



ACTUALITÉS SCIENTIFIQUES ET INDUSTRIELLES

1190

“ RHEOLOGIE ”

PUBLICATIONS DE L'INSTITUT NATIONAL DE TECHNOLOGIE
BRÉSIL

sous la direction du

Professeur E. L. da FONSECA COSTA

Rio de Janeiro

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MATHEMATICAL STRUCTURE OF THE
THEORIES
OF
VISCOELASTICITY

BY

BERNHARD GROSS

(Instituto Nacional de Tecnologia)
Rio de Janeiro



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HERMANN & C^{ie}, ÉDITEURS

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PRÉFACE

La Mécanique Appliquée a établi des théories générales pour résoudre les questions relatives aux solides « hookeiens » et aux fluides « newtoniens ».

Cependant, dans l'univers, les solides n'obéissent pas exclusivement aux lois de Hooke, ni les fluides, à celles de Newton. On observe fréquemment des phénomènes irréversibles, des déformations plastiques, le fluage des solides, etc., qui introduisent de la complexité dans les problèmes courants en mécanique. Plusieurs de ces phénomènes ont déjà été étudiés en Rhéologie, mais jusqu'à présent, ces études, n'envisageant, presque toujours, que des cas particuliers, ne donnent pas une théorie générale du sujet.

M. Bernhard Gross, Directeur de la « Divisão de Electricidade e Medidas Electricas » de l'Instituto Nacional de Tecnologia, de Rio de Janeiro et membre du « Centro de Estudos de Mecânica Aplicada », attaché au même Institut, présente, dans ce fascicule, les bases d'une théorie générale des phénomènes linéaires des corps « viscoélastiques ».

La théorie proposée par M. Gross est fondée sur les travaux de Volterra et sur le principe de superposition, dont la validité est incontestable dans l'étude des phénomènes de Rhéologie. Elle est ainsi une théorie phénoménologique. Quoiqu'elle ne s'occupe pas de l'explication intime du mécanisme viscoélastique, elle analyse ses conséquences avec justesse. De telles théories ont toujours été extrêmement fécondes au progrès de la science, puisque, en réalité, elles expriment le résultat de l'observation et par cela même servent de base à l'édification de nouvelles théories explicatives.

Nous pouvons rappeler ici que les théories explicatives de la physique moderne sont toutes appuyées sur des théories phénoménologiques comme, par exemple, la Thermodynamique, l'Electromagnétisme, etc.

Nous croyons ainsi que la théorie générale si bien conçue et

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établie par M. Bernhard Gross et exposée dans ce fascicule aura une grande importance dans l'étude des problèmes rhéologiques.

Le « Centro de Estudos de Mecânica Aplicada », du I. N. T., sous la direction du Professeur Edmond Brun, est le siège d'études et de discussions sur des problèmes de Rhéologie. Nous espérons pouvoir bientôt en divulguer les résultats de ces travaux par une autre publication de cette même série et apporter ainsi une nouvelle contribution à cet important chapitre de la Mécanique Appliquée.

E. L. DA FONSECA COSTA.

Directeur Général du I. N. T., Rio de Janeiro.



FOREWORD

In recent years an enormous amount of literature on viscoelastic properties of high polymeric solids has been published. So far as the mathematical background of the theory is concerned, many of these papers cover the same ground. The present exposition aims at a description of the foundation and structure of the mathematical framework that is common to all theories of linear viscoelastic behavior. The theory, at the present stage, is approaching completion. Further progress is likely to be made in applications rather than on fundamental principles. This situation seemed to justify a type of exposition which in a way may be called "dogmatic". Emphasis is definitely put on the purely mathematical side, however many intermediate developments are not given in detail, so the exposition is that of a formulary rather than of a textbook.

The author, for many years, has been associated with an electrical engineering department. He became familiar with the mathematics of dielectric phenomena and electrical network theory — the counterparts of viscoelastic effects — a long time before he had his attention directed to the latter. This will perhaps excuse his tendency of bringing into the discussion of viscoelastic theory concepts and methods which originated in electrical theory.

An explanation seems to be due for the fact that a book like the present came to be written in the electrical engineering department of an Institute of Technology. The main task of the Brazilian National Institute of Technology, like that of other congenerous institutions, is the study of technical problems

with the ultimate aim to further the industrial development of the country. But the Director General of the Institute, Professor E. L. da Fonseca Costa, has always stressed the importance of fundamental research. In spite of budget restrictions and other difficulties inherent in the structure of most Government Departments, he has been able to create a climate favorable for the growth of pure science, in the firm belief that any significant progress in science ultimately will advance technology too, directly when its results find immediate technical application, or indirectly by its formative and cultural value. His unerrant faith in science and unyielding support have been an invaluable encouragement to the author who feels deep gratitude for him.

During the last year science in Brasil has received a great impulse by the foundation of a National Research Council, headed by Admiral Alvaro Alberto, with the general program of furthering activity in all branches of science. In the preparation of this monograph the author had already the benefits of the Council, which put at his disposal a special grant allowing him to increase his technical and administrative staff and thus to free himself of part of his technical and administrative duties and to devote most of his time to scientific research. The help of the Council is gratefully acknowledged.

Rio de Janeiro, February, 1952

B. GROSS.



I

INTRODUCTION

1. ELASTIC AFTER-EFFECT AND VISCOELASTIC BEHAVIOR

In classical theory the behavior of an isotropic deformable medium is characterized by a set of constant coefficients. Observers more than 100 years ago found that most substances failed to fit into this simple pattern and exhibited a behavior that depended on the deformation and load history of the sample under test. In consequence such effects which were not accounted for by the classical theory were called elastic after-effect. The study of it occupied a great number of physicists. However for most of the materials with which their studies were made, the "anelastic" effects represented a rather small correction and the bulk of the observed data could still be satisfactorily explained by the classical concepts. The study of the after-effect for some time appeared to be a matter of academical rather than practical interest. The situation changed however with the development of the modern high polymeric and rubberlike materials, for which the "anelastic" effects are frequently so pronounced that they obliterate the "normal" behavior. The precise knowledge of the mechanical behavior of these substances became of greatest practical value and its investigation was undertaken intensively. It was found that these substances exhibit properties which are found in elastic and in viscous substances. Thus the term "viscoelasticity" was coined.

The situation of the research worker in this field nowadays is more favorable than was that of the scientists of the last century — not only because he can avail himself of the information which has piled up during a century of research (an opportunity of which apparently not everybody seems to be aware), but

7. — TABLE OF FUNCTIONS

The present paper usually employs a familiar terminology, except perhaps in that « plastic strain » (as opposed to elastic strain) is used as a convenient notation for what other authors have called Newtonian, viscous, or linear, flow. The subject of nomenclature is however too controversial to be discussed here.

