Iterative Calculation of Relaxation Spectrum from Free Vibration Data

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PART 1. COMPLEX MODULUS $G^*(\omega,a)$

It is customary to express the dynamic shear modulus of viscoelastic substances in terms of $G'(\omega)$ and $G''(\omega)$, where $G'(\omega)$ corresponds to the stiffness of the spring of a Voigt model and $G''(\omega)$ to the viscous resistance of the dashpot. Then the total modulus is $G^*(\omega) = G'(\omega) + iG''(\omega)$. Analogous expressions are used for other moduli, but the argument is general. For steady-state sinusoidal motion, $G'(\omega)$ and $G''(\omega)$ are, in terms of the relaxation spectrum $G(\tau)$, as follows:[1]

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

and

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

If the motion is damped sinusoidal as, for example, in the free oscillation of a torsional pendulum, the motion is characterized not only by the frequency ω but also by the damping factor a with the displacement, θ, given by:

$$\theta(t) = \theta_0 (\exp\{-at\}) \sin \omega t, \tag{3}$$

if nonperiodic transients are ignored.

The behavior of the viscoelastic material may here also be represented by a Voigt element,[2,3] and it is commonly known that the functions G' and G'' so derived are not the same as those for undamped oscillation at the same frequency,[4] the error increasing with a/ω. The Voigt equivalents G' and G'' are therefore functions not only of the frequency ω, but also of the damping factor a, and in the discussion to follow the storage and loss moduli will be designated $G'(\omega)$ and $G''(\omega)$ for undamped oscillation and $G'(\omega,a)$ and $G''(\omega,a)$ when damping is present. While no real difficulty arises when a/ω is small,[4] this restriction is not always observed, and the magnitude of the error has not, as far as the author is aware, been given. Values of logarithmic decrement in excess of 4 have been published,[5] corresponding to $a/\omega = \log \text{dec}/2\,\pi > {}^2/_3$.

In the sections to follow, the single Voigt element, the single Maxwell

element, and the general relaxation spectrum will be discussed, after which there will be an analytical treatment of the "box" spectrum[6] and a numerical treatment of the National Bureau of Standards polyisobutylene.[7,8]

1. Single Voigt Element

The derivation of the equations for the single Voigt element (Fig. 1) has been presented previously,[2,3] but for completeness and uniformity will be given here. The differential equation for free oscillation is

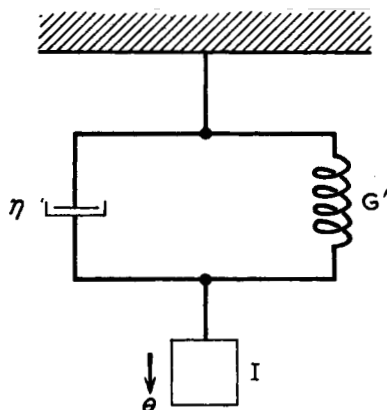$$I_1\theta'' + k\eta\theta' + kG'\theta = 0$$

Fig. 1. Voigt element: G' = spring modulus; η = dashpot viscosity; I = reduced inertia; θ = displacement.

where I_1 is the moment of inertia of the pendulum bob, η the viscosity, G' the storage modulus, and θ' and θ'' the first and second time derivatives, respectively, of θ. Hereafter, $I_1/k = I$ will be used, the equation above becoming

$$I\theta'' + \eta\theta' + G'\theta = 0 \tag{4}$$

I is then the reduced moment of inertia, and the form factor k no longer appears explicitly.

If the boundary conditions are

$$\theta(0) = 0, \theta'(0) = V$$

the complete solution for eq. (4) is

$$\theta(t) = (V/\omega)(\exp\{-at\})\sin\omega t \tag{5}$$

where
$$\omega = [(G'/I) - a^2]^{1/2} \tag{6}$$

and
$$a = \eta/2I = G'\tau/2I \tag{7}$$

Then
$$G' = I(\omega^2 + a^2) \tag{8}$$

and
$$G'' = \omega\eta = 2Ia\omega \qquad (9)$$

Also:
$$G' + G'' = I(\omega + a)^2$$

$$G' - G'' = I(\omega - a)^2$$

and $Q(\omega,a) = G'/G'' = (\omega^2+a^2)/2a\omega \geqslant 1$ for all $a > 0$, $\omega > 0$.

It will be shown later that it is sometimes desirable to couple a spring to aid the viscoelastic specimen; an example may be a torsion pendulum suspended from a hardened steel wire, the material under test coupled beneath the pendulum. Since the restoring torque in the spring is in phase with the displacement, it is simply additive to $G'(\omega,a)$. If the in-phase stiffness of the wire is g', then $G'(\omega,a)$ of eqs. (5) to (9) should be replaced by $G'(\omega,a) + g'$. Generally, the loss in a suitably chosen spring material is so low that it is negligible compared with that of the viscoelastic substance but, if desired, both g' and g'' can be determined in the absence of the viscoelastic material by the use of eqs. (8) and (9), substituting g' and g'' for G' and G''. Then g'' is additive to G'' in the same way that g' is to G'.

2. Single Maxwell Element

While the differential equation for the free oscillation of the single Maxwell element (Fig. 2) may be set up and solved by the same general procedure as in the case of the Voigt element, it will be useful to introduce here
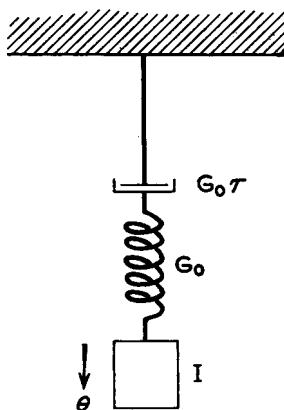

Fig. 2. Maxwell element: G_0 = spring modulus; $G_0\tau$ = dashpot viscosity; I = reduced inertia; θ = displacement.

the Boltzmann superposition equations.[9] If $T(t)$ is the torque T_1 reduced by the factor k, if $G(t)$ is the relaxation modulus, and if $G'(t) = dG(t)/dt$, then

$$T(t) = \theta(t)G(0) + \int_0^t G'(t)\theta(t - \tau)d\tau$$

Taking the Laplace transform:

$$LT(t) = G(0)L\theta(t) + LG'(t)L\theta(t) \tag{10}$$

But $LG'(t) = sLG(t) - G(0)$; substituting this into eq. (10) we have

$$LT(t) = sLG(t)L\theta(t) \tag{11}$$

If $\theta(0) = 0$, then $sL\theta(t) = \theta'(t)$ and Eq. (11) becomes

$$LT(t) = LG(t)L\theta'(t) \tag{12}$$

For the reduced moment of inertia, I,

$$I\theta'' = -T(t) \tag{13}$$

The transform of this is

$$LT(t) = -I[s^2L\theta(t) - \theta'(0)] \tag{14}$$

Then, from eqs. (11) and (14):

$$I[s^2L\theta(t) - \theta'(0)] + sLG(t)L\theta(t) = 0 \tag{15}$$

For a single Maxwell element, $G(t) = G_0 \exp\{-t/\tau\}$ and

$$LG(t) = G_0/(s + 1/\tau) \tag{16}$$

Then, combining eqs. (15) and (16):

