  $H^a(\tau)$ ; the highest accuracy is attained for  $N = 14$ . Better results are achieved by calculations based on the derivative of compliance (Eq. (12)) than by those based directly on its course (Eq. (11)). For the  $N$  given above,  $\bar{\varepsilon} \approx 10^{-4}$ , while Schwarzl-Staverman's method leads to  $\bar{\varepsilon} = 0.164$  ( $n = 1$ ) and  $\bar{\varepsilon} = 0.072$  ( $n = 2$ ), higher by more than two orders of magnitude. Also  $\varepsilon(\tau_i = 10^{10}) \approx 10^{-7}$  is lower by more than four orders of magnitude than the corresponding values obtained by using Schwarzl-Staverman's method,  $\varepsilon = 0.039$  ( $n = 1$ ) and  $\varepsilon = 0.016$  ( $n = 2$ ). The total, somewhat better accuracy of description of the spectrum  $L^a(\tau)$  compared to  $H^a(\tau)$  is probably given by the narrower interval of  $\log \tau$ . It follows from a detailed analysis of the dependence of  $\varepsilon$  on  $\tau$  (Fig. 2) that Schwarzl-Staverman's method leads to the right of the maximum to a systematic error in the absolute value of  $L(\tau)$  of 13% or 7% ( $n = 1$  or  $n = 2$  respectively, Figs 2 and 3), similarly to the case  $H(\tau)$ ; this issues from the fact that in this region the course of the  $L(\tau)$  spectrum is identical with the course of  $H(\tau)$ , with the exception of a constant shift (in Eq. (19)  $e^{2/\tau} \rightarrow 0$ ). To the left of the maximum, the average error in the value of  $L(\tau)$  is much greater (Fig. 2). The method used by us leads in the same region to an error  $\varepsilon < 10^{-4}$ , which gives an agreement between the approximative and the exact spectrum within five figures, also in the case of the retardation spectrum (Figs 2 and 3).

From the viewpoint of laboratory work without using computers, the application of the method described above with  $N$  as low as possible may be of importance. The necessity of improving Schwarzl-Staverman's method is evident especially in the case of the retardation spectrum  $L(\tau)$  (Fig. 2), because to the left of the maxi-

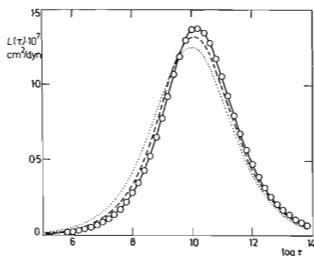


FIG. 3

Dependence of the Retardation Spectrum  $L(\tau)$  ( $\text{cm}^2 \text{dyn}^{-1}$ ) on Time  $\tau$  (s)

..... Schwarzl-Staverman,  $n = 1$ ; ---- Schwarzl-Staverman,  $n = 2$ ;  $\circ$  method used in this work,  $N = 14$ ; ——— exact spectrum, Eqs (19) and (20).

mum, *i.e.* in the main transition region  $\tau < 10^{10}$  there arises an error in the determination of the absolute value of  $L(\tau) = 75\%$  ( $n = 1$ ) and  $25\%$  ( $n = 2$ ). A decrease in this error in the region of the maximum accompanied by another change in its sign can also distort the whole dependence of  $L(\tau)$  on  $\tau$ . It can be seen from the Table that

$N$	2	4	6
$\bar{\varepsilon}$ (Eq. (11)):	0.155 (43%)	0.082 (20%)	0.012 (3%)
$\bar{\varepsilon}$ (Eq. (12)):	0.104 (27%)	0.006 (1.5%)	0.00035 (0.08%)

$N = 2$  (Eq. (11)) corresponds to the first Schwarzl–Staverman's approximation ( $n = 1$ ,  $\bar{\varepsilon} = 0.164$  (45%), and  $N = 4$  (Eq. (11) and  $N = 2$  (Eq. (12)) correspond to the second approximation ( $n = 2$ ,  $\bar{\varepsilon} = 0.072$  (18%)). The method described above has a sufficient accuracy for  $N = 6$  and the use of the course of compliance (Eq. (11)), or still better, for  $N = 4$  and the use of the derivative of compliance (Eq. (12)). In both cases,  $\bar{\varepsilon}$  is less than 5% within the whole region, which is the usual accuracy of the experimental determination of mechanical characteristics. The respective relationships applied in these cases are

$$L^a(\tau) = \ln 2[j(t)|_{t=\tau \ln 2} - 49j(t)|_{t=2\tau \ln 2} + 366j(t)|_{t=3\tau \ln 2} - 858j(t)|_{t=4\tau \ln 2} + 810j(t)|_{t=5\tau \ln 2} - 270j(t)|_{t=6\tau \ln 2}] \quad (21)$$

and

$$L^b(\tau) = \tau \ln 2[-2j(t)|_{t=\tau \ln 2} + 26j(t)|_{t=2\tau \ln 2} - 48j(t)|_{t=3\tau \ln 2} + 24j(t)|_{t=4\tau \ln 2}]. \quad (22)$$

Similar relationships with the same constants  $V_i$  can be written also for the calculation of  $H^a(\tau)$  from  $g(t)$  or  $dG(t)/dt$ .

Since the accuracy of the usual approximation methods for the calculation of  $H^a(\tau)$  or  $L^b(\tau)$  is of the same order of magnitude, and the numerical methods for the solution of  $H^a(\tau)$  have also led to an accuracy which was of the same order of magnitude as the second Schwarzl–Staverman's approximation, it can be said that the method described above means a marked improvement in accuracy of the  $H^a(\tau)$  or  $L^b(\tau)$  values, especially in the main transition and rubberlike regions, thus providing a possibility of comparing the detailed form of the spectrum with the modern molecular theories. A great advantage of this method can be seen in that, owing to the universal character of the coefficients  $V_i$ , such a high accuracy can be attained by using only a small number of arithmetic operations and thus also a small amount of the computer time.



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