

Lognormal Distribution Function for Describing Anelastic and Other Relaxation Processes

II. Data Analysis and Applications

Abstract: The present paper deals with the use of the theory and computations given in Part I for a relaxation process governed by a lognormal distribution of relaxation times. The experimental determination of the basic parameters appearing in the theory is shown to require the application of a number of corrections to the usual type of dynamical data. General expressions are derived for these corrections, and the data necessary for their use are presented in graphical form. Specific examples are given of the application of the theory to the analysis of anelastic relaxation phenomena.

Introduction

The previous paper¹ (which will be designated as I) has dealt with the behavior of a system which exhibits a lognormal distribution of relaxation times. In particular, methods were given for obtaining the three relaxation parameters, τ_m , δJ , and β , of such a system from the static response function $\psi(t)$, and the dynamic response functions $J_1(\omega)$ and $J_2(\omega)$. The purpose of the present paper is to deal with the use of the theory. We first consider, in the next section, a series of corrections required in the precise evaluation of relaxation parameters from actual dynamical data, taking cognizance of the fact that $J_1(\omega)$ and $J_2(\omega)$ are not quite the functions usually measured experimentally. Finally, the subsequent section deals with possible areas of application of the material contained in these papers, including a discussion of some specific anelastic relaxation processes.

Methods for the analysis of dynamical data*

The theory, as presented in Part I, gives a detailed description of the static and dynamic response functions when a Gaussian distribution in $\ln \tau$ prevails, including methods for evaluation of relaxation parameters (Part I, Table 5). Unfortunately, this theory is not always immediately applicable when dynamical data are involved because the theory assumes that J_1 and J_2 are measured as functions

of ω , while in practice deviations from this procedure usually occur, as follows:

(a) Other dynamic functions, such as $\tan \phi (=J_2/J_1)$, or $J = (J_1^2 + J_2^2)^{1/2}$, are often measured instead of J_1 and J_2 . For example, in dielectric relaxation, the loss angle ϕ is often measured directly, while in anelasticity the internal friction gives $\tan \phi$. The measurement of J instead of J_1 does not generally pose any problems, since the difference between J and J_1 is only of order $\phi^2/2$; thus for $\phi \leq 0.1$ (which is so often the case) this difference is unimportant. On the other hand, $\tan \phi = J_2/J_1$ is a more difficult quantity to interpret than J_2 .

(b) The dynamic response functions are more often measured as a function of T^{-1} than of the frequency. This approach is based on the validity of the Arrhenius relation (I-32),† which makes it possible to change the variable $x (= \ln \omega \tau_m)$ of Eqs. (I-16) and (I-17) by varying the temperature while keeping ω constant. It is clear from Eq. (I-32) that when ω is constant,

$$x = \frac{Q_m}{R} \left(\frac{1}{T} - \frac{1}{T_p} \right), \quad (1)$$

where T_p is the absolute temperature at which the J_2 peak occurs (corresponding to $x=0$). Thus, it appears that one need only insert (1) into Eqs. (I-16) and (I-17) to

*This section may be omitted on a first reading, particularly by a reader who seeks only an over-all picture of the content of these papers.

†The notation (I- π) will be used herein to refer to equation (π) in Part I. Similar notation will be used for the tables and Figures in Part I.

obtain $J_1(T^{-1})$ and $J_2(T^{-1})$. If this were strictly true it would mean that $J_1(T^{-1})$ and $J_2(T^{-1})$ differ from $J_1(x)$ and $J_2(x)$, respectively, only in that they are now centered about T_p^{-1} , and that the abscissa has undergone a change in scale factor (by Q_m/R). While this statement is approximately correct, the change-over from the frequency to the temperature variable leads to complications, resulting from the fact that the parameters δJ , ω , and β may each be explicitly dependent on temperature. (The simple scale change in converting from x to $1/T$ is based, of course, on the assumption that these three quantities are constant.)

The present section deals with the various corrections required in order to be able to utilize the results summarized in Part I, Tables 1 to 5 for the analysis of actual dynamical measurements. These corrections, though not unimportant, are usually small; they may, therefore, be handled as though each is independent of the others. We will be primarily concerned with the J_2 peak because measurements of this quantity (or of the related function $\tan \phi$) may be made with sufficient accuracy to justify making the various corrections. (In the case of the J_1 function, corresponding accuracy is not usually attained.) Involved in these corrections are the width, position, and height of the peak, since these are the quantities used to obtain β , τ_m , and δJ , respectively. The corrections to be considered are those due to: (1) the conversion from $\tan \phi$ to J_2 ; (2) the temperature dependence of δJ ; (3) the temperature dependence of ω ; (4) the temperature dependence of β .

In evaluating these corrections it is useful to consider first the general problem of the perturbation of a symmetric peak function $F(x)$, centered at $x=0$, by a function $G(x)$ to form a perturbed peak function $P(x)$ given by

$$P(x) = F(x)G(x), \quad (2)$$

where the perturbation $G(x)$ has the property that $G(0)=1$ and that $G(x)$ is a slowly varying function relative to $F(x)$. The effect of the perturbation will in general be to change the position, the height, and the width of the peak. A straightforward calculation shows that the position of the peak is shifted by an amount δx which, to first order, is given by

$$\delta x = a/A, \quad (3)$$

where a is the slope of the G -function at $x=0$,

$$a = G'(0), \quad (4)$$

and A is the negative curvature of the normalized function $F(x)/F(0)$ at the peak,

$$A = -F''(0)/F(0). \quad (5)$$

In making these calculations, it is convenient to take as the small quantity not the shift in peak position, δx , but rather the shift relative to the half-width of the peak; since the half-width is of order $1/\sqrt{A}$, the quantity $a/\sqrt{A}$ is taken to be small. Thus, for wide peaks δx may

