

Here,

$$\begin{aligned}
 t_1 &= r \sin \delta / q_{C \dots C_0} & t_4 &= r \sin \alpha / q_{O_I \dots O_{II}} & s_1 &= (D - r \cos \delta) / q_{C \dots C_0} & s_4 &= (r - r \cos \alpha) / q_{O_I \dots O_{II}} \\
 t_2 &= D \sin \delta / q_{C \dots C_0} & t_5 &= R \sin \beta / q_{O_I \dots O_{II}} & s_2 &= (r - D \cos \delta) / q_{C \dots C_0} & s_5 &= (r - R \cos \beta) / q_{O_I \dots O_{II}} \\
 t_3 &= D \sin \epsilon / q_{O_I \dots O_{II}} & t_6 &= r \sin \beta / q_{O_I \dots O_{II}} & s_3 &= (D - D \cos \epsilon) / q_{O_I \dots O_{II}} & s_6 &= (R - r \cos \beta) / q_{O_I \dots O_{II}} \\
 q_{C \dots C_0}^2 &= D_0^2 + r_0^2 - 2Dr \cos \delta, & q_{O_I \dots O_{II}}^2 &= 2D_0^2(1 - \cos \epsilon) = 2r_0^2(1 - \cos \alpha), & q_{O_I \dots O_{II}}^2 &= r_0^2 + R_0^2 - 2r_0R_0 \cos \beta.
 \end{aligned}$$

$q_{i \dots j}$  is the distance between nonbonded atoms  $i$  and  $j$ .

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## Restriction on the Form of Relaxation-Time Distribution Functions for a Thermally Activated Process\*

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When a distribution of relaxation times is associated with thermally activated processes in a material and arises solely from a distribution of activation energies, the form of the relaxation-time distribution may be restricted. In this case, the temperature dependence of some of the parameters which enter into the distribution function will be uniquely determined. The Wagner relaxation-time distribution function may be made entirely consistent with a distribution of activation energies by taking its shape parameter temperature dependent, but the Cole-Cole, Fuoss-Kirkwood, and Davidson-Cole distribution functions can only be made approximately consistent in the separate limits of very wide and narrow distributions of relaxation times. The temperature dependences of their parameters found experimentally for thermally activated processes is compared where possible with that required for the distribution of activation energies situation. A new relaxation-time distribution is proposed which is completely consistent with a distribution of activation energies in an activated process and which can describe a variety of experimental data.

### INTRODUCTION

THE temporal and frequency response of a variety of materials can be described by a distribution of relaxation times. Such a description, which can include the cases of a single or of many relaxation times and of either a discrete or continuous distribution, is only applicable when the material is linear for the process considered so that its response is directly proportional to the stimulus applied. Linearity often requires that there be no appreciable interaction between the microscopic processes whose resultant yields the macroscopic response measured. Although a time-varying system can be linear as well, the description of this kind of system, such as one in which irreversible structure changes occur during measurement, would require a distribution of relaxation times which itself changed with time. Such a complication will not be further considered herein.

The introduction of distributions of relaxation or retardation times has proved very useful in describing both the electrical behavior of dielectrics and the

mechanical behavior of linear viscoelastic solids.<sup>1-4</sup> For ease of exposition, the present discussion will be restricted to the dielectric case, although the analysis and conclusions apply equally to all situations where a time-invariant distribution of relaxation times occurs in a thermally activated linear system.

There are many relaxation models which may lead to a distribution of relaxation times (abbreviated DRT hereafter) in a physical system. For example, if the primary response arises from dipole orientation under the influence of an alternating applied field, a DRT may appear because each dipole finds itself in a slightly different environment from all others at a given instant. At a fixed temperature, the local environment, and hence the effective activation energy, may change with time because of thermal fluctuations, but the average environment may remain constant. In this case, a description by a time-invariant relaxation-time distribution may be appropriate. Were the environments and dipoles always all the same, each dipole

<sup>1</sup> C. J. F. Böttcher, *Theory of Electric Polarization* (Elsevier Publishing Company, New York, 1952), pp. 363-374.

<sup>2</sup> R. H. Cole, *J. Chem. Phys.* **23**, 493 (1955).

<sup>3</sup> B. Gross, *Theories of Viscoelasticity* (Hermann & Cie, Paris, 1953).

<sup>4</sup> J. R. Macdonald, *J. Appl. Phys.* **32**, 2385 (1961).

