SOME STATISTICAL ASPECTS OF
RELAXATION TIME DISTRIBUTIONS *)
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Synopsis

The distribution of relaxation times function, \( G(\tau) \), often used to describe the response of a linear mechanical, magnetic, or dielectric system is identified as a probability density. The situation is examined where either \( \tau \) or \( s \equiv \ln(\tau/\tau_0) \) is made up of a linear combination of new variables, some or all of which may be themselves distributed. When the probability densities of the individual variables are specified, it is shown how the overall density describing the distribution of \( \tau \) or \( s \) and the variance of the overall distribution can be calculated when the individual variables are either all statistically independent or all linearly related to a single distributed variable.

To illustrate the above general results, the important specific example of thermally activated processes is examined. It is assumed that \( \tau^{-1} \) obeys an Arrhenius equation and that both the pre-exponential factor and the heat of activation, or activation energy, may be separately distributed. For concreteness, the distributions of the two variables which combine to yield \( s \) are taken to be of the important exponential form, although many of the results apply as well for other distributions. Special attention is given to overall temperature dependence possibilities, and cases are described which lead to almost complete determination of the temperature dependence of the transient and frequency responses of the system. Finally, comparison is made between some of the temperature dependence predictions of the present work and internal friction and dielectric dispersion experimental results.

Introduction. Many magnetic, mechanical, and dielectric systems exhibit frequency dispersion. When the system is linear and non-resonant, its frequency response may be related to a distribution of relaxation times function, \( G(\tau) \). We may write

\[
Q(\phi) = \int_{0}^{\infty} \frac{G(\tau)\, d\tau}{1 + p\tau} \equiv \int_{-\infty}^{\infty} \frac{f(s)\, ds}{1 + (p\tau_0) e^s},
\]

where \( s \equiv \ln(\tau/\tau_0) \), \( \tau_0 \) is an arbitrary time constant, and \( \phi \) is a complex frequency variable. Here, \( Q(\phi) \) is a normalized frequency response function equal to \((\varepsilon^* - \varepsilon_{\infty})/(\varepsilon_u - \varepsilon_{\infty})\) in the dielectric case. The quantity \( \varepsilon^* \) is the

complex dielectric constant; \( \varepsilon_s \) the static dielectric constant; and \( \varepsilon_\infty \) the high-frequency dielectric constant beyond the dispersion region considered. The relation between \( G(\tau) \) and \( f(s) \), the distribution function for the logarithmic variable \( s \), may be obtained from the condition \( G(\tau) \, d\tau = f(s) \, ds \) and is \( \tau G(\tau) = F(\tau) = F(\tau_0 e^s) = f(s) = f[\ln(\tau/\tau_0)] \). It is evident from the normalization of \( Q(\phi) \) that \( Q(0) = 1 \) and that therefore \( G(\tau) \) and \( f(s) \) are themselves normalized. The response of many systems involves only a single time constant \( \tau_1 \) over the frequency range of interest and then \( G(\tau) = \delta(\tau - \tau_1) \), where \( \delta(\tau - \tau_1) \) is a Dirac delta function. In many cases, however, a number of time constants or a continuous distribution is necessary to characterize the system response.

Since \( G(\tau) \) and \( f(s) \) are probability density functions, we shall make use in the present work of the large body of statistical results dealing with such functions. We shall be specifically concerned with cases where \( \tau \) or \( s \) is given by a linear combination of other variables, \( x_i \), some of which are themselves distributed. This is a situation which is likely to be frequently encountered in physical systems involving a distribution of relaxation times. The presence of the individual \( x_i \) distributions then leads to overall distributions of \( \tau \) and \( s \).