not be $\ll 1$, yet the approximation $a/\sqrt{A} \ll 1$ may still be valid. The height of the peak is changed only to second order in the quantity $a/\sqrt{A}$, i.e.,

$$\frac{P(a/A)}{F(0)} = 1 + \frac{a^2}{2A}. \quad (6)$$

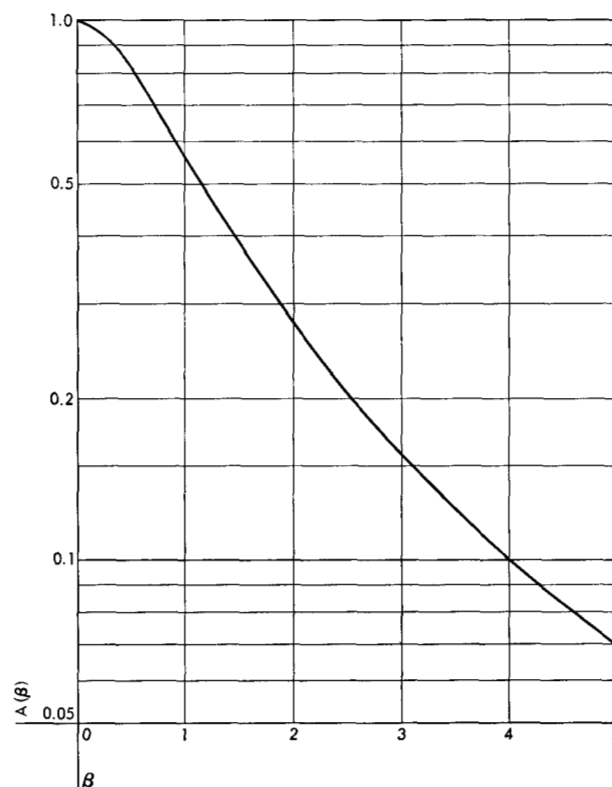
This change can, therefore, be neglected in what follows. For present purposes, the unperturbed peak $F(x)$ will be the J_2 function with constant values for δJ , ω , and β . The peak shift, δx , due to the perturbation $G(x)$, means that the condition $\ln \omega \tau_m = 0$, valid at the peak in the absence of a perturbation, is replaced by

$$\ln \omega \tau_m = \delta x = a/A \quad (7)$$

when the perturbation $G(x)$ is present. Thus, the correct value of τ_m may be located from the position of the peak using Eq. (7). Computation of δx for each type of perturbation will require a knowledge of A . Values of $A = -[\partial^2 f_2(x, \beta)/\partial x^2]/f_2(x, \beta)|_{x=0}$ computed as a function of β from the numerical tabulation of the function $f_2(x', \beta)$ in Table I-2, are plotted in Fig. 1. The quantity A goes from a value of unity at $\beta=0$ to an asymptotic value of $2/\beta^2$ at large values of β .

Finally, the effect of the perturbation on the peak

Figure 1 Quantity $A = -[\partial^2 f_2(x, \beta)/\partial x^2]/f_2(x, \beta)|_{x=0}$ as a function of β .



width must be considered. It is easy to show that if the function $G(x) - 1$ is an odd function of x , the width of the peak at half-maximum is unchanged by the perturbation to a first-order approximation. Using Eq. (1) combined with Eqs. (I-23) and (I-21) then gives for this width, in reciprocal temperature units

$$\Delta_2(T^{-1}) = 2.635 \frac{R}{Q_m} r_2(\beta), \quad (8)$$

where $r_2(\beta)$ is the quantity plotted in Fig. I-3. When $r_2 = 1$ in Eq. (8), we obtain the well-known result for the case of a single relaxation time. It is now possible to proceed to consider, in turn, each of the complexities mentioned above, which lead to perturbations of the simple J_2 peak.

Corrections for conversion from $\tan \phi$ to J_2

As shown in I, the quantity $\tan \phi = J_2/J_1$ involves, in general, a ratio of distribution integrals; therefore, the theory is more complicated for this quantity than for J_2 . Only when $\delta J \ll J_U$ can we write $\tan \phi$ as proportional to J_2 . Otherwise, it is desirable to convert the experimental results for $\tan \phi$ into the equivalent results for J_2 , the analysis of which has already been dealt with in Table I-5. Assuming that $\tan \phi$ and J_1 are being measured concurrently, one method of handling the data is to convert $\tan \phi$ into J_2 point for point, using the definition $J_2 = J_1 \tan \phi$. On the other hand, if it is only desired to obtain the three relaxation parameters, β , τ_m , and δJ from the peak width, location, and height, respectively, such a point-for-point conversion is not required; it is only necessary to apply small corrections to the results obtained directly from the $\tan \phi$ peak. The theory discussed in Eqs. (2) to (7) might then be applied to the present problem by taking $F(x) = J_2(x)/J_1(0)$, and the perturbation function $G(x) = J_1(0)/J_1(x)$.

The peak width remains unchanged to first order in the transformation from J_2 to $\tan \phi$, since $G(x) - 1$ is an odd function of x . The width obtained from the $\tan \phi$ peak may accordingly be used to obtain β from Eq. (8) and Fig. I-3.