\* Presented in part at the Chicago, Illinois meeting of the American Physical Society, November 25, 1961 [J. R. Macdonald, *Bull. Am. Phys. Soc.* **6**, 449 (1961)].

would have the same intrinsic relaxation time and the macroscopic response of the system could also be described by a single relaxation time. For many materials there also may be present several species of relaxing units, each with its own intrinsic relaxation time, and/or several states or equilibrium positions for each unit, resulting in several intrinsic times for each even in the absence of different environments around each unit.

Several authors<sup>5-7</sup> have considered dielectric dispersion and response in terms of an activated process with a distribution of activation energies (DAE). The purpose of the present work is to point out that the restriction to a thermally activated process in which only a DAE is present may impose interesting limitations on the form and parameters of the corresponding DRT. Several popular relaxation-time distributions will be considered from the standpoint of these restrictions and a new distribution consistent with them briefly mentioned.

#### THERMAL ACTIVATION AND RELAXATION

The intrinsic relaxation time  $\tau$  of a thermally activated process whose effective activation energy is  $E$  may be written as

$$\tau = B(T) \exp[E/kT], \quad (1)$$

where  $B(T)$  is independent of absolute temperature or a slowly varying function of it. For an assembly of charged particles each having two equilibrium positions separated by a high potential barrier of height  $E$ , (1) reduces to  $\tau = \tau_a \exp(E/kT)$ , where  $\tau_a$  is the vibration time of the charges in the potential wells, or equivalently,  $f \equiv 1/2\tau_a$  is the frequency of oscillations about either of the two identical equilibrium positions.<sup>8</sup> The situation is more complicated when dipolar molecules capable of internal excitation are considered.<sup>8</sup> The theory of rate processes leads to<sup>9,10</sup>  $B(T) \propto h/kT$ , where  $h$  is Planck's constant. At 25°C, this quantity is about  $1.6 \times 10^{-13}$  sec. Other approaches<sup>8</sup> indicate that  $\tau_a$  is of the order of  $10^{-14}$  to  $10^{-12}$  sec. A careful consideration of the frequency factors in thermally activated processes has recently been given by Landauer and Swanson.<sup>11</sup>

In the succeeding work we shall ignore the distinction between intrinsic, or microscopic, relaxation times and macroscopic, or directly measurable, relaxation times. A recent discussion of the relation between the two has been given by Glarum<sup>12</sup> for polar liquids. For

present purposes it will be assumed that Eq. (1) can describe the energy and temperature dependence of macroscopic relaxation times sufficiently well, and  $\tau$  will hereafter be understood to be a macroscopic quantity.

Since the relaxation (1) with  $E$  temperature independent has been repeatedly found for a wide variety of dielectric relaxation measurements,<sup>13,14</sup> it will be used herein as an empirical relation, and its applicability to detailed theoretical models not further considered. Most of the results of the present work are pertinent only when (1) or simple extensions of it apply and when  $B(T)$  is independent of  $E$ . The quantity  $E$  may then be interpreted as a temperature-independent apparent activation energy or heat of activation. Further discussion of equations like (1) has been given by the author in a paper submitted to *Physica*.

When there is a DAE, we may define  $E_1$  and  $E_2$  as the minimum and maximum energies possible. The shortest and longest relaxation times of the system,  $\tau_s$  and  $\tau_l$ , follow directly from (1) using  $E = E_1$  and  $E = E_2$ , respectively. The energy  $E_1$  may be zero but will usually be greater than zero. The maximum energy  $E_2$  must clearly be finite since only a finite energy is required for complete separation of all the atoms of a material to infinity. Possible effects of tunneling through barriers will not be considered herein.

If  $G(\tau)d\tau$  is the probability density of relaxation times in the interval  $d\tau$  and  $K(E)dE$  is the probability density of relaxation times having activation energies in the interval  $dE$ , then the complex dielectric constant may be written<sup>15</sup>

$$\epsilon^*(p) - \epsilon_\infty = (\epsilon_s - \epsilon_\infty) \int_0^\infty \frac{G(\tau)d\tau}{1 + p\tau} = (\epsilon_s - \epsilon_\infty) \int_0^\infty \frac{K(E)dE}{1 + p\tau(E)}, \quad (2)$$

where  $G(\tau)$  and  $K(E)$  are normalized so that

$$\int_0^\infty G(\tau)d\tau = \int_0^\infty K(E)dE = 1. \quad (3)$$

In Eq. 2,  $p$  is a complex frequency variable, and  $\epsilon_s$  and  $\epsilon_\infty$  are the low and high frequency limiting values, respectively, of the real part of the dielectric constant. Since  $p$  is arbitrary (except that its real part must be greater than or equal to zero), Eq. (2) leads to the condition  $K(E) = G(\tau)(d\tau/dE)$ . Because of the finite ranges of variation of  $\tau$  and  $E$  intrinsic to an activated process, the limits in (2) and (3) can clearly be replaced by  $\tau_s$  to  $\tau_l$  and  $E_1$  to  $E_2$ .