**General analysis.** Let us consider a variable \( z \), which may be either \( \tau \) or \( s \), given by

\[
z = \sum_{i=1}^{n} a_i x_i,
\]

where the probability density functions, \( p_{x_i}(x_i) \), of the \( x_i \) variables are assumed known and \( a_i \neq 0 \). We wish to obtain the overall probability density function \( p_z(z) \). It will be convenient to transform to the new variables \( y_t = a_i x_i \). In general, \( p_y(y_t) \) involves the Jacobian of the transformation \(^2\). In the present case of univariate distributions, one finds

\[
p_y(y_t) = |a_i^{-1}| \, p_{x_i}(a_i^{-1} y_t).
\]

When some or all of the \( x_i \) variables are partly correlated, the overall probability density function corresponds to a multivariate distribution whose variables are not all statistically independent. Since information concerning the details of such a multivariate distribution is usually lacking in physical cases of interest, we shall confine the present discussion to two situations which can be readily handled: that where all the \( x_i \) variables are statistically independent and that where they are all linearly dependent on a single variable, \( w \). An extension to combinations of these two cases can also be readily carried out, and the case where the individual variables depend nonlinearly as well as linearly on a single distributed variable may also be treated \(^3\).

When a probability density is known, its variance \( \sigma^2 \) may be calculated directly by integration or from the characteristic function (c.f.), an ex-
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Exponential Fourier transform of the probability density $^{2,3}$). One finds, for example, $\sigma_{yi}^2 = (a_i \sigma_{zi})^2$. When all $y_i$'s are statistically independent, the c.f. corresponding to $\phi_z(z)$ is the product of the individual-variable c.f.'s. The overall $\phi_z(z)$ may then be obtained by an inverse Fourier transform. It also follows in the independent case, irrespective of the forms of the $\phi_{yi}(y_i)$ densities, that

$$\sigma_z^2 = \sum_{i=1}^{n} \sigma_{yi}^2 = \sum_{i=1}^{n} (a_i \sigma_{zi})^2. \quad (2)$$

Note that when one of the $y_i$ variables, say the $j$th, is not distributed, $\phi_{yi}(y_j) = \delta(y_j - y_j^0)$ and $\sigma_{yi}^2 = 0$. Here $y_j^0$ is the non-distributed value of $y_j$ variable.

In the linearly dependent case, we have $x_i = a_i + \beta_i w$, where $w$ is a distributed variable. Then $z = a + bw$, equal to $c_i + dix_i$ when $\beta_i \neq 0$, where

$$a = \sum_{i=1}^{n} a_i \beta_i, \quad b = \sum_{i=1}^{n} a_i \beta_i, \quad c_i = (a_i \beta_i - b \alpha_i)/\beta_i,$$

and $d_i = b/\beta_i$. On defining all $\sigma$'s as positive quantities, it follows that $\sigma_z = |b| \sigma_w = |d_i| \sigma_{zi}$. Since $\sigma_z$ must be independent of the index $i$, one obtains $\sigma_{zi}/\sigma_{zi} = |\beta_i/\beta_i|$. The use of this relation finally allows $\sigma_z$ to be expressed as

$$\sigma_z = \sum_{i=1}^{n} \text{sgn} (a_i \beta_i) \sigma_{zi} = |\sum_{i=1}^{n} a_i \text{sgn} \beta_i \sigma_{zi}|. \quad (3)$$

The probability density $\phi_z(z)$ follows from either $\phi_z(z) = |b| \phi_{wi}[(b^{-1})(z-a)]$ or $\phi_z(z) = |d_i^{-1}| \phi_{zi}[(d_i^{-1})(z-c_i)]$ and must be independent of $i$. Note that the range of $z$ is not necessarily equal to that of $w$ or that of any $x_i$.