To obtain the shift in peak position, δx , requires calculation of the parameter a which appears in Eq. (3). From the definition of a , Eq. (4), and the form of $G(x)$ given above, we may write

$$a = G'(0) \cong - \frac{J_1'(0)}{J_1(0)} \equiv h \frac{\delta J}{J_1(0)}. \quad (9)$$

The last expression, which defines h , is adopted because $J_1'(0)$ is negative and proportional to δJ . Thus, $h = -\partial f_1(x, \beta)/\partial x|_{x=0}$ is a positive dimensionless parameter which is equal to 1/2 for the case of a single relaxation time and becomes smaller with increasing β . It is convenient now to introduce a dimensionless parameter called *relaxation strength*, Δ_J , and defined by

$$\Delta_J = \delta J/J_U. \quad (10)$$

When this definition and the result (obtained from Eq.

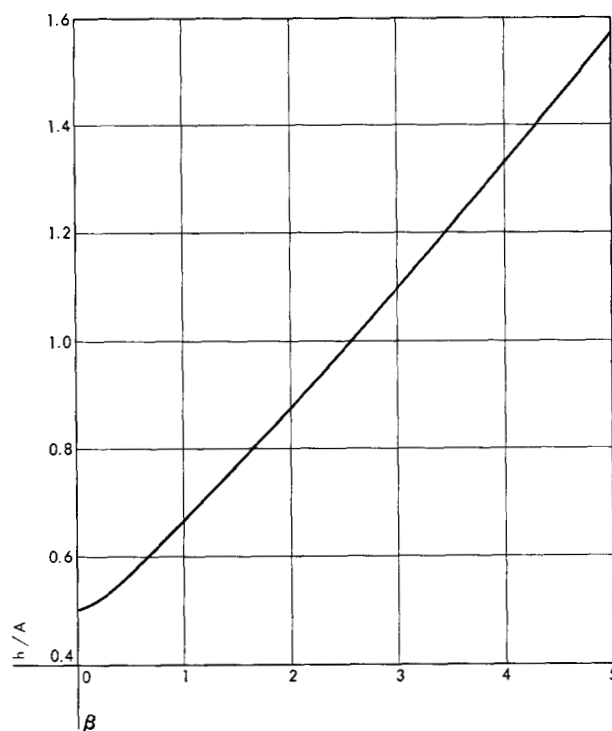


Figure 2 The quantity h/A as a function of β .

(I-16)) that $J_1(0) = J_U + \frac{1}{2}\Delta_J$ are inserted into Eqs. (3) and (9), we obtain, for the displacement of the peak position,

$$\delta x \cong \frac{h}{A} \frac{\delta J}{J_1(0)} = \frac{h}{A} \frac{\Delta_J}{1 + \frac{1}{2}\Delta_J}. \quad (11)$$

Values of h/A , for the case of a lognormal distribution, are plotted in Fig. 2 as a function of β . This graph is obtained from the values $A(\beta)$ plotted in Fig. 1, and values of h obtained from Yager's computations² of J_1 . For $\beta = 0$, $h/A = 1/2$, and Eq. (11) is in agreement (up to terms of order Δ_J^3) with the exact relation: $\delta x = \frac{1}{2} \ln(1 + \Delta_J)$ derived by Zener³ for the case of a single time of relaxation.⁴ Equation (11) extends Zener's result in that it permits the calculation of the peak shift when $\beta \neq 0$. The value of δx so obtained may then be used in Eq. (7) to obtain τ_m . It is worth noting that for large β , the quantity h/A approaches asymptotically $\beta/2\sqrt{\pi}$.

Finally, the peak height, $P(0)$ differs from the height of the unperturbed peak $F(0)$ only in terms of second order (see Eq. (6)), which difference may be neglected. Therefore, we obtain in the present case, with the help of Eq. (I-17):

$$\begin{aligned} (\tan \phi)_{\max} &= \frac{J_2(0)}{J_1(0)} = f_2(0, \beta) \frac{\delta J}{J_1(0)} \\ &= f_2(0, \beta) \frac{\Delta_J}{1 + \frac{1}{2}\Delta_J}. \end{aligned} \quad (12)$$

Equation (12), together with Fig. I-3 for the function $f_2(0, \beta)$ permits one to obtain δJ or ΔJ from the peak height of the function $\tan \phi$.

In summary, if $\tan \phi$ is measured as a function of $\ln \omega$ or of T^{-1} , the peak width, location, and height may be used to obtain β , τ_m , and ΔJ , respectively. The peak width is unchanged from that of the J_2 peak, while the height of the $\tan \phi$ peak is (to first order) the same as that of the J_2 peak divided by $J_1(0)$. The peak position is shifted, with the value δx given by Eq. (11). The column of Table 1 headed "tan ϕ to J_2 conversion" serves to summarize these corrections. The peak height will not appear in this table since, as shown in Eq. (6), the height is not affected, to first order, by the perturbations being considered.

Corrections for $\delta J(T)$

When measurements are made as a function of T^{-1} rather than of ω , the parameter δJ (or the strength, ΔJ) cannot be treated as constant, since it actually varies with T . To know how it varies, we must depart from the formal theory and consider the nature of the relaxation centers and the quantities which determine the energy of ordering of these centers. According to the simplest treatment, whereby the ordering energy depends only on σ , one obtains $\delta J \propto T^{-1}$; on the other hand, when the ordering energy is also allowed to depend on the existing state of order, the result may come out in the form $\delta J \propto (T - T_c)^{-1}$, where T_c is a critical temperature.^{3,4} (This last result is similar to that for the magnetic susceptibility of a ferromagnetic material above the Curie point.) We will use here the latter form for the temperature dependence of δJ , recognizing that the simpler form may always be obtained by setting $T_c = 0$.