Table I gives the functions and coefficients mentioned in the foregoing discussion. It includes also the distribution functions to be discussed in the next chapter.



III

THE RELAXATION FUNCTION
AS A LAPLACE INTEGRAL

The relaxation function is a continuous, decreasing function which for $t \rightarrow \infty$ goes to 0. Thus it can be represented in integral form as

$$(11 a) \quad \bar{\psi}(t) = \int_0^{\infty} \bar{\beta} \bar{F}(\tau) e^{-t/\tau} d\tau$$

The normalization factor $\bar{\beta}$ is determined in such a way that

$$(12 a) \quad \int_0^{\infty} \bar{F}(\tau) d\tau = 1,$$

that is

$$(12 b) \quad \bar{\beta} = \bar{\psi}(0).$$

$\bar{F}(\tau) d\tau$ is the relaxation spectrum. This may be a continuous or a line spectrum. In the last case it is written

$$(13) \quad \bar{F}(\tau) = \sum \bar{A}_i \delta(\tau - \bar{\tau}_i)$$

and eq. (11 a) degenerates into

$$(11 b) \quad \bar{\psi}(t) = \sum \bar{\beta} \bar{A}_i e^{-t/\bar{\tau}_i}$$

$\bar{\tau}_i$ being the characteristic relaxation times.

Introducing a relaxation frequency $s = 1/\tau$, and a frequency function $\bar{N}(s)ds$,

$$(14) \quad \bar{N}(s) = \bar{\beta} \bar{F}(1/s)/s^2 \quad s = 1/\tau$$

eq. (11 a) is transformed into

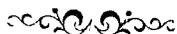
$$(15) \quad \bar{\psi}(t) = \int_0^{\infty} \bar{N}(s) e^{-ts} ds.$$

For a line spectrum one has $\bar{N}(s) = \sum \bar{\beta} \bar{A}_i \delta(s - \bar{s}_i)$ and the integral (15) transforms into $\bar{\psi}(t) = \sum \bar{\beta} \bar{A}_i \exp(-\bar{s}_i t)$.

In this deduction the existence of the distribution function $F(\tau)$ appears merely as a result of the mathematical properties of the relaxation function and not of any assumptions about a molecular mechanism. Conversely the possibility of finding a function that actually fits into eq. (11) cannot be considered as proof for such a mechanism.

Inspection of the integral (15) shows that this is a Laplace integral. Indeed the reason for the substitution (14) was to transform eq. (11) into this form. Therefore, when $\bar{\psi}(t)$ is given as an analytical expression, standard methods for the inversion of the Laplace integral can be applied as was pointed out by Gross (16). The technique of using known Laplace pairs for the analysis of the relaxation spectrum was discussed in length by H. H. Macey (17). Such methods are found in numerous textbooks of which here reference is made to Van der Pol and Bremmer (18).

The integral inversion formulae do not lend themselves easily to numerical computation. Thus the solution becomes difficult, when it seems impossible to find an analytical expression which fits sufficiently well the data and at the same time allows for an inversion of the Laplace transform in analytical form. However a method of computation has been developed by C. Eckart (19), in which the experimental data are represented by a polynomial of a simple function of t . By this power expansion method the distribution function can be calculated to any degree of approximation, provided $\bar{\psi}(t)$ is given over a sufficiently wide interval of t . Eckart himself has applied this method successfully to the formally identical problem of the analysis of the absorption curve of cosmic radiation. Another expansion method was given by Macey (17).



IV

APPROXIMATION METHODS FOR THE DETERMINATION OF THE RELAXATION SPECTRUM

The relaxation function, according to eq. (11) is expressed in terms of the relaxation spectrum as an integral transform, with the range of integration extending from 0 to ∞ . The value of $\bar{\psi}(t)$ at a given point t_0 therefore depends on all the values of the distribution in the interval $0 - \infty$. Thus it cannot *in general* be expressed in terms of the value of the relaxation spectrum at one point. Conversely, the rigorous inversion methods will not *in general* allow to express the value of the distribution function at one given point as a function of the relaxation function at some other single point, but will give a functional expression in which appear all values of the relaxation function in the interval $0 - \infty$. Therefore, the spectrum can be determined *rigorously* if, and only if the relaxation function is known over the entire time scale. Of course not all values contribute to the same extent. The "weighing" factor $\exp(-ts)$ reduces the influence of the far-off end of the spectrum upon a given $\bar{\psi}(t)$. For the application of the analytical methods the relaxation function must therefore be given in the form of an analytical expression in the interval $0 - \infty$.

Experiment, however, does not provide one with analytical expressions, but with a set of experiment data, plots in a graph, which of course extend over a limited interval of time only. One has therefore to find a suitable formula which fits those data sufficiently well and is also amenable to further treatment. Apart from the possible difficulty to find such an expression, this method necessarily implies in an extrapolation of the experimental data into a region where the behavior of the under-

lying function is unknown. However, since theoretically *all* values of this function contribute to the spectrum, the result of the analysis will depend to some extent on the form of the extrapolation. In certain instances some uncertainty will therefore result in the determination of the spectrum.

For these reasons many tentatives were made to obtain an inversion method which would give the relaxation spectrum by the application of some numerical or graphical operation on the experimental data. This would imply in the establishment of a direct one-to-one relationship between one point of the relaxation function and one point of the relaxation spectrum. Since this was shown to be impossible, one can only hope to get an approximation method. The error depends on the form of the (true) relaxation spectrum and can hardly be estimated properly. The methods are more reliable when the spectrum is broad and resembling a power law than when it is sharp. Thus when applying these methods one should always keep in mind that they will give a general idea of the shape of the spectrum, but that the result should be confirmed by independent theoretical or experimental methods, if it is to be used for further treatment or discussion.

Approximation methods were given by Alfrey and Doty (9), Ter Haar (20), C. Zener (9), and F. Schwarzl (21) to whom the most comprehensive treatment is due. So far as these methods apply to the inversion of the integral (15) the exponential function is substituted by some suitable expression which permits inversion by differentiation. Alfrey's method is obtained by substitution of $\exp(-ts)$ by a rectangle of the same area, Ter Haar's method by substituting for $s \exp(-ts)$ a delta function $\delta(s - 1/t)/t^2$. A further and possibly better approximation is obtained when $\exp(-ts)$ is substituted by the first term of its series expansion and the integral taken from $s = 0$ to $s = 1/t$. Table II summarizes these methods and also shows the results when they are applied

a) to $\bar{\psi}(t) = \exp(-\mu t)$

b) to $\bar{\psi}(t) = At^{-n}$.