Specific examples. It is very often found in dielectric$^{4,5,6,7}$ and mechanical$^{8,9,10}$ dispersion experiments that the relaxation frequencies of the system satisfy an Arrhenius type of equation. For such thermally activated processes, one may frequently write$^{8,9}$ $\tau = \tau_d \exp(\Delta G/kT)$, where $\tau_d = v_d^{-1}$ is an inverse vibrational frequency or attack time, and $\Delta G$ is the difference in work required for a transition from minimum to maximum Gibbs free energy in surmounting a potential barrier. Both $\tau_d$ and $\Delta G$ may depend somewhat on temperature because of such effects as straining of the crystal lattice as the temperature changes. The experimental determination of any small temperature dependence of $\tau_d$ is very difficult, and this quantity will here be taken temperature independent$^{10a}$. Experimentally, the apparent activation energy is often found to be temperature independent as well; therefore, we shall assume $\Delta G = E[1 - (T/T_0)]$, the only form which can lead to such independence. Here, $E$ is temperature independent, $T < T_0$, and $T_0$ is of the order of the melting point or above for most solids$^8$ and
near the boiling point or above for most liquids. Such linear dependence for $\Delta G$ has been used by Ze-ner(8)\(^1\) in a theory of diffusion and has been found also for semiconductor energy gaps(12)(13).

The above expressions, plus the relations

$$\Delta H = \Delta G + T\Delta S = d(\Delta G/T)/d(1/T),$$

lead to $\Delta H = E$, the enthalpy increment or heat of activation, and $\Delta S = \equiv E/T_0$, the entropy increment for the process. Such direct dependence of $\Delta S$ on $E$ follows also from a diffusion theory of Zener and Wert(11), whose predictions agree excellently with experiment(9). In addition, it is consistent with a large body of dielectric data on liquids(7), which seems to indicate a surprisingly small variation in $T_0$ from material to material.

We may now write

$$s = \ln \left( \frac{T}{T_0} \right) = z = \ln(\tau_d/\tau_0) + \left[ \left( \frac{1}{kT} \right) - \left( \frac{1}{hT_0} \right) \right] E, \quad (4)$$

and identify $x_2 = E/hT_n = \xi$, and $a_2 = (T_n/T) - (T_n/T_0)$, where $T_n$ is an arbitrary normalization temperature. The variable $x_1$ may alternatively be either $\ln(\tau_d/\tau_0)$ with $a_1 = 1$ or $\ln(\nu_d/\nu_0)$ with $a_1 = -1$. When $x_1$ and $x_2$, which may or may not be distributed, are statistically independent, they cannot depend on a common parameter such as temperature. When $\xi$ is temperature independent but $\tau_d$ temperature dependent, $x_1$ and $x_2$ can be independent or at most partly correlated. Finally, some perturbing factor in the material may act on $\ln(\tau_d/\tau_0)$ or $\ln(\nu_d/\nu_0)$ and $\xi$ in the same way, making it possible for both $x_1$ and $x_2$ to be distributed and linearly related if they depend on temperature similarly.

For concreteness sake, we shall select(6) $p_{x_1}(x_i) = \xi_i \exp(-\xi_i x_i)$ and take $\xi_i$ and $x_i$ temperature independent. When a given $x_i$ is independent of temperature, it is physically reasonable to expect that its distribution also will be so independent(6). Note that the distributions of $x_1$ and $x_2$ need not be of the same form in general in the statistically independent case. The exponential distribution law can lead to system behaviour in agreement with many experimental results such as the frequently found $t^{-n}$ discharge-current time dependence(14)(15) and dispersion data usually described by the Cole-Cole(16), Davidson-Cole(17) or Fang(18) relaxation-time distribution functions. Some more basic justification for a exponential probability density is that it is the only Markovian, or memoryless, distribution(19) and is the probability density for the waiting time for the first of a series of events obeying a Poisson probability law(20).

For simplicity of exposition, the range of $x_i$ has here been taken $(0, \infty)$, requiring $\xi_i > 0$, although a finite range is actually physically required for a thermally activated situation(6)(21). When the range is finite, $\xi_i$ may be $\leq 0$ and the normalization of $p_{x_i}(x_i)$ is different from that above. When $\xi_i \to \infty$, $p_{x_i}(x_i) \to \delta(x_i)$. Application of the general analysis to the present
distributions leads to $\sigma_{\tau} = \xi_i^{-1}$, $\sigma_{\nu} = |a_i| \xi_i^{-1}$, and to the results of table I. Here, $\phi \equiv a_2$ is a normalized, shifted, inverse temperature variable, taken positive on physical grounds. From (4), $p_2(z) \equiv f(s)$, and $G(\tau)$ may be readily calculated from any of the present results. In Case 1, it is $\xi_1 \tau_0^{-1} (\tau_0/\tau)^{1+\xi_i}$, itself a well-known distribution\(^6\)\(^7\). Note that there is no temperature dependence in cases 1 and 2; thus, the only dependence observed in dispersion and transient response measurements will arise from that of the $(\varepsilon_\infty - \varepsilon_0)$ term, which can be measured directly or obtained from application of a Kronig-Kramers relation to loss-frequency data\(^1\).