In order to apply the results of Eqs. (3) and (5), we again develop the exact peak function as the perturbation of a symmetrical peak $F(x)$, following the notation of Eq. (2). In the present case, the function J_2 may be written in terms of the temperature as

$$J_2(x) = \delta J(T) f_2(x, \beta) \\ = \{ \delta J(T_p) f_2(x, \beta) \} \left\{ \frac{\delta J(T)}{\delta J(T_p)} \right\}, \quad (13)$$

where the variables T and x are interconvertible by means of Eq. (1). The first factor on the right-hand side of Eq. (13) may then be taken as the unperturbed peak, $F(x)$, while the second factor is the perturbation, $G(x)$. In view of the proposed form $\delta J \propto (T - T_c)^{-1}$, it is easily shown that this second factor is expressible as

$$G(x) = \frac{1 - (T_c/T_p)}{(1 + \alpha x)^{-1} - (T_c/T_p)}, \quad (14)$$

where

$$\alpha = RT_p/Q_m. \quad (15)$$

For $T_c = 0$, Eq. (14) goes into the simple form: $G(x) =$

$1 + \alpha x$, which obeys the condition that $G(x) - 1$ is an odd function of x .

Thus, as before, the peak width remains unchanged by the perturbation $G(x)$. In the more general case, where $T_c \neq 0$, this same result will be obtained, provided that the peak width is not very great and T_c is not comparable to T_p , since then $G(x)$ can be expressed to sufficient accuracy over the range of the peak by a Taylor expansion about $x = 0$. Accordingly, we conclude that, except for very wide peaks or in cases where T_c/T_p is close to unity, the perturbation due to $\delta J(T)$ does not appreciably affect the peak width. In cases where this approximation is not valid the best procedure is probably to make a point-for-point correction, i.e., to multiply each data point by $\delta J(T_p)/\delta J(T)$.

As for the peak position, we again use Eq. (7) where now

$$a = G'(0) \frac{\alpha}{1 - (T_c/T_p)}. \quad (16)$$

This result, together with values of A given in Fig. 1, permits the calculation of the shift in peak position, δx , using Eq. (3). It is noteworthy that the sign of the correction is the same as that for the conversion of $\tan \phi$ to J_2 , given by Eq. (11). Unlike this earlier correction, however, the quantity a is here independent of β . An estimate of a is readily obtained, for the case in which $T_c/T_p \ll 1$, by utilizing Eq. (I-32) combined with the fact that $x = 0$ at $T = T_p$ to give

$$\alpha^{-1} = Q_m/RT_p = -\ln \omega \tau_{0m}. \quad (17)$$

For τ_{0m} , the typical value of 10^{-14} sec may be inserted, so that, for a typical frequency range of $10^{3 \pm 2}$ cps, we obtain $\alpha = 0.043 \pm 0.008$. Thus, for example, for a case in which $\beta = 2$ and the quantity $A = 0.27$ (from Fig. 1), we find $\delta x \approx 0.15$. Such a correction needs to be taken into account for precise work.

Finally, the peak height requires no correction, to first order, as a result of Eq. (6). It is, therefore, expressed by $J_{2\max} = \delta J(T_p) \cdot f_2(0, \beta)$, or by Eq. (12).

A summary of these results is given in the column of Table 1 headed " $\delta J(T)$."

Corrections for $\omega(T)$

The problem to be considered here is unique to anelastic relaxation measurements. It occurs as a result of the fact that, in measuring internal friction as a function of temperature, it is experimentally convenient to work with a constant inertia rather than at a constant frequency; changes in the compliance (i.e., of the elastic modulus) and in dimensions of the sample accordingly produce small changes in the frequency. The quantity ω , therefore, is not a constant but a slowly varying function of temperature. The consequence of a change in ω as we traverse the peak is that each point can be regarded as belonging to a peak for which ω is constant but which is centered at a temperature different from T_p . To see what effect this dependence of ω on T has on the peak width,

we may compare the value $\omega(T')$ of ω at temperature T' , at which the function is equal to half its maximum value, with the value $\omega_p = \omega(T_p)$. The point at T' appears to be part of a peak centered at reciprocal temperature $T_p^{-1} + \delta'(T^{-1})$, where

$$-\frac{Q_m}{R} \delta'(T^{-1}) = \ln \frac{\omega(T')}{\omega_p} = \frac{\delta\omega}{\omega_p} \left(1 - \frac{\delta\omega}{2\omega_p} + \dots \right) \quad (18)$$

and $\delta\omega = \omega(T') - \omega_p$. Since the elastic moduli of a material always decrease with increasing temperature, $\delta\omega$ will be >0 on the low-temperature (high T^{-1}) side of the peak, and <0 on the high-temperature side of the peak. Therefore, the effect of the temperature dependence of ω is to make the peak narrower relative to one measured at constant frequency. Accordingly, the correction required, which is the negative of $\delta'(T^{-1})$, must serve to widen it.⁵ Note that if $\delta\omega/\omega_p$ is equal in absolute magnitude on the two sides of the peak, the second-order correction in Eq. (18) cancels out exactly. In any case, if the two half-maximum values are attained at temperatures T' and T'' , the peak width must be increased, to first order, by the amount $\delta(T^{-1})$ given by

$$\delta(T^{-1}) = \frac{R}{Q_m} \frac{|\omega(T') - \omega(T'')|}{\omega_p} \quad (19)$$

This correction may also be expressed as a fraction of the total peak width $\Delta_2(T^{-1})$, which is given by Eq. (8), as follows:

$$\frac{\delta(T^{-1})}{\Delta_2(T^{-1})} = \frac{|\omega(T') - \omega(T'')|}{2.635 r_2(\beta) \omega_p} \quad (20)$$

The correction involved in Eqs. (19) or (20) may be obtained directly from the measured values of ω ; nevertheless, it is worthwhile to get an idea of its magnitude by considering the two principal effects which contribute to it. These are as follows:

(a) The dependence of compliance on frequency due to the δJ -effect, i.e., the relaxation process itself. (When δJ is appreciable compared to J_U this will be the principal effect.)