TABLE II. — Approximation Methods

Author	Type of Approximation	Inversion Formula $\bar{\psi}(\tau)$	Method applied to	
			$e^{-\mu t}$	At^{-n}
Ter Haar	$se^{-ts} = \delta(s - 1/t)/t^2$	$\bar{\psi}(\tau)/\tau$	$e^{-\mu\tau/\tau}$	$A\tau^{-(1+n)}$
Alfrey	$e^{-ts} = \begin{cases} 1 & s \leq 1/t \\ 0 & s > 1/t \end{cases}$	$-\bar{\psi}'(\tau)$	$\mu e^{-\mu\tau}$	$nA\tau^{-(1+n)}$
Gross	$e^{-ts} = \begin{cases} 1 - ts & s \leq 1/t \\ 0 & s > 1/t \end{cases}$	$\tau \bar{\psi}''(\tau)$	$\mu^2 \tau e^{-\mu\tau}$	$n(n+1)A\tau^{-(1+n)}$
Rigorous Solution			$\delta(\tau - 1/\mu)$	$A\tau^{-(1+n)}/\Gamma(n)$



V

RELATIONS BETWEEN COMPLEX
MODULUS FUNCTION,
RELAXATION FUNCTION, AND RELAXATION
SPECTRUM

Having defined the distribution function of relaxation times we shall now discuss the relations existing between the quantities belonging to group II. This is possible with the aid of form (10 b) of the principle of superposition, convenient for all applications in which the strain is given.

1. — COMPLEX MODULUS FUNCTION
AND RELAXATION FUNCTION

The complex modulus function was defined as the stress developed under a sinusoidally varying strain, applied for a very long time so that the transient has disappeared. Taking $\alpha = \exp(i\omega t)$ and substituting into (10 b) one gets

$$(16) \quad E^*(i\omega) = i\omega \int_0^{\infty} e^{-i\omega\tau} \bar{\psi}(\tau) d\tau + E_0$$

or separating into real and imaginary component

$$(17 a) \quad E_1(\omega) = \omega \int_0^{\infty} \bar{\psi}(\tau) \sin \omega\tau d\tau$$

$$(17 b) \quad E_2(\omega) = \omega \int_0^{\infty} \bar{\psi}(\tau) \cos \omega\tau d\tau$$

where $E^* = (E_0 + E_1) + iE_2$. Mathematically these integrals are one-sided Fourier transforms. They enable one to calculate

the complex modulus function or the real or imaginary component of it from the relaxation function. The integrals (17) are easily inverted and give then expressions for the relaxation function in terms of the dynamic modulus or the dynamic friction. Applying the Fourier inversion one has

$$(18 a) \quad \bar{\psi}(t) = \frac{2}{\pi} \int_0^{\infty} \frac{E_1(\omega)}{\omega} \sin(\omega t) d\omega$$

$$(18 b) \quad \bar{\psi}(t) = \frac{2}{\pi} \int_0^{\infty} \frac{E_2(\omega)}{\omega} \cos \omega t d\omega$$

These expressions allow calculation of the relaxation function, that is, of the behavior under static strain, from dynamical data.

2. — RELATIONS BETWEEN DYNAMIC MODULUS
AND DYNAMIC VISCOSITY

The simultaneous existence of the two equs. (18) implies in a relationship between E_1 and E_2 ; otherwise it would be impossible that two different integrals yield the same expression for $\bar{\psi}(t)$. This relation has a physically more interesting aspect if for $E_2(\omega)/\omega$ one substitutes $\eta(\omega)$. Then it shows the connection between the dynamic modulus and the dynamic viscosity. It can be obtained by substituting $\bar{\psi}(t)$ from eq. (18 b) into eq. (17 a). The result is

$$(19 a) \quad E_1(\omega) = \frac{2}{\pi} \int_0^{\infty} \eta(\alpha) \frac{\omega^2}{\omega^2 - \alpha^2} d\alpha$$

$$(19 b) \quad \eta(\omega) = \frac{2}{\pi} \int_0^{\infty} E_1(\alpha) \frac{1}{\alpha^2 - \omega^2} d\alpha$$

The integrals are principal values. They can frequently be evaluated by analytical methods. But they are also amenable to numerical or graphical computation. Thus it is not necessary that the dynamical data be given in analytical form and represented by mathematical expressions. It is sufficient when they are given graphically. The weighing factor $1/\omega^2$ gives an automatic cut-off at the high frequency end.

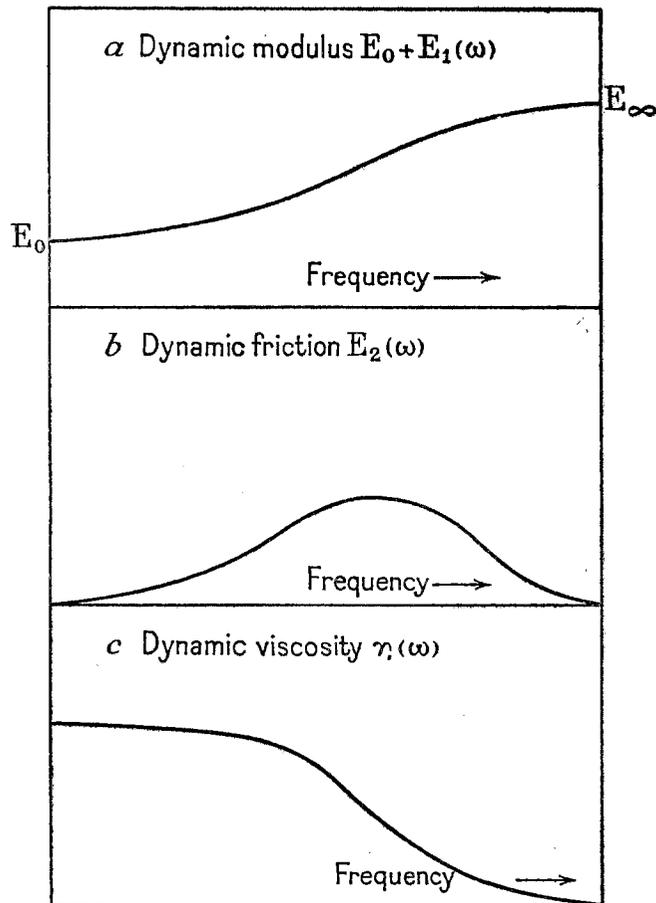


FIG. 5. — Components of complex modulus function and dynamic viscosity.