Cases 1 and 2 are distinguished by taking $a_1 = 1$ or $-1$, respectively, and indicate whether the logarithm of $\tau_d$ or of its inverse, the vibrational frequency $v_d$, is exponentially distributed with range $(0, \infty)$. The same choice has been used for cases 4 and 5, but in 6 and 7 $x_1 = \ln(\tau_d/\tau_0)$ and $a_1 = 1$ have been taken, and the distinction between $\tau_d$ and $v_d$ introduced by means of the signs of $\beta_1$ and $\beta_2$ in the relation $x_i = \alpha_i + \beta_i v$. In the table, $A \equiv \xi_2/\xi_1$ in cases 4 and 5, and $\beta_1/\beta_2$ in cases 6 and 7.

![Fig. 1. Normalized dispersion parameter $\lambda = \xi_2 \sigma_\lambda$ versus normalized and shifted inverse temperature variable $\phi = \left[(T_n/T) - (T_n/T_0)\right]$. The various cases of table I and values of $A$ are shown as (case no., $A$) on each curve.](image)

In fig. 1, the quantity $q = \xi_2 \sigma_\xi$ has been plotted versus $\phi$ for cases 3–7. A number of points are of interest. First, it is noteworthy that the quite different distributions of cases 4 and 5 can have the same variance. The expressions for $p_2(z)$ in cases 4 and 5 are also different in form from the individual $p_2(x_i)$'s. In the independent case, only for a few distributions, such as the Gaussian, will the overall distribution be of the same form as the individual ones\(^3\). Were it possible for $\phi$ to equal zero, case 3 would then lead to $p_2(z) = \delta(z)$ and $\tau = \tau_0 = \tau_d$, yielding simple Debye dispersion with the single time constant $\tau_d$. A physically more reasonable possibility in case
7 is \((A + \phi) = 0\). At this temperature, \(T = (T_0^{-1} + T_n^{-1} |\beta_1/\beta_2|)^{-1}\), which may be considerably below \(T_0\), and again simple Debye dispersion is obtained\(^{21}\). Above this temperature, more than one time constant is again effective and in the formal limit of high temperatures \((A + \phi)\) approaches \(-[(T_n/T_0) + |\beta_1/\beta_2|]\). Although it has been experimentally found that frequently dispersion with a wide distribution of relaxation times tends toward simple Debye dispersion as the temperature is increased\(^6\), no instances are known to the author where dispersion with a single time constant is reached and then the distribution widens again at higher temperatures. Such behavior should be searched for, however, since there seems to be no theoretical reason to believe that case 6 should be more likely than case 7.

Some consideration of case 3 (with \(T_0 = \infty\)) has been given previously\(^{6}\)\(^{22}\), and it was found that most of the usual relaxation-time distribution functions such as that of Cole and Cole\(^{18}\), cannot be made consistent with the assumption of a temperature-independent distribution of activation energies. The present work shows that they also cannot be made consistent with the situation where both \(\&\) and \(\tau_d\) are simultaneously distributed with temperature-independent distributions. Luckily, the present exponential distribution with finite limits can usually describe the same data as well at a given temperature and describe measurements at different temperatures more satisfactorily\(^{21}\).