(b) The dependence of J_U on temperature. (This will be important only if $\Delta_J \ll 1$.)

The calculation of these two contributions is relatively straightforward; therefore, only the results will be quoted here. For the relative change in peak width due to the δJ effect, we find

$$\frac{\delta(T^{-1})}{\Delta_2(T^{-1})} \cong \frac{0.15}{r_2(\beta)} \frac{\Delta_J}{1 + \frac{1}{2}\Delta_J} \quad (21)$$

For a single relaxation time, $r_2 = 1$, this correction is approximately $0.15\Delta_J$, which is only about 3% for Δ_J as large as 0.2. As β increases, the increase in r_2 makes the correction still smaller. For the correction due to the tem-

perature dependence of J_U , we obtain

$$\frac{\delta(T^{-1})}{\Delta_2(T^{-1})} = \frac{\eta R T_p^2}{2Q_m} \quad (22)$$

where $\eta = -J_U(T_p)(dJ_U^{-1}/dT)$ is the temperature coefficient of the reciprocal compliance (i.e., of the elastic modulus). Typical values of the right-hand side of Eq. (22) are obtained using $RT_p/Q_m \sim 0.04$, $T_p \sim 500^\circ\text{K}$, $\eta \sim 3 \times 10^{-4}/^\circ\text{K}$, to get 3×10^{-3} , or less than 0.5% change in peak width due to this effect. This correction will, therefore, generally be negligible.

Having disposed of the question of the correction to the peak width due to the $\omega(T)$ dependence, we now turn to the question of peak position and height. From the discussion of the correction to the width, leading to Eq. (21), it is clear that the $\omega(T)$ dependence produces a symmetrical narrowing of the J_2 peak, so that the peak position and height remain unchanged. The narrowing due to the second effect, which led to Eq. (22) is not exactly symmetrical, but since this entire effect is small, the shift in peak position which it produces is completely negligible for all but extremely wide peaks.

The column headed $\omega(T)$ in Table 1 summarizes the corrections discussed in this section.

Corrections for $\beta(T)$

The final source of complication, which appears when relaxation data are obtained as a function of temperature, comes from the temperature dependence of the parameter β . As shown in Part I, this distribution parameter will be independent of temperature when the distribution is entirely in the quantity τ_0 , and it will show the strongest temperature dependence (i.e., $\beta \propto T^{-1}$) when the distribution is entirely in the activation energy, Q . A more general result, Eq. (I-33), was shown to apply to intermediate cases.

To calculate δx , the shift in peak position, we may use the method of treating the actual peak as a perturbation of a simpler peak, in accordance with Eq. (2). In the present case, the unperturbed function $F(x)$ and the perturbation function $G(x)$ are, respectively, given by

$$F(x) = \delta J \cdot f_2(x, \beta_p) \quad (23)$$

$$G(x) = f_2(x, \beta) / f_2(x, \beta_p) \quad (24)$$

In these equations x is again regarded as related to T^{-1} by Eq. (1), β depends on T according to (I-33) and β_p is a constant, equal to $\beta(T_p)$. To utilize Eq. (7) requires a knowledge of $a = G'(0)$. Straightforward manipulation of Eq. (24) using Eq. (I-17) which defines the $f_2(x, \beta)$ function, shows that

$$a = G'(0) = \frac{\beta_q}{Q_m} \frac{df_2(0, \beta)/d\beta}{f_2(0, \beta)} \Big|_{\beta=\beta_p} \quad (25)$$

Furthermore, it is not hard to show that

$$\frac{d^2 f_2(x, \beta_p)}{dx^2} \Big|_{x=0} = \frac{2}{\beta_p} \frac{df_2(0, \beta)}{d\beta} \Big|_{\beta=\beta_p} \quad (26)$$

Consequently, when we take the ratio a/A , where A is defined by Eq. (5), we obtain the simple result

$$\delta x = a/A = -\frac{\beta_p \beta_q}{2Q_m} \quad (27)$$

Under the condition of strongest dependence of β on temperature, where the distribution is only in Q , we have, from Eq. (1-28), $\beta_q = \beta_p RT_p$. Equation (27) then becomes

$$\delta x = -\beta_p^2 \left(\frac{RT_p}{2Q_m} \right) \quad (28)$$

The magnitude of δx increases rapidly with increasing β_p . For example, for $\beta=2$, and taking $RT_p/Q_m \sim 0.04$, we obtain, from (28), $\delta x \sim -0.08$, which is for most purposes quite a small correction. For larger β -values, however, this correction becomes more significant.

The peak width is essentially unaffected by the $\beta(T)$ dependence, because of the linear variation of β with T^{-1} as given by Eq. (1-33). This linearity assures that the half-maximum points on both sides of the peak are shifted by the same amount and in the same direction.⁶ The fact that the width is unaffected by the temperature dependence of β means that the value β_p can be obtained from the width without corrections, as outlined in Table I-5. Values of β so obtained may then be plotted vs T^{-1} , to obtain β_q explicitly. Finally, the β_q -value so obtained can be used to correct the peak position, in accordance with Eq. (27), when this correction is of sufficient magnitude to merit attention.

The column headed $\beta(T)$ in Table 1 summarizes the corrections discussed in this section.