An important relation that follows from (19 b) is

$$(19c) \quad \eta(0) = \frac{2}{\pi} \int_0^{\infty} \frac{E_1(\alpha)}{\alpha^2} d\alpha$$

Mathematically these integrals are known as Hilbert transforms. They are closely connected with the theory of Fourier integrals and of analytical functions. A detailed discussion is given by Titchmarsh (22) and by Gross (23), Gama (24) and Levi (25). In physics they now have become a matter of great importance in consequence of many applications in electrical network theory and have been studied by Bode (26), but were already

discussed in connection with optical dispersion by Kronig (27) and Kramers (28), and in connection with dielectrics by Gross (29) and Silva and Gross (30), who have made practical applications and shown how the integrals are computed graphically. The present exposition follows the same lines as that of Gross (29) for dielectrics. The literature has already become too extensive for a complete bibliography of all important papers on the subject to be given here.

2. — COMPLEX MODULUS FUNCTION IN TERMS OF RELAXATION SPECTRUM

The integral (16) is an one-sided complex Fourier transform equivalent to a Laplace transform. Since $\bar{\psi}(t)$ was given as a Laplace transform, $E^*(i\omega)$ is essentially an iterated Laplace or Stieltjes transform. Carrying out the iteration process one gets

$$(20) \quad E^*(i\omega) = i\omega \int_0^{\infty} \frac{N(s)}{s + i\omega} ds + E_0$$

and separating into real and imaginary part (fig. 5)

$$(21a) \quad E_1(\omega) = \int_0^{\infty} \bar{N}(s) \frac{\omega^2}{\omega^2 + s^2} ds$$

$$(21b) \quad E_2(\omega) = \int_0^{\infty} \bar{N}(s) \frac{\omega s}{\omega^2 + s^2} ds$$

These expressions give dynamic modulus and dynamic friction in terms of the frequency spectrum \bar{N} , or the relaxation spectrum \bar{F} when use is made of eq. (14).

For a line spectrum one has

$$(22a) \quad \bar{N}(s) = \sum \bar{\beta} \bar{A}_i \delta(s - \bar{s}_i)$$

Making use of the known properties of the delta function the integral (20) transforms into :

$$(22b) \quad E^*(i\omega) = \sum \left[\bar{\beta} \bar{A}_i \frac{\omega^2}{\omega^2 + \bar{s}_i^2} + i \bar{\beta} \bar{A}_i \frac{\omega \bar{s}_i}{\omega^2 + \bar{s}_i^2} \right] + E_0$$

Usually one starts with such an expression and then obtains the integrals (20) as a generalization. We prefer to give first the

general formulae and to derive from them the relations for discontinuous spectra.

4. — RELAXATION SPECTRUM FROM DYNAMICAL DATA

These integral transforms have been known for a long time. The problem one is faced with now is their inversion. In a way this corresponds to the inversion of the Laplace transform (15) and what was said before about different types of methods in part applies here too.

Approximation methods were developed (31) and in some cases successfully applied (32). They are essentially equivalent to Alfrey's Laplace inversion method and consist in substituting the expression $\omega^2/(\omega^2 + s^2)$ by 1 for $s < 1/\omega$ and 0 for $s > 1/\omega$. The eqs. (21) can then be inverted by differentiation.

A rigorous inversion method was however given by Fuoss and Kirkwood (4) and discussed by Weinberg and Householder (33) and by Gross (34). It is very much simpler and more direct than are the inversion methods for the Laplace integral. For this reason the relative importance of rigorous and approximate methods is now different from what it was in the former case. The availability of a simple rigorous method makes approximation dispensable. These formulae are :

$$(23) \quad \bar{N}(\omega) = \pm \frac{1}{\pi\omega} \text{Im } E^*(\omega e^{\pm i\pi})$$

and

$$(24 a) \quad \bar{N}(\omega) = \pm \frac{2}{\pi\omega} \text{Im } E_1(\omega e^{\pm i\pi/2})$$

$$(24 b) \quad \bar{N}(\omega) = \pm \frac{2}{\pi\omega} \text{Re } E_2(\omega e^{\pm i\pi/2})$$

They invert, respectively, equ. (20), (21 a), (21 b). The meaning of the symbols "Re" and "Im" is "Real part" and "Imaginary part".

Eq. (23) is of importance for analytical purposes. Eqs. (24) are important for both analytical and practical applications. For the discussion of experimental dynamical data one has again to represent the experimental curves by mathematical expressions.

But while in the former case this was only the first step in a complicated mathematical process (except of course when the chosen function was identical with a component of a known Laplace pair), now it gives already the solution of the problem. Indeed, the distribution functions now follow by a trivial mathematical operation, the substitution of the variable $i\omega$ by $\omega \exp(\pm i\pi)$, or ω by $\omega \exp(\pm i\pi/2)$, calculation of the resulting complex expression and separation into real and imaginary part. This needs some practice in complex algebra, but no knowledge of higher mathematics. In the interpretation of dielectric measurements the method has become commonplace. Examples for its application have been given profusely. For this reason it is believed that its application to the discussion of the dynamical behavior of viscoelastics would be of no less importance.

When measurements have been made of both E_1 and E_2 , \bar{N} may be determined from either of them, or from both these quantities. Following the receipt given above, in the lastnamed case one will represent both E_1 and E_2 by suitable expressions and derive from them \bar{N} . The resulting formulae for \bar{N} usually will be different but when represented graphically should give functions of the same shape. This will constitute a test for the theory. Alternatively one may choose an expression for say E_1 , calculate E_2 with the aid of eq. (19 b) and see how far the resulting curve fits the measurements.

In conclusion it results that the determination of the relaxation spectrum from dynamical data is much simpler than from static data.

5. — MATHEMATICAL PROPERTIES [OF THE INVERSION FORMULA

In view of the somewhat unusual form of the eqs. (23) and (24) here a simple way for deducing them shall be given. Starting with equ. (20) one makes the substitution :

$$(25) \quad \omega \rightarrow i\omega \pm \epsilon \quad i\omega \rightarrow -\omega \pm i\epsilon.$$

Then

$$(26) \quad E^*(-\omega \pm i\epsilon) = (-\omega \pm i\epsilon) \int_0^\infty \bar{N}(s) \left[\frac{s - \omega}{(s - \omega)^2 + \epsilon^2} \mp \frac{i\epsilon}{(s - \omega)^2 + \epsilon^2} \right] ds + E_0$$

Now consider this expression for $\lim_{\epsilon \rightarrow 0}$. Then one has

$$(27) \quad \lim_{\epsilon \rightarrow 0} (-\omega \pm i\epsilon) = \omega e^{\pm i\pi} \quad \lim_{\epsilon \rightarrow 0} E^*(-\omega \pm i\epsilon) = E^*(\omega e^{\pm i\pi}).$$