$$L\theta(t) = \theta'(0)(s + 1/\tau)/s(s^2 + s/\tau + G(0)/I)$$

whose solution is

$$\theta(t) = [\theta'(0)\tau^2/(\omega^2\tau^2 + {}^1\!/_4)]\{1/\tau - [(1/\tau)\cos\omega t + (1/\omega)(1/4\tau^2 - \omega^2)$$
$$\sin\omega t]\exp\{-at\}\} \tag{17}$$

where $\omega = (G/I - 1/4\tau^2)^{1/2}$ and $a = 1/2\tau$. The first term in the bracket is constant and may be ignored. Then, according to eqs. (8) and (9):

$$G'(\omega,a) = I(\omega^2 + a^2) = G(0) \tag{18}$$

and

$$(G''\omega,a) = 2I\omega a = (I/\tau)(G/I - 1/4\tau^2)^{1/2}$$

Since $I = G(0)/(\omega^2 + a^2)$ from eq. (18), and $a = 1/2\tau$,

$$G''(\omega,a) = G(0)\omega\tau/({}^1\!/_4 + \omega^2\tau^2) \tag{19}$$

and

$$\tan\delta(\omega,a) = G''(\omega,a)/G'(\omega,a) = \omega\tau/({}^1\!/_4 + \omega^2\tau^2) \tag{20}$$

From eqs. (1) and (2), for a single element,

$$G'(\omega) = G(0)\omega^2\tau^2/(1 + \omega^2\tau^2), \tag{21}$$

$$G''(\omega) = G(0)\omega\tau/(1 + \omega^2\tau^2), \text{ and} \tag{22}$$

$$\tan\delta(\omega) = G''(\omega)/G'(\omega) = 1/\omega\tau \tag{23}$$

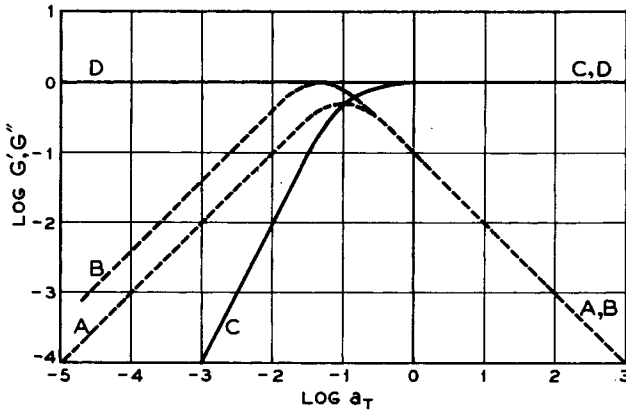The functions of eqs. (18), (19), (21), and (22) are shown in Figure 3.

Fig. 3. Single maxwell element: A = $G''(\omega)$; B = G'', (ω, a), a uncontrolled; C = $G'(\omega)$; D, $G'(\omega, a)$, a uncontrolled.

Torsional pendulum experiments usually cover only a small frequency range, typically around 1 cycle/sec. ($\omega = 2\pi$), and the variation in properties is achieved by means of temperature variations; or, with some degree of idealization, frequency is held constant at, say, $\omega = 10$, and the relaxation spectrum is shifted, by temperature changes, through the factors a_T or $\kappa(T)$.[10,11] Thus for the single Maxwell element, it may be assumed that $G(0) = 1$, $\omega = 10$, and τ, the relaxation time, is varied between 10^{-5} and 10^4 in steps of $\Delta \log \tau = 0.5$. In any case, including the most general (to be discussed later), varying τ is equivalent to varying ω and a with constant τ, as all appear in the equations only as the products $\omega\tau$ and $a\tau$ and their powers. For this reason the ordinate of Figure 3 and those of all such plots to follow are in terms of $\log a_T$, where a_T is the multiplying factor applicable either to the τ's of the relaxation spectrum or to ω and a.

3. The General Relaxation Spectrum

Equation (12) may be solved by obtaining the inverse transform,

$$T(t) = \int_0^t \theta'(\lambda) G(t - \lambda) d\lambda x \tag{24}$$

where $G(t - \lambda)$, the relaxation modulus, is

$$G(t - \lambda) = \int_0^\infty G(\tau) \exp \{(t - \lambda)/\tau\} d\tau \tag{25}$$

Let us *assume* that $\theta(\lambda) = (\exp\{-a\lambda\}) \sin \omega\lambda$; then

$$\theta'(\lambda) = (\exp \{-a\lambda\})(\omega \cos \omega\lambda - a \sin \omega\lambda) \tag{26}$$

Substituting eqs. (25) and (26) into eq. (24), we have

$$T(t) = \int_0^\infty \int_0^t (\exp \{-a\lambda\})(\exp \{-(t - \tau)/\tau\})(\omega \cos \omega\lambda$$
$$- a\sin \omega\lambda) G(\tau) d\tau d\lambda \tag{27}$$

This may be integrated with respect to λ; the result, after dropping a non-periodic transient, is

$$T'(t) = (\exp\{-at\}) \sin \omega t \int_0^\infty \frac{[\tau^2(\omega^2 + a^2) - a\tau]G(\tau)d\tau}{(1 - a\tau)^2 + (\omega\tau)^2}$$

$$+ (\exp\{-at\}) \cos \omega t \int_0^\infty \frac{\omega\tau G(\tau)d\tau}{(1 - a\tau)^2 + (\omega\tau)^2} \quad (28)$$

In terms of the single Voigt element of Figure 1,

$$T(t) = G'\theta(t) + (G''/\omega)\theta'(t) = (\exp\{-at\}) \sin \omega t(G' - aG''/\omega)$$

$$+ (\exp\{-at\}) \cos \omega t(G'') \quad (29)$$

Then equating coefficients of $(\exp\{-at\}) \sin \omega t$ and $(\exp\{-at\}) \cos \omega t$ in eqs. (28) and (29), we have

$$G'(\omega,a) - (a/\omega)G''(\omega,a) = \int_0^\infty \frac{(\tau^2(\omega^2 + a^2) - a\tau)G(\tau)d\tau}{(1 - a\tau)^2 + (\omega\tau)^2} \quad (30)$$

and

$$G''(\omega,a) = \int_0^\infty \frac{\omega\tau G(\tau)d\tau}{(1 - a\tau)^2 + (\omega\tau)^2} \quad (31)$$

By substituting eq. (31) into eq. (30), we eliminate G'' from the latter, and

$$G'(\omega,a) = \int_0^\infty \frac{(\omega^2 + a^2)\tau^2 G(\tau)d\tau}{(1 - a\tau)^2 + (\omega\tau)^2} \quad (32)$$

Comparison of eqs. (32) and (1) show that the integrand of the former is always the greater, for given finite values of ω and τ; therefore, at a given frequency, $G'(\omega,a) > G'(\omega)$. Numerical results indicate that $G''(\omega,a) > G''(\omega)$, although this is more difficult to prove. From eqs. (8) and (9):

$$G''(\omega,a) = 2Ia\omega$$

$$G'(\omega,a) = I(\omega^2 + a^2)$$

whence

$$I = \int_0^\infty \frac{\tau^2 G(\tau)d\tau}{(1 - a\tau)^2 + (\omega\tau)^2} \quad (33)$$

and

$$I = (1/2a) \int_0^\infty \frac{\tau G(\tau)d\tau}{(1 - a\tau)^2 + (\omega\tau)^2} \quad (34)$$