Applicability of the theory

In the present section we will outline some of the applications of the theory contained in the previous sections of this paper. To some extent, this material will draw together suggestions made at various points in the earlier sections; however, it will also include some applications not mentioned earlier, as well as applications to specific

relaxation phenomena. This discussion of applications is most conveniently subdivided along the lines of the three relaxation parameters, β , δJ , and τ_m , which are derivable from the experimental measurements. It must be emphasized that the use of the lognormal distribution is only justified when it is shown that a *complete* static or dynamic response function can be fitted by the theory.

Determination of β

Knowledge of the quantity β represents a knowledge of the width of the Gaussian distribution in $\ln \tau$ and, as such, can be useful in ascertaining the atomistic mechanisms of relaxation. As shown in I, however, more complete information is obtained when β is known as a function of temperature; it then becomes possible to tell how much of the distribution is in the quantity $\ln \tau_0$ and how much in the activation energy. Such information is much more informative than the simple knowledge of β at one temperature.

By way of illustration, let us begin with the well-known anelastic relaxation process which occurs in substitutional solid solutions (the "Zener relaxation"). This effect has been studied extensively by the authors and their collaborators for the solid solutions of Zn in Ag⁷. The effect manifests itself as a $\tan \phi$ peak which is relatively narrow, corresponding to β -values in the range below unity. The data for the Ag-Zn alloys is fitted very well by assuming the lognormal distribution in relaxation times. The results for β , obtained by the methods of Table I-5 and Table 1 of this paper, are shown in Fig. 3. In this Figure, both static (creep) data and dynamic ($\tan \phi$) data are used to obtain results over a range of temperatures. At the same time, data for solid solutions of two slightly different compositions are included, since there is every reason to believe that the results for these two compositions lie on essentially the same curve. The scatter is rather large partly because, in this range of comparatively small β -values, the quantities $r_2(\beta)$ and $\Delta y'(\beta)$ are not as strongly dependent on β as is the case for larger β -values. Nevertheless, it is possible to see from Fig. 3 that the

Table 1 Corrections to the location and width of the J_2 peak

Correction for:	$\tan \phi$ to J_2 conversion	$\delta J(T)$	$\omega(T)$	$\beta(T)$
Peak location*	$\delta x = \frac{h}{A} \frac{\Delta J}{1 + \frac{1}{2}\Delta J}$ with h/A from Fig. 2	$\delta x = \frac{RT_p}{AQ_m} \frac{1}{(1 - T_c/T_p)}$ with A from Fig. 1	None†	$\delta x = -\beta_p \beta_q / 2Q_m$
Peak width	None†	None†	Increase width by $\delta(T^{-1})$ given by Eq. (20) or (21)	None†

*Peak location obtained from Eq. (7) using δx given here.

†No correction to first order.

distribution in $\ln \tau$ is most likely made up both of a distribution in the activation energy and one in $\ln \tau_0$. The significance of this result will be discussed in more detail in another paper.⁸

The above remarks concerning the Zener relaxation suggest that a more precise evaluation of $\beta(T)$ may be obtained from relaxation processes involving broader distributions. An example is the "grain-boundary relaxation" observed in polycrystalline metals. The most complete study of this phenomenon has been made by Kê⁹ using both static and low-frequency dynamic experiments. The results are complicated by the presence of an additional internal friction which increases monotonically with increasing temperature and is superimposed on the peak. This so-called "background" internal friction is hard to separate unequivocally from the peak. One way of carrying out such a separation is to assume that the peak is symmetrical in T^{-1} with its width given by twice the observed half-width of the lower temperature (high T^{-1}) side of the peak. This procedure, which should not be far wrong, gives for the grain-boundary relaxation a value of $\beta=3.30$ at 280°C. Since it can be shown that the relaxation time for a given boundary is proportional to its linear dimension,¹⁰ it seems reasonable to suggest that the distribution responsible for the width of the peak is a distribution in grain diameters. It is, therefore, interesting to note the work of Feltham¹¹ who shows that grain diameters in polycrystalline aluminum vary according to a log-normal distribution. Quantitatively, however, the above suggestion fails, since the β -value derived by Feltham from the grain-size distribution is only 0.39, which is far lower than the value 3.30 quoted above from the relaxation measurements. Although a grain-size distribution count was not made on the specimens used for the relaxation studies, it is nevertheless hard to believe that the distribution would change so appreciably as to account for

the difference in β -values. It must, therefore, be concluded that the distribution in relaxation times will have an entirely different explanation. One way of shedding light on this problem is to determine β_0 and β_Q separately from $\beta(T)$. Unfortunately, Kê's work allows only one other value of β to be obtained in addition to that obtained from the peak, viz., a value from static runs carried out near 200°C. Again the results are complicated by the "background" contribution, but by using only the early part of the creep curve (specifically, the ratio $t_{1/2}/t_{1/4}$, where $t_{1/4}$ is the time for relaxation to go 1/4 of the way to completion), the authors obtain $\beta=3.65$ at 200°C. This result, compared with the value of 3.30 at 280°C, suggests that a distribution in both Q and in $\ln \tau_0$ is involved. Nevertheless, this result must be regarded as tentative in view of the limited temperature range covered. More extensive measurements of this kind would be helpful in our attempt to understand the reason for the broad distribution and, at the same time, the atomistic mechanisms involved in the relaxation process.

Another broad anelastic relaxation effect which has been studied in some detail is the Bordoni relaxation due to dislocations introduced into a crystal by plastic deformation. A recent paper by Niblett¹² attempts to distinguish between a distribution in $\ln \tau_0$ and one in activation energies by an approach similar to that of the present paper (i.e., by examining whether the peak width is or is not a function of temperature). Niblett concerns himself only with distinguishing the two extreme possibilities, i.e., a distribution entirely in $\ln \tau_0$ vs one entirely in Q . He concludes that the results fit better to a distribution in the activation energies.