And

$$(28 a) \quad \lim_{\epsilon=0} \int_0^{\infty} \bar{N}(s) \frac{s - \omega}{(s - \omega)^2 + \epsilon^2} ds = \int_0^{\infty} \frac{\bar{N}(s)}{s - \omega} ds,$$

where the integral is a principal value.

$$(28 b) \quad \lim_{\epsilon \rightarrow 0} \frac{1}{\pi} \frac{\epsilon}{(s - \omega)^2 + \epsilon^2} = \delta(s - \omega),$$

where $\delta(\omega)$ is Dirac's Delta function (cf. Van der Pol and Bremmer, ref. 18). Therefore

$$(28 c) \quad \lim_{\epsilon \rightarrow 0} \int_0^{\infty} \bar{N}(s) \frac{\epsilon}{(s - \omega)^2 + \epsilon^2} ds = \pi \bar{N}(\omega),$$

$$(28 d) \quad \lim_{\epsilon \rightarrow 0} \int_0^{\infty} \bar{N}(s) \frac{(s - \omega) \epsilon}{(s - \omega)^2 + \epsilon^2} ds = 0$$

because according to known properties of the Delta function

$$(28 c) \quad \lim_{\epsilon \rightarrow 0} \frac{1}{\pi} \frac{(s - \omega) \epsilon}{(s - \omega)^2 + \epsilon^2} = (s - \omega) \delta(s - \omega) = 0$$

The remaining term is to be multiplied by ϵ and disappears for $\lim_{\epsilon \rightarrow 0}$. Therefore, finally,

$$(29) \quad E^*(\omega e^{\pm i\pi}) = -\omega \int_0^{\infty} \frac{\bar{N}(s)}{s - \omega} ds \pm i\pi\omega \bar{N}(\omega) + E_0$$

and

$$(30) \quad \bar{N}(\omega) = \pm \frac{1}{\pi\omega} \text{Im } E^*(\omega e^{\pm i\pi}).$$

It must be emphasized that $E^*(\omega e^{\pm i\pi})$ is actually a symbolic way for writing $\lim_{\epsilon=0} E^*(-\omega \pm i\epsilon)$. Usually, there is no need to bother about this. For applications it will be sufficient to substitute in the formula for E^* , the variable $i\omega$ by $\omega \exp(\pm i\pi)$. A complex expression will result which has a real and an imaginary part. However it may happen that one of these components disappears. When this is the imaginary component, application of the formula would give zero. For this to occur, the

expression for $E^*(i\omega)$ would have to be rational. In such a case one has indeed to take the rigorous way and calculate the limit precisely. One will then always find a *line* in the relaxation spectrum.

The eqs. (21) can be reduced to the form (20) by a substitution of variables. They therefore are inverted in the same way.

The method which has been given here is not the only, and certainly not the most general method of inversion. It was already mentioned that the eqs. (20) and (21) are Stieltjes transforms. These integrals resemble Cauchy's integral. They can be transformed into a generalized form of Cauchy's integral by a substitution of variables. The inversion is then possible by a generalization of Cauchy's formula, $\bar{N}(\omega)$ being considered as the residue of the function E^* at the point $-\omega$ (35).

The application of the method to the inversion of the Laplace integral, and therefore to the determination of the relaxation spectrum from the relaxation function, was discussed by Gross (36).

The inversion formulae of course involve the principle of analytical continuation. Experiment gives values of a function along the positive real axis. Representing these values as a branch of an analytical function, one then obtains values of this function on the whole complex plane. The one-to-one relationship between one point of the relaxation spectrum and one point of the complex modulus function therefore represents no contradiction to previous remarks about the impossibility of obtaining such relations in the inversion of infinite integrals, because the point of the modulus function is not an experimental point, not being situated along the real axis.

The interesting properties of these formulae would invite a more complete and more rigorous discussion; however, this has to be given elsewhere.



degenerate into a series of deltafunctions. This will be shown presently.

Suppose that according to eq. (33)

$$(51) \quad F(\tau) = \sum_1^M A_i \delta(\tau - \tau_i).$$

Substitution into (49 a) gives

$$(52) \quad \bar{\beta} \bar{F}(\tau) = \frac{1}{\pi \tau^2} \frac{\pi \beta \sum A_i \delta(\tau - \tau_i)}{[K(\tau)]^2 + [\pi \beta \sum A_i \delta(\tau - \tau_i)]^2}$$

This is an expression involving deltafunctions, of a novel type that was recently discussed by Gross and Pelzer (38) and Gross (39). Eq. (52) has the form

$$\frac{1}{\pi} \frac{\epsilon}{[K(\tau)]^2 + \epsilon^2}$$

It is known that for $\lim \epsilon \rightarrow 0$, this expression is equal to $\sum \delta(\tau - \bar{\tau}_i)/|K'(\bar{\tau}_i)|$, where the $\bar{\tau}_i$ are the roots of the eq. $K(\tau) = 0$. It has been shown by Gross (39) that the same result is obtained when ϵ is substituted by $\delta(\tau - \tau_i)$, provided the roots of $K(\tau) = 0$ do not coincide with one of the τ_i . Eq. (52) gives therefore

$$(53) \quad \bar{F}(\tau) = \sum_1^{\bar{M}} \bar{A}_i \delta(\tau - \bar{\tau}_i),$$

where the amplitudes are given by

$$(54 a) \quad \bar{\beta} \bar{A}_i = \frac{1}{\tau_i^2 |K'(\bar{\tau}_i)|},$$

the time constants $\bar{\tau}_i$ are the roots of the equation

$$(54 b) \quad K(\tau) = 0,$$

and $K(\tau)$ is given by

$$(54 c) \quad K(\tau) = \epsilon_\infty/\tau - 1/\eta_0 + \beta \sum_1^M A_i/(\tau - \tau_i).$$

Conversely, if $\bar{F}(\tau)$ is given by expression (53), $F(\tau)$ is given by eq. (51); the amplitudes are

$$(55 a) \quad \beta A_i = \frac{1}{\tau_i^2 |K'(\tau_i)|},$$

the time constants τ_i are the roots of the eq.

$$(55 b) \quad \bar{K}(\tau) = 0$$

and $\bar{K}(\tau)$ is given by

$$(55 c) \quad \bar{K}(\tau) = [E_0 - \bar{\beta} \sum_1^{\bar{M}} \bar{A}_i \bar{\tau}_i/(\tau - \bar{\tau}_i)]/\tau$$