Equations (31) and (32) give the dynamic properties when the viscoelastic material is subjected to the arbitrary displacement $(\exp\{-at\})$ $\sin \omega t$; eqs. (33) and (34) give further conditions that must be met if the

force-displacement relation is to be that provided by the inertial reaction of a mass or of a moment of inertia alone. Finding appropriate values of a to reconcile eqs. (33) and (34) for a given spectrum and frequency is essentially a cut-and-try process, although fortunately it is one that can be arranged for rapid convergence in a successive approximation program for a computing machine. First, $G'(\omega)$ and $G''(\omega)$ are computed by means of eqs. (1) and (2), with the use of either analytic or discrete spectral approximations. Then, assuming that $a \ll \omega$, in eqs. (8) and (9)

$$G' \approx I\omega^2$$

$$G'' = 2Ia\omega$$

whence $a = 5G''/G'$ if, as before, $\omega = 10$. With this tentative value of a, I is calculated by means of eq. (33), and a function W, equal to the right side of eq. (34) with the factor $1/2a$ omitted, is also calculated. Then a second approximation to a is obtained by $a = W/2I$. It is perhaps not obvious that this should be a better approximation than the first, but experience shows that it is. New values of I and W are calculated, from which a third approximation to a is found, and so on, until, if a_j is the jth approximation $(a_j-a_{j-1})/a_j$ is less than any desired value; the limit 0.0001 was used in the calculations described here. A maximum limit of twenty iterations was specified, and was reached occasionally, but the average number was four or five. When the value of a was thus found, $G'(\omega,a) = I(\omega^2 + a^2)$ and $G''(\omega,a) = 2Ia\omega$, from eqs. (8) and (9).

The ratios a/ω thus found for the single Maxwell element, over the range of frequencies considered, range from 5000 to 5×10^{-6}. If we assume, as a practical limit, a damping in which each peak has half the amplitude of its immediate predecessor, then $-2\pi a/\omega = \ln (0.5)$, from which $a/\omega = 0.110$. Let us assume, then, that the maximum ratio a/ω is to be 0.1. Thus, since $\omega = 10$, $a_{max} = 1$. We may calculate the necessary values of I and g' as follows. First, $G'(\omega,a)$ and $G''(\omega,a)$ are calculated by means of eqs. (31) and (32). From eq. (9):

$$I = G''/2a\omega = G''/20 \tag{35}$$

From eq. (8), substituting $(G'(\omega,a) + g')$ for G':

$$G'(\omega,a) + g' = I(\omega^2 + a^2) = 101(I)$$

whence

$$g' = 101(I) - G'(\omega,a) \tag{36}$$

In cases in which the iterative calculations would have resulted in a/ω less than 0.1, g' will be negative; g' is of course not needed in these cases, but the fact serves as a check of the calculations. The results for the single Maxwell element are shown in Figure 4. Here it will be seen that the ratio $g'/G'(\omega,a)$ becomes very large at low values of a_T. In an experimental measurement, $G'(\omega,a)$ would be determined by means of eq. (36),
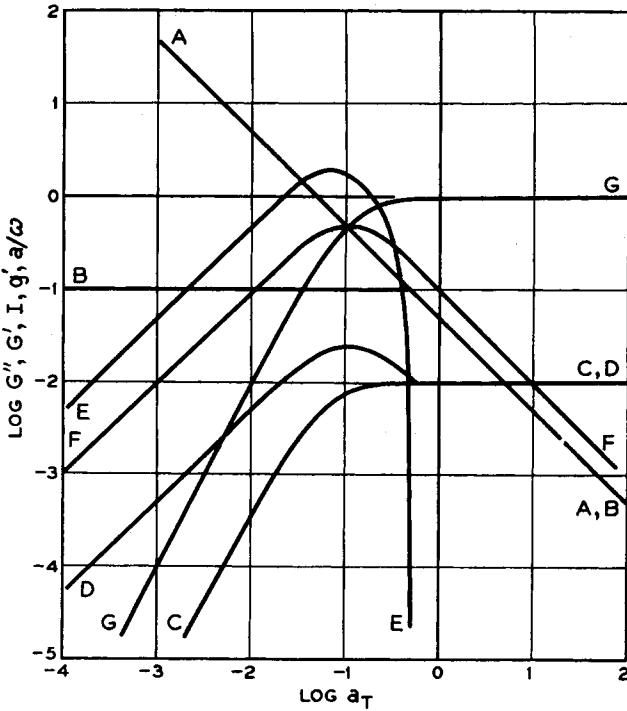
Fig. 4. Single maxwell element: $A = a/\omega$, a uncontrolled; $B = a/\omega \leqslant 0.1$; $C = I$, a uncontrolled; $D = I$, $a/\omega \leqslant 0.1$; $E = g'$, $a/\omega = 0.1$; $F = G''(\omega,a)$, $a/\omega \leqslant 0.1$; $G = G'(\omega,a)$, $a/\omega \leqslant 0.1$.

all the other elements being known. $G'(\omega,a)$ is then the small difference between two large experimentally determined quantities, and precision cannot be expected. But the calculation of $G''(\omega,a)$ via eq. (35) does not suffer this handicap—a fortunate circumstance, since $G''(\omega,a)$ is the more useful for calculating the relaxation spectrum, as will be discussed later.

4. "Box" Distribution of Relaxation Times

The "box" distribution[6] is of the form

$$G(\tau) = K/\tau \qquad \tau_1 \leqslant \tau \leqslant \tau_2 \tag{37}$$
$$= 0 \qquad \tau < \tau_1, \quad \tau > \tau_2$$

If $K = 1/\ln(\tau_2/\tau_1)$, then $G(t)$ is normalized to unity at $t = 0$.

Substituting eq. (35) into eqs. (31) and (32), and integrating, we find

$$G''(\omega,a) = K(\arctan \{[\tau_2(\omega^2 + a^2) - a]/\omega\} - \arctan \{[\tau_1(\omega^2 + a^2) - a]/\omega\}) \tag{38}$$

$$G'(\omega,a) = (K/2) \ln \{[\tau_2^2(\omega^2 + a^2) - 2a\tau_2 + 1]/[\tau_1^2(\omega^2 + a^2) - 2a\tau_1 + 1]\} + (a/\omega)G''(\omega,a) \tag{39}$$

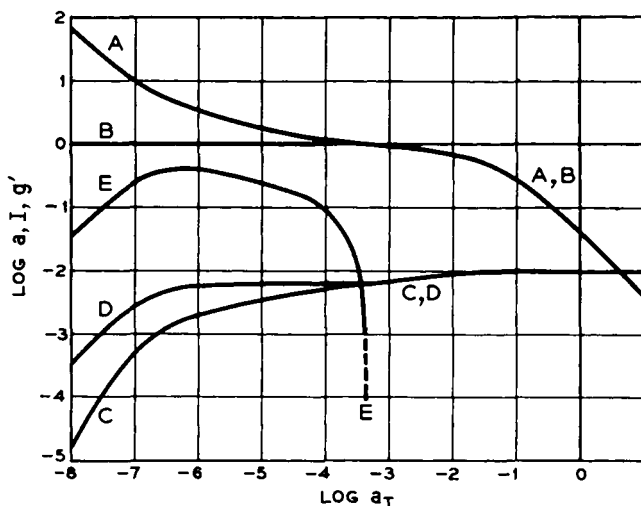Figures 5 and 6 show the results of the calculations of these functions.

Fig. 5. "Box" distribution: A = a, uncontrolled; B = $a/\omega \leqslant 0.1$; C = I, a uncontrolled; D = I, $a/\omega \leqslant 0.1$; E = g', $a/\omega = 0.1$.