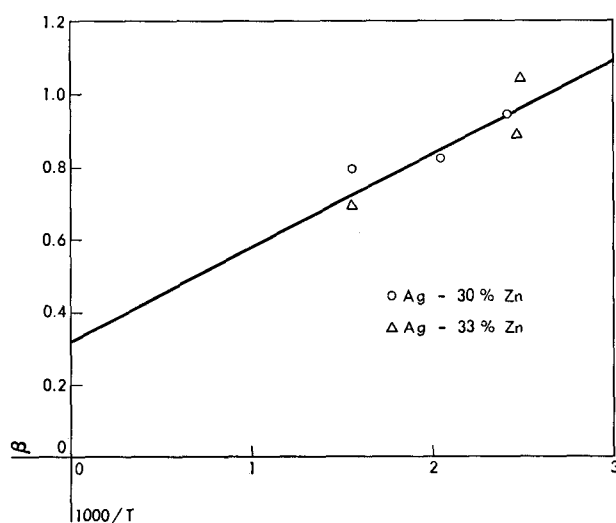
Precise determination of δJ

One method of obtaining an increased understanding of a relaxation phenomenon in a crystal is in terms of the temperature, orientation, and composition dependence of δJ (or of the relaxation strength, Δ_r). The usefulness of such information is shown, for example, by a recent series of papers dealing with the Zener relaxation.⁷ When the relaxation strength is large and the distribution is relatively narrow, δJ is conveniently obtained by measuring the function J_1 at relatively high temperatures (where it equals J_R) and at relatively low temperatures (where $J_1=J_U$). When the distribution is broad, however, and especially if Δ_r is also small, this method will fail. The best way to attain precision in the measurement of the relaxation strength is then to obtain δJ from the height of the J_2 peak (see Table I-5), or Δ_r from the height of the $\tan \phi$ peak using Eq. (12). The advantage of these methods is that they give directly the strength at one temperature, T_p , without the requirement of advance knowledge concerning the dependence of δJ on temperature.

Precise determination of τ_m

Probably the widest use of relaxation studies is to obtain information on the kinetics of the process producing the

Figure 3 Variation of β with T^{-1} for two Ag-Zn solid solutions.



relaxation, as typified by the most probable relaxation time, τ_m , and the associated activation energy, Q_m , and frequency factor, τ_{0m}^{-1} . The importance of precise determinations of τ_m are illustrated by recent concern over discrepancies between the activation energy, Q_m , obtained from relaxation studies and values obtained from the diffusion of radioisotopes in the same materials.^{13,14} In a typical investigation, relaxation times are measured over about three decades. A systematic error of 20% in a value of τ_m due to failure to take the various corrections into account, can give an error in Q_m of the order of 3%, which is not insignificant by current standards of precision.

The corrections in the calculation of τ_m from dynamical data are summarized in Table 1 in the row headed *Peak location*. The correction for the conversion of $\tan \phi$ to J_2 is important when ΔJ is large, even for small β -values. On the other hand, the corrections for the temperature dependence of δJ and of β become important only for broad relaxations ($\beta > 2$).

In the case of static measurements it is noteworthy that $t_{1/2}/\tau_m$ drops from 0.693 to 0.615 (a change of 13%) in going from $\beta=0$ to $\beta=2$ (see Fig. 1-6). An even greater source of error in static measurements comes about when the "after-effect" rather than the ψ function is measured. Though not discussed in this paper so far, the after-effect is experimentally a very convenient method for studying relaxation behavior. (In fact, most of the early studies of both anelastic and dielectric relaxation in the last century were by means of such measurements.) It therefore seems appropriate to review this type of measurement briefly and to consider how it is affected by the existence of a lognormal distribution. Specifically, the procedure is to apply a "force," σ_0 , to the system for a time t_0 (called the *hold time*) according to the schedule

$$\sigma = \begin{cases} \sigma_0 & (-t_0 < t < 0) \\ 0 & (t < -t_0 \text{ and } t > 0) \end{cases} \quad (29)$$

and then to observe the "displacement" $\varepsilon(t)$ for $t > 0$. Note that the time scale is chosen so that σ_0 is released at $t=0$. Since we are only dealing in the range where all responses of the system are linear, the quantity of interest is $\varepsilon(t)/\sigma_0$. This ratio is used to define the "after-effect" function $\chi_{t_0}(t)$ by the equation

$$\varepsilon(t)/\sigma = \delta J \cdot \chi_{t_0}(t) \quad (30)$$

The subscript t_0 relates to the fact that the after-effect function depends on how long the "force" σ_0 had been applied. The well-known superposition principle of Boltzmann³ may be used to relate the after-effect functions to the static function $\psi(t)$. Specifically, it shows that

$$\chi_{t_0}(t) = \psi(t+t_0) - \psi(t) \quad (31)$$

Note that for $t_0 \rightarrow \infty$, $\chi_{\infty}(t) \rightarrow 1 - \psi(t)$. Now, it is easy to show that for the case of a single relaxation time ($\beta=0$), $\chi_{t_0}(t)$ is always an exponential, proportional to $e^{-t/\tau}$, regardless of the value of the hold time, t_0 . In this case,