The meaning of $K'(\tau_i)$ is

$$K'(\tau_i) = \left[\frac{d}{d\tau} K(\tau) \right]_{\tau_i}$$

The expressions for K and \bar{K} are easily obtained when eqs. (51) and (53) are substituted into the integrals in (50). Both K and \bar{K} are now polynomials in τ . When no component of plastic strain exists, $1/\eta_0 = 0$ and $E_0 \neq 0$; then the polynomial K is of order M and the polynomial \bar{K} of order \bar{M} . When a component of plastic strain exists, $1/\eta_0 \neq 0$ and $E_0 = 0$; then K is of order $M + 1$ and \bar{K} of order $\bar{M} - 1$. It follows that

$$(56) \quad \bar{M} = \begin{cases} M + 1 & \text{with plastic strain} \\ M & \text{without plastic strain.} \end{cases}$$

The general conclusions are :

- a) When one of the spectra is a line spectrum, the other is a line spectrum too.
- b) When a component of plastic strain exists, the number of lines in the relaxation spectrum always exceeds by 1 the number of lines in the retardation spectrum. When no plastic component exists, the number of lines in both spectra is the same.
- c) The general relations between the amplitudes and time constants for an arbitrary number of lines is given by eqs. (54) and (55).

For the simple exponential functions the relations between the spectra, or the equivalent ones between the creep and the relaxation functions, could have been obtained by application of

the more orthodox methods of Whittaker (40) now found in many textbooks. For dielectrics, such methods were used by Graffi (41) and Gross (42). But it seemed more interesting to give a deduction based on the general eqs. (49) which shows that these are indeed of a very general type and allow one to synthesize in a single expression the relation between the distribution functions for both continuous and discontinuous spectra.

3. — MIXED SPECTRA

A still more general case would be that F or \bar{F} is given by a superposition of a continuous and a line spectrum, that is by an expression of the form

$$(57) \quad F(\tau) = \sum A_i \delta(\tau - \tau_i) + f(\tau),$$

where $f(\tau)$ is a continuous spectrum. It can be shown that under such conditions $\bar{F}(\tau)$ is given by a similar expression which can be calculated without much difficulty. However this shall not be given here, because so far no practical application has been found.

4. — CONCLUDING REMARKS

It was shown that all viscoelastic functions can be represented as integrals over one or the other of the two distribution functions. The establishment of the direct relations between those two functions is therefore of fundamental importance. The *validity* of these relations is general, they apply to continuous, discontinuous, and mixed spectra, that is to creep and relaxation functions which are integrals or series over exponential functions, or both. *Computation* is possible by analytical, graphical, or numerical methods. *Applications* include a) discussion of the difference in shape of typical relaxation and retardation spectra b) influence of plastic strain on the form of the relaxation spectrum c) transformations between corresponding models d) determination of the creep function belonging to a given relaxation spectrum, or the relaxation function belonging to a given retardation spectrum. An *example*, it is possible to calculate the retardation spectrum and the creep function of a substance the relaxation spectrum of which is given by a Wiechert distribution.

IX

THE VOLTERRA INTEGRAL EQUATION BETWEEN THE CREEP FUNCTION AND THE RELAXATION FUNCTION

There remains now only the task of giving a relation between the creep and the relaxation function. It is however found that no direct relation exists, but that both functions are correlated by an integral equation which is not easily solved by elementary methods. The eq. is closely related to the principle of superposition; it plays an important rôle in Volterra's theory of "anelastic" effects and viscoelastic phenomena. So it can hardly be omitted here. It can be obtained either from eq. (45), or directly from the principle of superposition by substitution of (10 b) into (10 a). The ultimate result is

$$(58) \quad E_0 \epsilon_\infty - 1 + \epsilon_\infty \bar{\psi}(t) + E_0 [t/\tau_0 + \psi(t)] + \int_0^t \bar{\psi}(\tau) \left[1/\tau_0 + \frac{d\psi(t-\tau)}{d(t-\tau)} \right] d\tau = 0$$

It is possible, though sometimes cumbersome, to solve this equation with Volterra's method of iterated kernels (15). For the case of no plastic strain, the Volterra integral equation between the rate of creep and the rate of relaxation was given by Gross (ref. 7, 1946) and later by Sips (43) (in a slightly different form which however is easily seen to be equivalent). For dielectrics, a solution by the original Volterra method was given by F. M. de Oliveira Castro (44). Important applications of the superposition theory were recently given by Henderson (45) who calculated the relaxation function belonging to Andrade's creep function. Comparison between the theoretical and experimental results gave so satisfactory an agreement that according to Henderson "the empirical stress relaxation formulae, which often involve several constants, and are never completely satisfactory, may be dispensed with".

c) On the bottom level, a reversible integral transform connects the retardation and the relaxation spectrum.

X

GENERAL STRUCTURE OF THE THEORY

One is now in a position to give a picture of the general structure of the theory.

Visco-elastic effects and functions are classified in 2 groups, group I referring to creep effects and measurements made under given stress, and group II referring to relaxation effects and measurements made under given strain.

Inside each group one distinguishes 3 levels :

- a) The top level, with the complex compliance function in group I and the complex modulus function in group II.
- b) The medium level with the creep function in group I and the relaxation function in group II.
- c) The bottom level, with the retardation spectrum in group I and the relaxation spectrum in group II.

To go from one level to that immediately above, one has to apply a Laplace transform (the one-sided complex Fourier transform being equivalent to a Laplace transform). To go from one level to that immediately below one has to apply an inverse Laplace or Fourier transform. It is however possible to reach from the bottom level directly the top level by means of a Stieltjes transform. Conversely, one may descend from the top level to the bottom level directly by means of an algebraic (complex) relation.

Between the two groups there are several relations which allow one to shift from one group to the other. These relations connect functions lying on the same level. According to the existence of 3 different levels, there are 3 types of functional relationships.

- a) On the top level, a complex algebraic relation connects the complex modulus and the complex compliance function.
- b) On the medium level, a Volterra integral equation connects the creep and the relaxation function.