5. Polyisobutylene

The integrals of eqs. (31)–(34) may be replaced by summations of discrete spectral lines. The line spectrum for polyisobutylene as given by Tobolsky and Catsiff[8] was recalculated to have but two lines per decade, instead of the five lines of the original data. Here, Young's modulus, $E'(\omega)$, $E''(\omega)$, etc., are used instead of the shear modulus. The salient characteristics of this system are given in Figures 7, 8, and 9. In plots to this scale, the functions $G'(\omega)$ and $G'(\omega,a)$ cannot be distinguished from each other when $a/\omega \leqslant 0/1$, and the same is true for $G''(\omega,a)$ and $G''(\omega)$. Figure 7 shows the rather close similarity between $G''(\omega)$ and $G''(\omega,a)$ with a unrestricted. In Figure 8, the effect of unrestricted a on the values of $G'(\omega,a)$ at low values of a_T is shown to be marked by the leveling off at $G'(\omega,a) = 2.121 \times 10^5$. The values of a dip below $\omega/10 = 1.0$ at the rub-
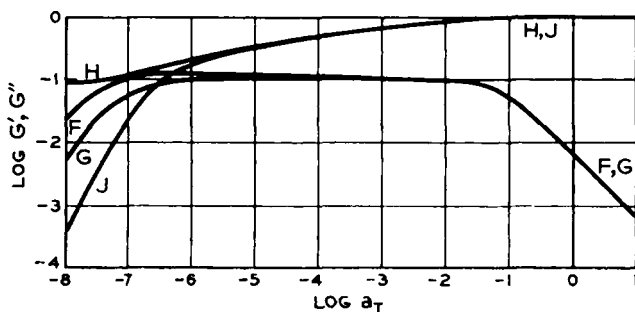

Fig. 6. "Box" distribution: F = $G''(w/a)$, a uncontrolled; G = $G''(\omega) \approx G''(\omega,a)$, $a/\omega \leqslant 0.1$; H = $G'(\omega,a)$ a uncontrolled; J = $G'(\omega) \approx G'(\omega,a)$, $a/\omega \leqslant 0.1$.
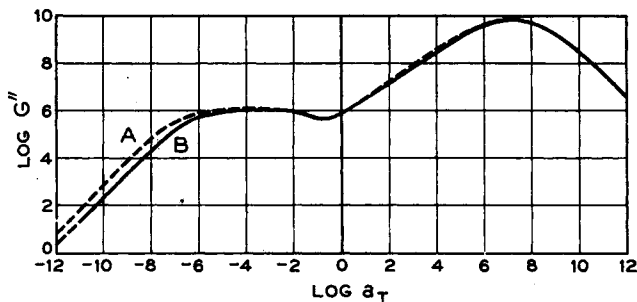
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Fig. 7. Polyisobutylene:　A = $G''(\omega,a)$, a uncontrolled;　B = $G''(\omega) \approx G''(\omega,a)$, $a/\omega \lessgtr$ 0.1.
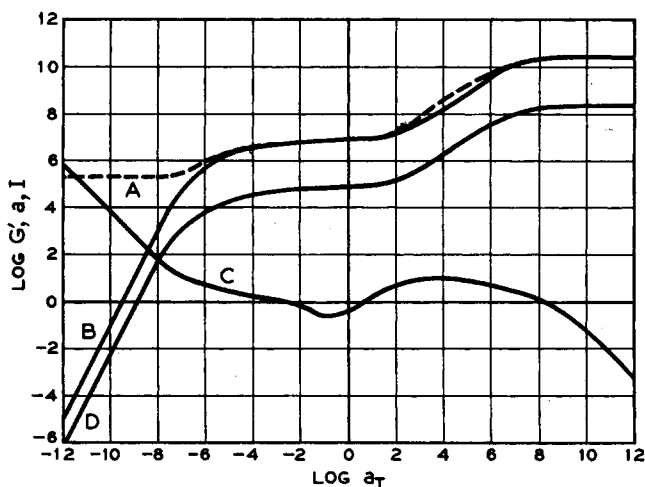

Fig. 8. Polyisobutylene:　A = $G'(\omega,a)$, a uncontrolled;　B = $G'(\omega) \approx G'(\omega,a)$, $a/\omega \lessgtr$ 0.1;　C = a, uncontrolled;　D = I, a uncontrolled.

bery and the glass plateaus; the corresponding values of I, G', and G'' are used in the computations for Figure 9, where $a \lessgtr \omega/10$. At these points, g' would have to be negative if a/ω were to be held at 0.1; instead, g' is permitted to go to zero, and a/ω is somewhat less than 0.1.

PART 2. CALCULATION OF SPECTRA

Ninomiya and Ferry[12] have discussed approximate methods of calculating relaxation spectra from $G'(\omega)$ and $G''(\omega)$ (see their Equation 12). The success of an iterative scheme for successive approximations to the spectrum in the case of stress relaxation[13] suggested that iteration might also be useful here. $G''(\omega)$ is theoretically more effective than $G'(\omega)$;[12] a preliminary trial showed this to be definitely the case at the first calculation and more strongly so at each iteration. As a result, the rest of the work was confined to $G''(\omega)$ and $G''(\omega,a)$.
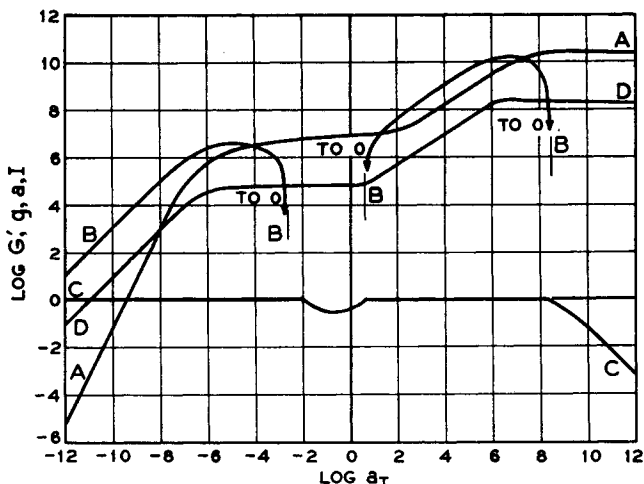
Fig. 9. Polyisobutylene: A $= G'(\omega) \approx G'(\omega,a)$, $a/\omega \lessgtr 0.1$; B $= g'$, $a/\omega = 0.1$; C $= a/\omega \lessgtr 0.1$; D $= I$, $a/\omega \lessgtr 0.1$.

The successive approximations to the spectrum are calculated as follows. Equation (12) of Ninomiya and Ferry[12] is arranged for $\Delta \log \omega = 0.5$; this involves their parameter a (not to be confused with the a of this paper) and also requires that their F''_2 be multiplied by $|\Delta \ln \tau| = |\Delta \ln \omega| = 2.303 \times 0.5 = 1.1515$ to change from their continuous spectrum to our discrete one.   The results of this calculation, $H1(\tau)$, are substituted in eqs. (31) and (32) (arranged as sums rather than integrals), to yield the first approximation, $G1''(\omega,a)$.   Then the difference $\Delta G1''(\omega,a) = G''(\omega,a) - G1''(\omega,a)$ is found, and from this the first correction to the spectrum, $\Delta H1(\tau)$, is calculated.   This is added to $H_1(\tau)$ to yield $H2(\tau)$, from which $G2''(\omega,a)$ is calculated, and so on for as many iterations as desired (in this case twenty).   This was programmed for the IBM 7090 computer; a typical calculation with twenty iterations required 20 sec.   Success in reproducing the spectra is discussed below.