Cases 1, 3, 4, and 6 have recently been independently considered by Nowick and Berry\(^{23}\) for the combination of Gaussian distributions only. Their \(\sigma_z\) expressions are equivalent to the present ones, in agreement with the general results of eqs. (2) and (3), when \(\phi\) is replaced by \((T_n/T)\), a simplification appearing because they did not take explicit account of the entropy contribution which leads to the \(T_0\) term in (4). The resulting expression for \(\sigma_z\) in Case 6 was used to fit results derived from creep and internal friction measurements on Ag-Zn alloys, but because of appreciable scatter in the points the \(\sigma_z\) expression for the independent case also gave as good a representation of the data. Had an overall exponential distribution instead of a Gaussian been used to determine \(\sigma_z\) from the data, the temperature dependence found might have been somewhat different. There are very little data available as yet where dispersion has been evaluated on the assumption of actual distributions such as those of table I. However, Vaughan, Lovell, and Smyth\(^{24}\) recently analyzed dielectric dispersion data on alkyl halides on the basis of the \(\sigma_z\) and \(p_z(z)\) of case 3 with \(T_0 = \infty\) and found considerable evidence of the temperature dependence predicted.

Since the temperature dependence of \(p_z(z)\) or \(G(\tau)\) is entirely determined for the cases of table I, a full comparison of theory and experiment would require evaluation of the temperature dependence of either \(Q(\phi)\) or normalized transient response as well as that of the pertinent shape parameter related
### Table I

<table>
<thead>
<tr>
<th>Case</th>
<th>Variables Distributed</th>
<th>Dependence</th>
<th>$\xi_2$</th>
<th>Range of $z$</th>
<th>$p(z)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\tau_d$</td>
<td>$-$</td>
<td>$\xi_1^2$</td>
<td>$0, \infty$</td>
<td>$\xi_1 e^{-\xi_1 z}$</td>
</tr>
<tr>
<td>2</td>
<td>$\nu_d$</td>
<td>$-$</td>
<td>$\xi_1^2$</td>
<td>$-\infty, 0$</td>
<td>$\xi_1 e^{\xi_1 z}$</td>
</tr>
<tr>
<td>3</td>
<td>$\sigma$</td>
<td>$-$</td>
<td>$(\xi_2/\xi_2)^2$</td>
<td>$0, \infty$</td>
<td>$(\xi_2/\xi_2) e^{-\phi \xi_2 z}$</td>
</tr>
<tr>
<td>4</td>
<td>$\sigma$ and $\tau_d$</td>
<td>Independent</td>
<td>$\xi_2^2(A^2 + \phi^2)$</td>
<td>$0, \infty$</td>
<td>$[\xi_2^{-1}(\xi_2 + \phi)] [\xi_2^{-1}(\xi_2 + \phi)] e^{-\phi \xi_2 z}$</td>
</tr>
<tr>
<td>5</td>
<td>$\sigma$ and $\nu_d$</td>
<td>Independent</td>
<td>$-\infty, \infty$</td>
<td>$-\infty, \infty$</td>
<td>$[\xi_2^{-1}(\xi_2 + \phi)]$ $\left{ \begin{array}{ll} e^{\xi_2 z} &amp; z &lt; 0 \ e^{-\phi \xi_2 z} &amp; z &gt; 0 \end{array} \right.$</td>
</tr>
<tr>
<td>6</td>
<td>$\sigma$ and $\tau_d$</td>
<td>Linearly dependent</td>
<td>$\xi_2^2(A^2 + \phi^2)$</td>
<td>$0, \infty$</td>
<td>$[\xi_2^{-1}(\xi_2 + \phi)] e^{-\phi \xi_2 z}$</td>
</tr>
<tr>
<td>7</td>
<td>$\sigma$ and $\nu_d$</td>
<td>Linearly dependent</td>
<td>$-\infty, 0$</td>
<td>$A + \phi &lt; 0$</td>
<td>$[\xi_2^{-1}(\xi_2 + \phi)] e^{-(A + \phi) \xi_2 z}$</td>
</tr>
</tbody>
</table>

To $\sigma_d$. First, one must pick an overall distribution of a form such that transient and frequency response results at a given temperature are well described. Then, results at different temperatures may be compared with those predicted from the overall distribution for one of the possible cases. Such comparison, using a modified exponential distribution, will be published elsewhere.21)

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