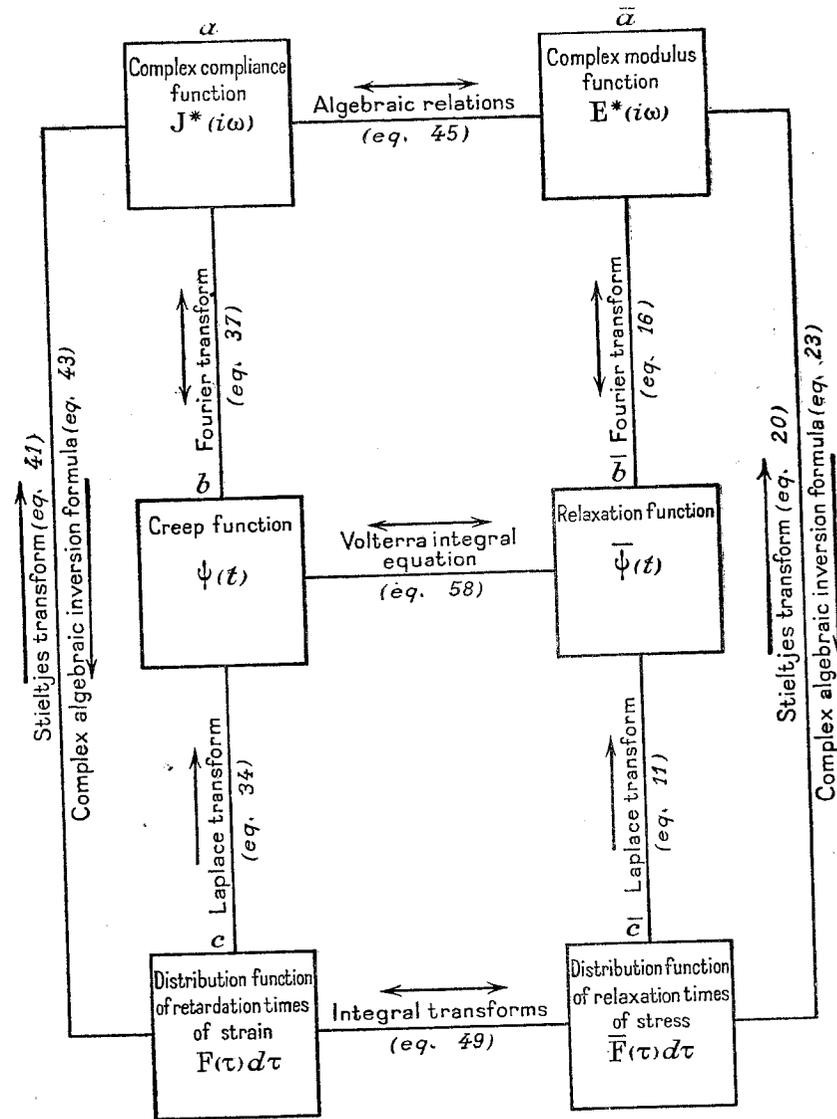


Fig. 8. — Diagram showing structure of theory.

This structure is shown in fig. 8, not for its possible academic interest, but because it is of very real value for all practical calculations. It shows the various possibilities which exist for

the form (51) and (53). But as was shown these can always be duplicated by a Voigt or a Maxwell model, which therefore represent the general case.

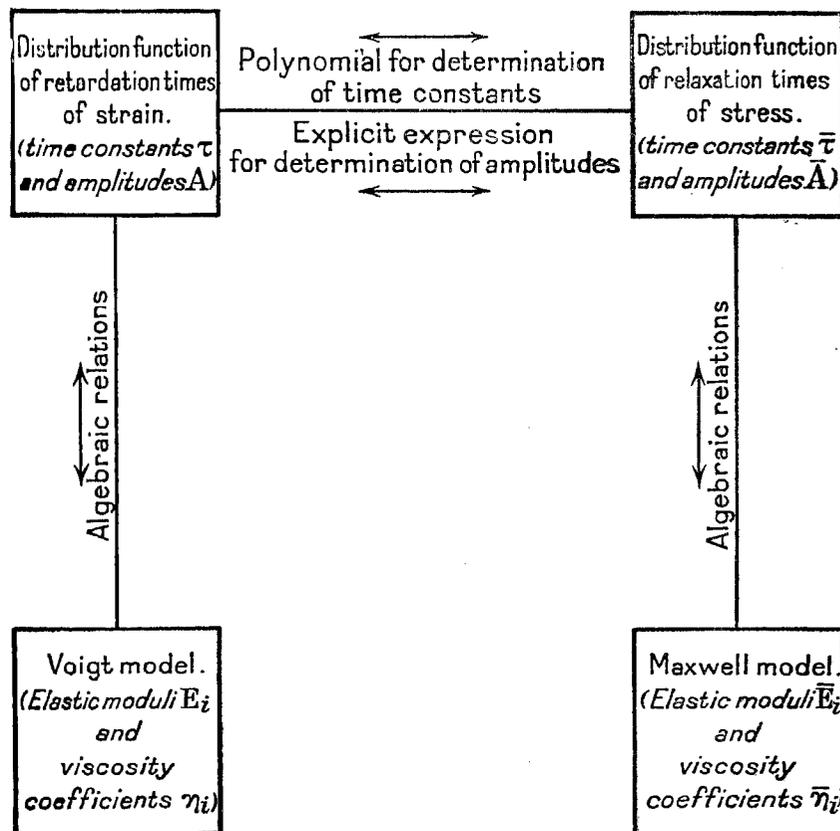


FIG. 12. — Diagram showing relation between equivalent models.

7. — RELATIONS BETWEEN SIMPLE VOIGT AND MAXWELL MODELS

As a simple example a Voigt and a Maxwell model both constituted by a single spring and a branch shall be treated. Considering given the coefficients ϵ_∞ , E_1 and τ_1 of the Voigt model, one wants to determine the coefficients E_0 , \bar{E}_1 and $\bar{\tau}_1$ of the Maxwell model. Both the retardation and the relaxation spectrum are given by single lines, of amplitudes βA_1 and $\bar{\beta} \bar{A}_1$, and time constants τ_1 and $\bar{\tau}_1$. The relations between these ampli-

tudes and time constants shall be calculated first. The function $K(\tau)$ of equ. (54) is given by

$$(86) \quad K(\tau) = \epsilon_\infty/\tau + \beta A_1/(\tau - \tau_1).$$

The condition $K(\tau) = 0$ gives

$$(87) \quad \bar{\tau}_1 = \tau_1 \epsilon_\infty / (\epsilon_\infty + \beta A_1).$$

Differentiating eq. (86) gives

$$(88) \quad K'(\tau) = -\frac{1}{\tau^2} \frac{\epsilon_\infty (\tau - \tau_1)^2 + \beta A_1 \tau^2}{(\tau - \tau_1)^2}$$

Substituting $\bar{\tau}_1$ from eq. (87) into the last eq. and applying eq. (54 a) gives for the amplitude $\bar{\beta} \bar{A}_1$

$$(89) \quad \bar{\beta} \bar{A}_1 = \frac{1}{\epsilon_\infty} \frac{\beta A_1}{\beta A_1 + \epsilon_\infty}$$

With the aid of eqs. (85) one obtains finally the relations between the constants of the models in the form

$$(90) \quad \bar{E}_1 = \frac{1}{\epsilon_\infty} \frac{1}{1 + E_1 \epsilon_\infty} \quad \bar{\eta}_1 = \eta_1 \frac{1}{(1 + E_1 \epsilon_\infty)^2}$$

The constant E_0 is obtained from table III as

$$(91) \quad E_0 = \frac{1}{\epsilon_\infty + 1/E_1}$$

In a case as simple as that the relations of course could have been obtained in a more direct way. But the point to be made is that the theory provides for a general formula which gives the relations between the constants of equivalent models for any number of branches and which has been brought into a form which allows for numerical applications. With increasing number of branches the degree of the polynomial $K(\tau) = 0$ increases and accordingly increases the difficulty of determination of its roots. However if necessary numerical methods of computation can be applied. The problem of shifting from one model to the other has therefore found a general solution.