1. Single Maxwell Element

Spectrum from $G''(\omega)$

Through the twenty iterations there is a gradual but positive approach to the spectral line of unit strength at $\tau = 1$.   This is summarized in Table I, where the strengths of the central line and the two adjacent ones are given.

In the case of experimental data, in which the form of the spectrum is not known in advance, the only test is of how closely the calculated spectrum will reproduce the original data.   For the single Maxwell unit at hand, the maximum values of $G'(\omega)$ and $G''(\omega)$ are 1.0 and 0.5, respectively.   The

TABLE I

H_i at and Adjacent to Central Line as a Function of the Trial Number; Single Unit Maxwell Element, $\tau = 1$

Trial	τ				
	0.1	0.3162	1.0	3.162	10.0
1	0.005765	0.1670	0.5235	0.1670	0.005765
2	−0.02240	0.1572	0.7171	0.1573	−0.02243
3	−0.03498	0.1250	0.8129	0.1251	−0.03503
5	−0.03378	0.07305	0.9062	0.07317	−0.03387
10	−0.01294	0.01924	0.9780	0.01939	−0.01305
15	−0.004098	0.005383	0.9940	0.005548	−0.004215
20	−0.001263	0.001578	0.9982	0.001745	−0.001381

table below shows how the maximum values of $\Delta G'(\omega)$ and $\Delta G''(\omega)$ for each trial decrease as the number of trials increases.

Trial	Max. $\Delta G'(\omega)$	Max. $\Delta G''(\omega)$
1	0.1780	0.1410
2	0.04925	0.05558
3	0.01949	−0.02843
5	−0.005496	0.01106
10	−0.0008481	0.002087
15	0.0002170	0.0005166
20	0.00007619	0.0001404

Duplicate calculations were made with $\Delta \log \omega = 0.2$. The grouping of spectral lines as well as the maximum $\Delta G'(\omega)$ and $\Delta G''(\omega)$ are given below for the twentieth trial.

τ_i	H_i
0.1	−0.009988
0.1585	0.01083
0.2512	0.02645
0.3891	−0.1152
0.6310	0.2173
1.0	0.7373
1.585	0.2161
2.512	−0.1143
3.981	0.02705
6.310	0.009117
10.	0.008164

Max. $\Delta G'(\omega) = 0.0004205$
Max. $\Delta G''(\omega) = 0.0005147$

This spectrum is considerably less sharply peaked than that summarized in Table I and, in fact, the envelope of the H_i's suggests the analytic curves of Ninomiya and Ferry.[12] Further, the spectrum when $\Delta \log \tau = 0.5$ is almost perfectly symmetrical about $\tau = 1$, but is less so when $\Delta \log \tau = 0.2$. The reason appears to be in roundoff errors in the fourth significant figure. This suggests that the balance between precision of data and

magnitude of $\Delta \log \tau$ may be at somewhat larger values for the latter than the range 0.2–0.4 suggested by Ninomiya and Ferry.[12]

Spectrum from $G''(\omega,a)$, a unrestricted

In this case, by following eq. (17) it is shown that $a = 1/2\tau$, or 0.5, since $\tau = 1$. From eq. (19):

$$G''(\omega,a) = G(0)\omega\tau/(^1/_4 + \omega^2\tau^2)$$

$$= 2G(0)(2\omega\tau)/(1 + (2\omega)^2\tau^2) \qquad (40)$$

From Eq. (2), for the single line spectrum at $\tau = 1$, $G''(\omega) = G(0)\omega\tau/(1 + \omega^2\tau^2)$; comparing this with eq. (40), we see that $G''(\omega,a) = 2G''(2\omega)$. The result is that the spectrum as calculated from $G''(\omega,a)$ will have twice the strength at half the frequency (corresponding to twice the relaxation
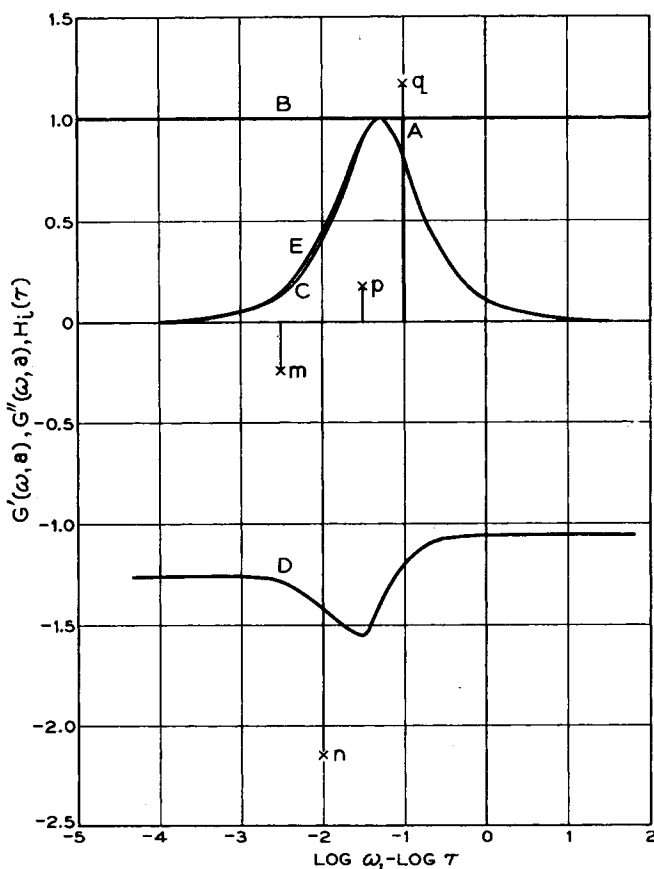

Fig. 10. Single maxwell element. Calculation of spectrum from $G''(\omega,a)$, a uncontrolled: A = true spectral line; B = $G'(\omega,a)$, a uncontrolled; C = $G''(\omega,a)$, a uncontrolled; m, n, p, q = chief spectral lines at twentieth trial; D = $G1'(\omega,a)$ at twentieth trial; E = $G1''(\omega,a)$ at twentieth trial.

time) as that calculated from $G''(\omega)$. If the sole criterion of success were
the finding of a spectrum that would duplicate $G''(\omega,a)$, then this would be
fairly successful (Fig. 10). The principal lines in the spectrum after the
twentieth trial were:

τ_i	H_i (20th trial)	H_i (true)
1.000	1.179	1.000
3.162	0.1617	0.0
10.000	−2.140	0.0
31.62	−0.2530	0.0
$\Sigma H_i = $ −1.052		1.000

Other spectral lines of small magnitude resulted in a sum for all H_i's of
−1.059. The four main lines and the resulting $G'(\omega,a)$ are shown in Figure
10. The gross failure to reproduce the pure-single-line spectrum at $\tau = 1$,
and $G'(\omega,a)$, is perhaps not as surprising as the success in reproducing G''-
(ω,a), since the inversion formula of Ninomiya and Ferry applies strictly
only to $G''(\omega)$, not to $G''(\omega,a)$. This serves to demonstrate the power of
the iterated application of the Ninomiya and Ferry approximation in
reproducing $G''(\omega,a)$ even when very large a/ω ratios appear. However,
since such calculations will never be practically necessary, no further
examples of calculations with unrestricted a will be given.