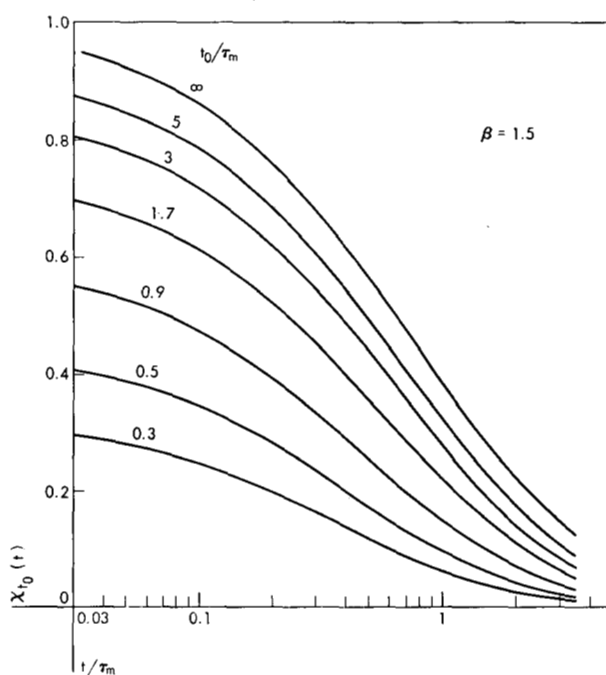


Figure 4 After-effect function plotted vs $\log t/\tau_m$ for various values of the hold time, t_0 , for the case of $\beta=1.5$.

therefore, the relations $\tau = t_{1/e} = 1.44 t_{1/2}$ provide a convenient way to get τ from after-effect measurements, where now $t_{1/2}$ is the time for the after-effect function to fall to half of its value at $t=0$. When $\beta \neq 0$, on the other hand, this simplicity is lost. For low values of t_0/τ_m , the very short relaxation times in the distribution will be relaxed during the hold time, but not the longer relaxation times. This means that the mean relaxation time contributing to the after-effect is less than τ_m , except when t_0/τ_m is very large. This result is illustrated in Fig. 4, where a group of after-effect functions have been computed, using Eq. (31) and the functions in Table I-3, for the case of $\beta=1.5$. The latter value was selected as typical of a distribution which is not especially broad. The plot of $\chi_{t_0}(t)$ vs t/τ_m for different values of the hold time, designated by the dimensionless parameter t_0/τ_m , are given in the Figure. The plots show that not only does the magnitude of the after-effect increase with increasing hold times, but also the decay time of the after-effect distinctly increases. This latter point is shown graphically in Fig. 5 which plots $t_{1/2}/\tau_m$, obtained from after-effect curves such as those in Fig. 4, as a function of t_0/τ_m . The limiting value $t_{1/2}/\tau_m = 0.63$ is shown by the dashed horizontal line at the top of the curve. Note that even for $t_0 = 5\tau_m$, the limit is not yet reached, while for $t_0 = 2\tau_m$ the value $t_{1/2}/\tau_m$ is 24% lower than the limiting value. Curves such as those of Fig. 4 and Fig. 5 for other β -values can be computed with the help of Table I-3 and Eq. (31). Such curves are necessary if precise values of τ_m are to be obtained from after-effect data.

Summary

The substance of this second paper is as follows:

- 1) The various corrections required in order to determine precise values of the relaxation parameters from actual dynamical data are evaluated. Most important of these is the shift in location between the J_2 and the $\tan \phi$ peaks, which generalizes a formula of Zener valid only for the case of a single time of relaxation.
- 2) Applications of the theory are discussed. Methods for utilizing after-effect data, and of avoiding error in the evaluation of τ_m therefrom, are included. Finally, application to some specific anelastic relaxations are discussed.

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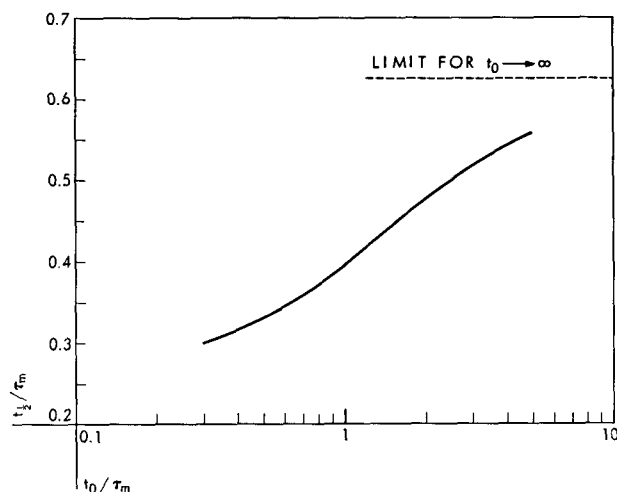


Figure 5 Variation of $t_{1/2}/\tau_m$ with relative hold time t_0/τ_m for the case of $\beta=1.5$.

References and footnotes

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2. W. A. Yager, *Physics* **7**, 434 (1936).
3. C. Zener, *Elasticity and Anelasticity of Metals*, U. Chicago Press, Chicago, 1948.
4. Zener actually obtains an effective relaxation time $\bar{\tau}$ from the $\tan \phi$ peak, given by $\bar{\tau} = \tau / (1 + \Delta\epsilon)^{1/2}$, where τ is the relaxation time at constant stress. It follows that $\delta x = \frac{1}{2} \ln(1 + \Delta\epsilon)$.
5. This same correction may be applied for any point on the peak (not just at half maximum). Equation (18) may therefore be used to make a point for point correction to convert the measured peak into one corresponding to a constant frequency, $\omega = \omega_p$.
6. It is interesting to note, however, that the shift at the half-maximum position involves a positive δx , while that at the peak is negative, as given by Eq. (27). This means that the $\beta(T)$ dependence serves to distort the shape of the peak when the δx correction is large enough to be significant.
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