XIII

TABLE OF DISTRIBUTION FUNCTIONS

The following table lists a number of expressions which have been used in the discussion of viscoelastic and dielectric behavior. It does not aim to be complete. It includes some formulae which were not found in the literature but derived from given creep functions or which represent obvious generalizations of known expressions. The order is not chronological, but follows rather the type of function indicated. Most functions are not normalized.

Dielectric relaxation spectra correspond to viscoelastic retardation functions. This is a consequence of the viscoelastic-dielectric analogy, which makes current correspond to rate of strain and voltage to stress.

Table V. — Distribution functions

$$(1) \quad \frac{b}{\sqrt{\pi}} e^{-(bu)^2} du \quad u = \log_e (\tau/\tau_0)$$

Viscoelastic relaxation spectrum of Wiechert (1). Tables for corresponding rate of relaxation given by Jahnke-Emde (46). Methods for deriving coefficients from dynamical data given by Yager (53).

$$(2) \quad \beta e^{-(\tau_0/\tau)} d\tau/\tau$$

Viscoelastic retardation spectrum derived from creep data of Bennewitz (54) and Lyons (55).

$$(3) \quad \beta e^{-(\tau/\tau_1 + \tau_2/\tau)} d\tau/\tau$$

Viscoelastic relaxation spectrum derived by Macey (17) with method of Laplace pairs.

$$(4) \quad \beta (e^{-\tau_1/\tau} - e^{-\tau_2/\tau}) d\tau/\tau$$

Viscoelastic relaxation spectrum derived by Gross (56) from relaxation data of Andrews *et al.* (57). Gross (56) gives also the corresponding retardation spectrum.

$$(5) \quad \begin{cases} \frac{\beta}{\tau^2} \frac{e^{(\tau_1/\tau - \tau_2/\tau)}}{[c e^{(\tau_1/\tau - \tau_2/\tau)} - 1]^2} d\tau & 0 < \tau < \tau_2 \\ 0 & \tau_2 < \tau < \infty \end{cases}$$

Dielectric relaxation spectrum derived by Kuhn (58) for high polymers.

$$(6) \quad \beta \frac{e^{-u}}{(e^{-u} + 1)^2} du \quad u = \log_e \tau/\tau_0$$

Relaxation spectrum derived by Kirkwood and Fuoss (59).

$$(7) \quad \beta e^{-(\tau_0/\tau)} d\tau/\tau^n$$

Dielectric relaxation spectrum derived by Voglis (60) from experimental dynamical data on dielectric after-effect.

$$(8) \quad \begin{cases} \frac{\sin \alpha \pi}{\pi} \left[\frac{\tau}{\tau_0 - \tau} \right]^{1-\alpha} d\tau & \tau_0 < \tau < \infty \\ 0 & 0 < \tau < \tau_0 \end{cases}$$

Dielectric relaxation spectrum derived by Cole (61) from data on dielectric dispersion.

$$(9) \quad \beta d\tau/\tau^n \quad 0 < n < 1$$

Dielectric relaxation spectrum derived by Schweidler (3) for dielectric after-effect. Corresponds also to Andrade's creep function (62) and to the (linear) Nutting equation (63).

$$(10) \quad \begin{cases} 0 & 0 < \tau < \tau_1 \\ \beta d\tau/\tau & \tau_1 < \tau < \tau_2 \\ 0 & \tau_2 < \tau < \infty \end{cases}$$

This expression was introduced by Becker (10) who used it indistinctively for both the retardation and the relaxation spectrum. It was applied by Richter (49) in the discussion of the magnetic after-effect. Tobolsky and co-workers (64) used it recently as an expression for the relaxation spectrum, and Buchthal and Kulser (65) for the retardation spectrum. In a less general way, with the restriction $\tau_2 = \infty$ it was used by Lethersich (48) and Gross (66).

$$(11) \quad \left\{ \begin{array}{l} 0 \\ \beta d\tau/\tau^n \\ 0 \end{array} \right. \quad \left\{ \begin{array}{l} 0 < \tau < \tau_1 \\ \tau_1 < \tau < \tau_2 \\ \tau_2 < \tau < \infty \end{array} \right. \quad n \text{ a positive integer}$$

Generalization of formula (10) above, discussed as relaxation spectrum with $n = 0, 1, 2$, by R. D. Andrews (21 b).

$$(12) \quad \left\{ \begin{array}{l} 0 \\ \beta \\ 0 \end{array} \right. \quad \left\{ \begin{array}{l} 0 < \tau < \tau_1 \\ \tau_1 < \tau < \tau_2 \\ \tau_2 < \tau < \infty \end{array} \right. \quad \left[c + \log_e \frac{\tau/\tau_1 - 1}{1 - \tau/\tau_2} \right]^2 + \pi_2$$

Relaxation spectrum corresponding to a retardation spectrum given by formula (10) above, calculated by Buchthal and Kaiser (65), and with the restriction $\tau_2 = \infty$ by Kuhn (8) and Gross (66).

$$(13) \quad \frac{1}{\pi} \frac{\cos(\alpha\pi/2) \cosh(\alpha u)}{\cos^2(\alpha\pi/2) + \sinh^2(\alpha u)} du \quad u = \log_e \tau/\tau_0$$

Dielectric relaxation spectrum derived by Fuoss and Kirkwood (4) from dielectric loss data.

$$(14) \quad \frac{1}{2\pi} \frac{\sin(\pi m)}{\cosh(mu) + \cos(m\pi)} du \quad u = \log_e \tau/\tau_0$$

Dielectric relaxation spectrum derived by Cole and Cole (65) from dielectric dispersion. The function was proposed by Gross (7) as expression for the retardation spectrum; it was shown that it can be used simultaneously for both the retardation and the relaxation spectrum (without plastic deformation) provided the value of the constant τ_0 is adjusted. When plastic deformations are taken into account, the retardation spectrum remains unchanged, but the relaxation spectrum is altered. The modified relaxation spectrum was given by Pelzer and Gross (7). The function is also discussed by Nolle (9).



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