Spectrum from $G''(\omega,a)$, $a/\omega \leqslant 0.1$

The results of this calculation are fully as satisfactory as those from
$G''(\omega)$. Table II shows the central tendency and the gradual improve-
ment in the spectrum through the twentieth iteration.

TABLE II
H_i at and Adjacent to Central Line as a Function of the Trial Number; Single Unit
Maxwell Element, $\tau = 1$

Trial	τ				
	0.1	0.3162	1.0	3.162	10.0
1	0.0003215	0.1637	0.5929	0.1674	0.0008872
2	−0.02468	0.1325	0.7795	0.1361	−0.02719
3	−0.03097	0.09378	0.8659	0.09665	−0.03351
5	−0.02362	0.04527	0.9432	0.04666	−0.02468
10	−0.005950	0.007639	0.9914	0.007906	−0.005773
15	−0.001145	0.001075	0.9987	0.001379	−0.001161
19	−0.0001436	0.00007774	0.9999	0.0002894	−0.0003019
20	−0.00002939	−0.0002001	1.000	0.0001778	−0.0002109

The total strength of the spectrum, ΣH_i, is 0.9246 at the first trial,
increases to 0.9999 at the ninth, and remains at this value for the remainder
of the twenty trials. It therefore appears likely both from this observa-

tion and from the way in which H_i at $\tau_i = 1$ converges to 1.0, that further iterations would not lead to any further significant change in the spectrum.

The maximum values of $\Delta G'(\omega,a)$ and $\Delta G''(\omega,a)$ for these trials are given below.

Trial	Max. $\Delta G'(\omega,a)$	Max. $\Delta G''(\omega,a)$
1	0.1317	0.1224
2	0.03151	0.04563
3	−0.01377	0.02259
5	−0.003886	0.007905
10	0.004404	0.001038
15	0.0001441	0.0001769
19	−0.0001300	0.00004650
20	−0.0001310	−0.00003366

2. "Box" Spectrum

Spectrum from $G''(\omega)$

Since the box spectrum covers six decades, with a total strength of unity, each decade must account for $^1/_6$ and, since each decade is divided into two equal parts on a logarithmic basis, each of the eleven spectral lines within the spectrum should have a strength of $^1/_{12} = 0.08333$. Exactly what should be expected at the two boundaries is perhaps not clear, but the two should have a mean value of $0.08333/2 = 0.04167$. In the table below are listed the two boundary values and both the highest and lowest interior values found at various trials.

Interior Values of H_i

Trial no.	H_i at $\tau = 1.0$	Highest	Lowest	H_i at $\tau = 10^6$
1	0.03619	0.07250	0.06761	0.03619
2	0.04093	0.08276	0.08125	0.04092
3	0.04155	0.08519	0.08281	0.04154
4	0.04164	0.08640	0.08292	0.04162
9	0.04167	0.08867	0.08204	0.04163
14	0.04167	0.08888	0.08177	0.04164
20	0.04167	0.08892	0.08171	0.04164
Expected value	0.04167	0.08333	0.08333	0.04167

The maximum values of $\Delta G'(\omega)$ and $\Delta G''(\omega)$ for the above trials were:

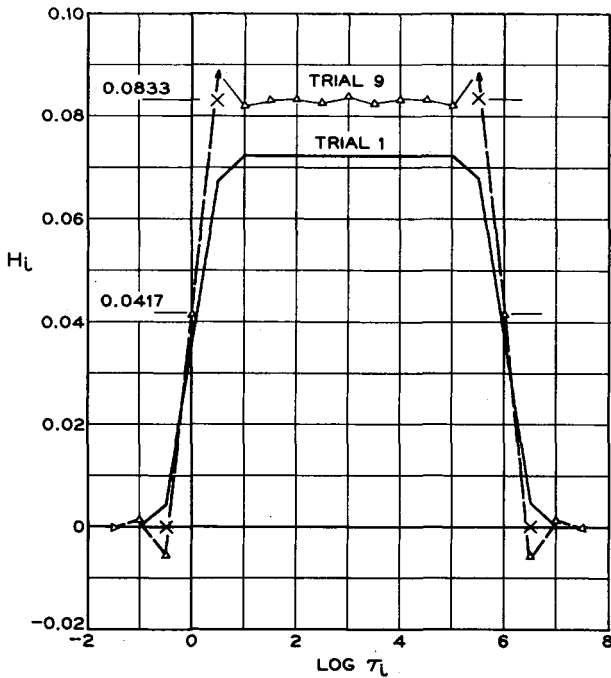| Trial no.	Max. $\Delta G'(\omega)$	Max. $\Delta G''(\omega)$
1	0.1358	0.01578
2	0.02112	0.003435
3	0.003004	0.001090
4	0.002337	0.0004720
9	0.001577	0.00004239
14	0.001524	−0.00001118
20	0.001510	−0.00001639

Fig. 11. "Box" distribution. Calculation of spectrum from $G''(\omega)$. The X's are the smoothed points at the spectral boundaries at the ninth trial (see text).

From the point of view of $\Delta G''(\omega)$, trial 14 is the best. The evolution of this spectrum brings out quite clearly one of the main problems in such iterative processes, namely, where to stop. Since the spectrum is being calculated from $G''(\omega)$, it might be thought that the best spectrum would be that associated with the least deviation of the recalculated $G''(\omega)$ from the original, that is, with the lowest value of $\Delta G''(\omega)$ in the above table. This occurs at the fourteenth trial. Figure 11 shows spectra to correspond with the table. Knowing in advance that the spectrum is the "box," one would be inclined to use a trial earlier than the fourteenth. But in ignorance of the true spectrum, which trial should one use? Though there is no simple answer, a few observations may be pertinent. First, with data to a certain number of significant figures there may be errors of 0.5 in the last digits. The calculated spectrum will reflect these errors, and upon iteration will try, not to smooth them, but to accommodate them. This must result in "noise" in the spectrum. There would seem, then, to be no advantage in iteration beyond the point where the error in the reproduced experimental function has been reduced to 0.5 in the last digit. For the "box" spectrum, this occurs at the ninth trial. Second, at this trial, and in fact in all trials after the second, there are positive peaks at the ends of the spectrum, compensated for by negative peaks just outside the spectrum. These pairs of positive and negative peaks denote the

discontinuities at the ends of the spectrum, and it may be permissible to smooth, by adding enough to the negative peak to eliminate it and subtracting the same amount from the adjacent positive peak. Such a spectrum is shown in Figure 11, and it is submitted that it represents the desired discrete spectrum rather successfully.

The above considerations about roundoff errors are applicable in this case of a fairly short spectrum. Different conditions apply in the case of extended spectra, particularly those in which important relaxation phenomena of quite different orders of magnitude occur at widely separated relaxation times. This will be discussed further in the section on polyisobutylene.

Spectrum from $G''(\omega,a)$, $a/\omega \leqslant 0.1$

In the table below are, as before, the boundary values and the highest and lowest interior values for H_i at various trials.

Interior Values of H_i

Trial no.	H_i at $\tau = 1.0$	Highest	Lowest	H_i at $\tau = 10^4$
1	0.03620	0.07728	0.07029	0.03881
2	0.04045	0.08395	0.08214	0.04174
3	0.04111	0.08601	0.08231	0.04200
5	0.04138	0.08710	0.08231	0.04210
10	0.04157	0.08887	0.08161	0.04218
15	0.04162	0.08894	0.08149	0.04220
20	0.04164	0.08894	0.08147	0.04220
Expected value	0.04167	0.08333	0.08333	0.04167

The maximum values of $\Delta G'(\omega,a)$ and $\Delta G''(\omega,a)$ for the above trials were:

Trial no.	Max. $\Delta G'(\omega,a)$	Max. $\Delta G''(\omega,a)$
1	0.08820	0.0133
2	0.01130	0.001971
3	0.003801	0.0008724
5	0.002543	−0.0002256
10	0.002321	0.00002881
15	0.002293	−0.00002551
20	0.002288	−0.00002677

The comments made above in relation to spectra from $G''(\omega)$ are also pertinent here; the differences are only a matter of small degree.

3. Polyisobutylene

Spectrum from $G''(\omega)$

The progressively improving reproduction of $G''(\omega,a)$ is illustrated in Figure 12. The upper curve is that to be duplicated. The curves for the
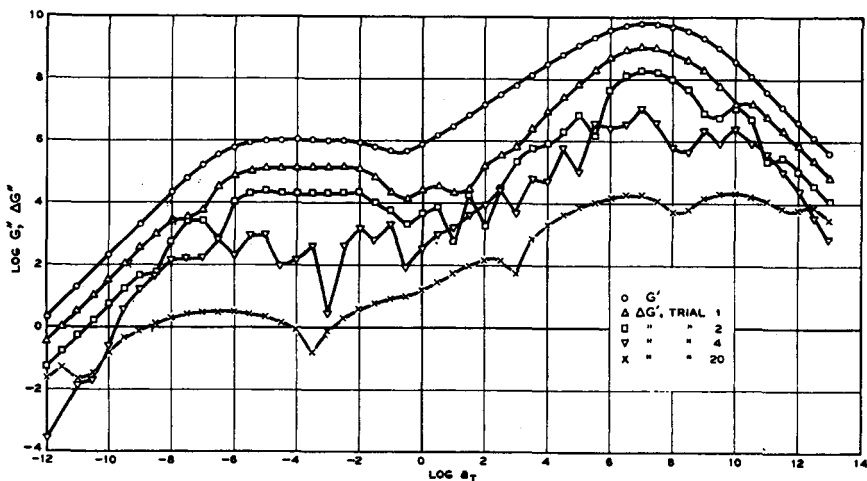
Fig. 12. Polyisobutylene. $G''(\omega,a)$ calculated from the original spectrum; the errors in its reproduction, from the approximate spectra. Upper curve: $G''(\omega,a)$. The other curves show the errors in the reproduction of $G''(\omega,a)$ at trial numbers as indicated on the curves.
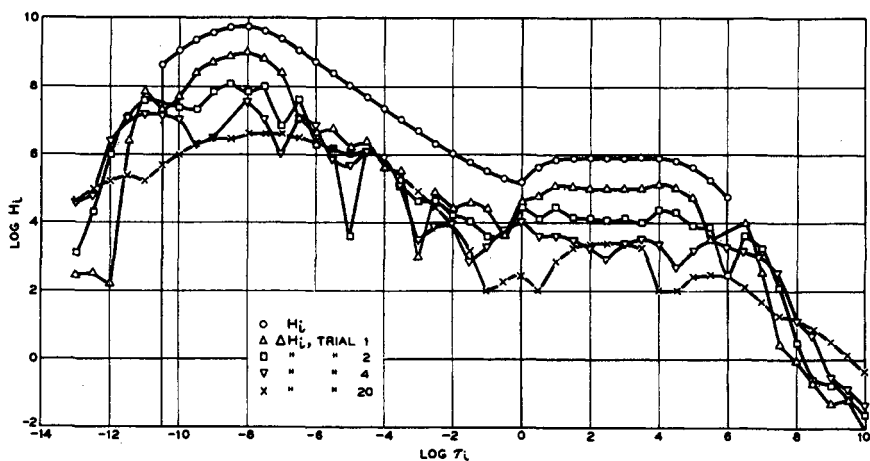

Fig. 13. Polyisobutylene. Original spectrum (upper curve), and errors in its calculation from $G''(\omega,a)$ at trial numbers as indicated on the curves.

first, fourth, and twentieth trials represent $|\Delta G''(\omega,a)|$, or the absolute value of the difference between the functions $G''(\omega,a)$ calculated from the spectra obtained in those trials and the "true" $G''(\omega,a)$, in other words, the error in the reproduced $G''(\omega,a)$. In the first trial, the error is about 1 part in 10; in the fourth, 1 in a 1000; and in the twentieth, it is between 1 in 10^4 and 1 in 10^5.

(The "true" and reproduced functions are generally identical with the fourth significant figure in the twentieth trial. The computing machine, however, works to seven or eight significant figures, and the errors are com-
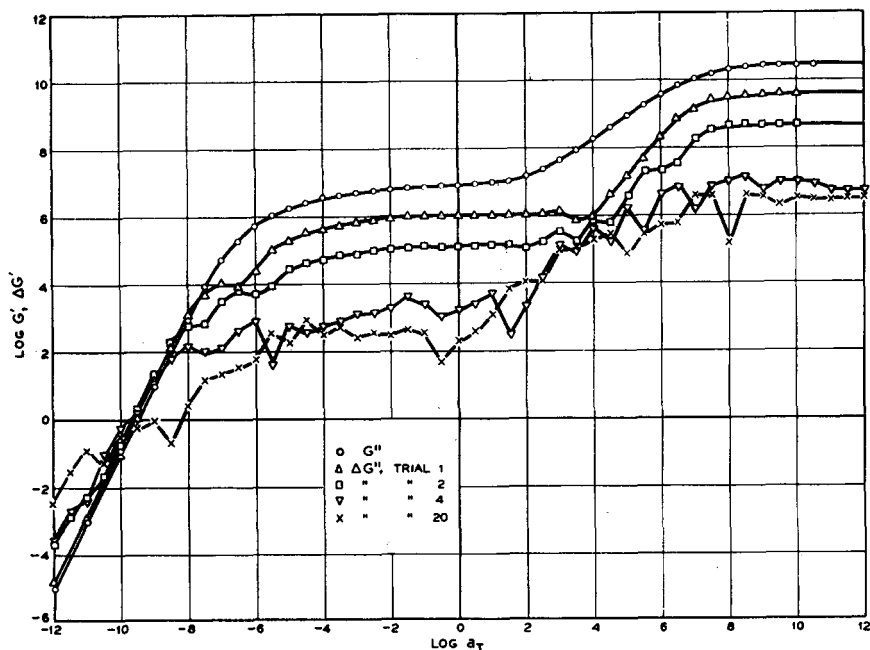
Fig. 14. Polyisobutylene. $G'(\omega,a)$ calculated from the original spectrum; the errors in its reproduction, from the approximate spectra. Upper curve: $G'(\omega,a)$. The other curves show the errors in the reproduction of $G'(\omega,a)$ at trial numbers as indicated on the curves.

puted by the machine before the superfluous figures are curtailed for print-out. The four significant figures that are printed are not obtained by rounding, but by merely suppressing all digits beyond the fourth.)

Figure 13 shows similarly the progressive improvement in the spectrum. Within the limits of the initial spectrum, the first trial is in error by about 1 part in 10; the fourth, by about 1 part in 10^2; and the twentieth, by roughly 1 part in 10^3. Outside these limits, the initial spectrum is assumed to vanish. The sum of all the H_i's found outside the initial spectrum is 8.76×10^7 at the first trial, and 6.34×10^4 at the 20th. Figure 14 is a similar plot for $G'(\omega,a)$. The errors here are of about the same magnitude as those of Figure 13.

Spectrum from $G''(\omega,a)$, $a/\omega \lessgtr 0.1$

The results in this case are so nearly the same as those from $G''(\omega)$ that except for the details of the noise the same plots can serve for both.

DISCUSSION

If $a/\omega = 0.1$, the maximum ratios of the integrands of eqs. (32) and (1) and of eqs. (31) and (2) are, respectively, 1.116 and 1.105, occurring at $\tau = 0.9512/\omega$. These ratios are the extremes, and will be found only in the case of single Maxwell units. In the case of polyisobutylene, for ex-

ample, the maximum ratios $G'(\omega,a)/G'(\omega)$ and $G''(\omega,a)/G''(\omega)$ are 1.093 and 1.073, respectively. These discrepancies are not very great when we consider uncertainties in measurement and in the derivation of other functions from G' and G'' by the usual approximations, but they are, on the other hand, hardly so small as to be dismissed. There seems to be no practicable way to calculate functions of (ω) directly from those of (ω,a), but we have shown that the relaxation spectrum can be found by iteration to a high degree of accuracy from either $G''(\omega)$ or $G''(\omega,a)$, and any other desired function then can be calculated from it.

Free vibration tests in which a spring (g' in our nomenclature) or thread supports the specimen are not new,[14-16] although in these cases the value of g' was regarded as negligible. Ferry[4] has suggested larger values of g' for the purpose of reducing damping. In this paper it is shown how appropriate values of g' may be derived for materials whose relaxation spectra are known. In the calculations, we have shown that when a is nonrandom—that is, is either made equal to 0.1ω or is found as a function satisfying eqs. (33) and (34)—the relaxation spectrum may be found. Experimentally, a/ω would vary more or less erratically as different values of I or sample dimensions were used to keep the frequency within bounds at different temperatures. One such case was calculated, for the single Maxwell element, with a variable but always $< 0.1\omega$. The convergence to the true specimen was fully as satisfactory as in the case of $a = 0$ or $a \leqslant 0.1\omega$. It therefore seems that for materials in which a_T may be assumed known—for instance, those whose a_T may be predicted through the WLF relation[17]—an apparatus, providing variable I and g' and means of varying the specimen size and shape over rather wide limits, can be made to operate at a reasonably small range of frequencies, and with suitable damping. Then with a_T assumed known, temperature changes can be translated into terms of frequency, and the resulting $G''(\omega,a)$ can be used to determine the relaxation spectrum. The absurd spectrum obtained with a single Maxwell unit with a unrestricted might instill a fear that faults might occur in less obvious ways. In a normal case, the first trial gives a good first approximation of the ultimate spectrum, and the subsequent trials merely refine it progressively; in the absurd case, the first trial spectrum bore no resemblance to that of the twentieth trial. Thus detection of abnormality appears easy.

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Synopsis

The complex elastic modulus $G^*(\omega) = G'(\omega) + iG''(\omega)$ is shown to be a function not only of the frequency (ω) but also of the damping factor a if the strain is of the form $x = x_0 \exp\{-at\} \sin \omega t$. The general equations for $G^*(\omega,a) = G'(\omega,a) + iG''(\omega,a) =$ are derived in terms of the relaxation spectrum. The use of a spring to aid the specimen and reduce the ratio a/ω is discussed, and its desirability demonstrated. If data are thus available in terms of either $G''(\omega)$ or $G''(\omega,a)$ the iterated second approximation of Ninomiya and Ferry provides a rapid and powerful method of finding the relaxation spectrum. To the accuracy to which the time–temperature reduction factor a_T is known or can be predicted by means such, for example, as the WLF equation, the function $G''(\omega,a)$ over a temperature range at nearly constant frequency can be translated into terms of $G''(\omega,a)$ at constant temperature and varying frequency. In such cases, the relatively simple torsional pendulum, or some analogue of it, can economically provide a characterization of the viscoelastic behavior of the material over an extended time or frequency range.

Résumé

On montre que le module d'élasticité complexe $G^*(\omega) = G'(\omega) + iG''(\omega)$ est une fonction non seulement de la fréquence (ω) mais aussic du facteur d'amortissement a si la deformation est de la forme $x = x_0 \exp\{-at\} \sin \omega t$. Les èquations gènèrales de $G^*(\omega,a) = G'(\omega,a) + iG''(\omega,a)$ sont dérivées en termes de spectre dè relaxation. L'emploi d'un ressort pour aider le modèle et réduire le rapport a/ω est discuté et on démontre son utilité. Si donc les données sont utilisables en termes soit $G''(\omega)$ soit $G''(\omega,a)$ la seconde approximation répétée de Ninomiya et Ferry fournit une méthode rapide et puissante pour trouver le spectre de rélaxation. En ce qui concerne la précision avec laquelle on connait, ou on peut prédire au moyen par exemple de l'équation WLF, le facteur de réduction temps–température a_T, on peut traduire la fonction $G''(\omega,a)$ dans un domaine de température a une fréquence à peu près constante, en termes de $G''(\omega,a)$ a température constante et fréquence variable. Dans pareils cas, le pendule de torsion relativement simple, ou tout analogue à lui, peut fournir à peu de frais, une caractérisation du comportement viscoélastique du matériau pendant un long laps de temps ou gamme de fréquence.

Zusammenfassung

Es wird gezeigt, dass der komplexe Elastizitätsmodul $G^*(\omega) = G'(\omega) + iG''(\omega)$ nicht nur eine Funktion der Frequenz (ω) sondern auch des Dämpfungsfaktors a für eine Verformung von der Form $x = x_0 \exp\{-at\} \sin \omega t$ ist. Die allgemeinen Beziehungen für $G^*(\omega,a) = G'(\omega,a) + iG''(\omega,a)$ werden anhand des Relaxationsspektrums abgeleitet. Die Benützung einer Feder zur Unterstützung der Probe und zur Verkleinerung des Verhältnisses a/ω wird diskutiert und als wünschenswert betrachtet. Wenn auf diese

Weise Daten für $G''(\omega)$ oder $G''(\omega,a)$ zugänglich sind, liefert das Zweite-Iterations-Näherungsverfahren von Ninomiya und Ferry eine rasche und wirksame Methode zur Auffindung des Relaxationsspektrums.   Mit der gleichen Genauigkeit, mit welcher der Zeit–Temperaturreduktionsfaktor a_T bekannt ist oder anhand von Beziehungen, wie etwa der WLF-Gleichung, erhalten werden kann, kann die Funktion $G''(\omega,a)$ in einem Temperaturbereich mit nahezu konstanter Frequenz in $G''(\omega,a)$ bei konstanter Temperatur und variierender Frequenz übergeführt werden.   In solchen Fällen kann das relativ einfache Torsionspendel, oder eine analoge Vorrichtung, in ökonomischer Weise eine Charakterisierung des viskoelastischen Verhaltens des Materials in einem ausgedehnten Zeit- oder Frequenzbereich liefern.