When  $\tau$  can be described by (1), the above expres-

<sup>5</sup> M. Gevers and F. K. DuPré, *Trans. Faraday Soc.* **A42**, 47 (1946).

<sup>6</sup> C. G. Garton, *Trans. Faraday Soc.* **A42**, 56 (1946).

<sup>7</sup> H. Fröhlich, *Theory of Dielectrics* (Clarendon Press, Oxford, 1958), 2nd ed., pp. 92-98.

<sup>8</sup> Reference 7, pp. 78-81.

<sup>9</sup> S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), Chap. IX.

<sup>10</sup> W. Kauzmann, *Revs. Modern Phys.* **14**, 12 (1942).

<sup>11</sup> R. Landauer and J. A. Swanson, *Phys. Rev.* **121**, 1668 (1961).

<sup>12</sup> S. H. Glarum, *J. Chem. Phys.* **33**, 1371 (1960).

<sup>13</sup> Reference 1, pp. 378-388.

<sup>14</sup> C. P. Smyth, *Dielectric Behavior and Structure* (McGraw-Hill Book Company, Inc., New York, 1955).

<sup>15</sup> J. R. Macdonald and M. K. Brachman, *Revs. Modern Phys.* **28**, 393 (1956).

sion for  $K(E)$  leads immediately to<sup>4</sup>

$$K(E) \equiv K_1(\tau) = \tau G(\tau)/kT. \quad (4)$$

However, the distribution function  $K(E)$  will be time invariant and is most likely to be temperature independent in the temperature range where no configurational or internal structure changes occur. When  $K(E)$  is temperature independent, the only case to be considered herein, it is necessary that the quantity on the right also be correspondingly independent of time and temperature. In the next section, implications of this requirement for various forms of  $G(\tau)$  will be considered. Note that  $K_1(\tau)$  is directly related to the DRT function  $F(\tau) \equiv \tau G(\tau)$  sometimes used in the discussions of relaxation time distributions.<sup>2</sup>

It is quite possible for a thermally activated process to obey Eq. (1), exhibit a DRT, and yet not involve a DAE. If a number of different processes with the same activation energy,  $E_0$ , but with different frequency factors are simultaneously present in a material, then there will be a distribution of the quantity  $B(T)$  in (1). The dielectric response can then be described by the usual relaxation-time distribution function  $G(\tau)$  since the distribution of  $B(T)$  leads directly to a simple DRT. Alternatively, a DRT can appear even when there is normally only a single relaxation time if a spatial temperature variation occurs in the sample being measured. Since this possibility does not correspond to the usual experimental situation, it will not be further considered. Finally, when distributions of both  $B(T)$  and  $E$  simultaneously occur in an experimental material, the temperature dependence of the appropriate  $G(\tau)$  is no longer restricted by the relation (4). Although the above two-distribution case is often a physically likely possibility when there is a DRT, we shall limit further attention herein to the DAE case alone since it may lead to definite and simple temperature dependence of the parameters of  $G(\tau)$  when the latter's form is specified. Consideration of this temperature dependence and comparison with experiment should help in determining when a description in terms of only a DAE is appropriate.

*Note added in proof.* Since this paper was written, it has been found that D. W. Davidson [Can. J. Chem. **39**, 1321 (1961)] has considered the temperature dependence of the parameter  $m$  of the Cole-Cole DRT from a point of view somewhat similar but different in an important way from that of the present work. The general situation where  $\tau$  or  $\ln(\tau/\tau_0)$  is made up of a linear combination of other distributed variables, such as activation energy and frequency factor, has been considered in a paper by the author submitted to *Physica*, and the results applied to the thermally activated case. A less general analysis restricted to Gaussian distributions has been given by A. S. Nowick and B. S. Berry [IBM J. Research Develop. **5**, 297 (1961)].

## RELAXATION-TIME DISTRIBUTION FUNCTIONS

The simplest distribution function is that for a single relaxation time  $\tau_0$ . Let the corresponding activation energy in (1) be  $E_0$ . The pertinent  $G(\tau)$  is then  $\delta(\tau - \tau_0)$ , where  $\delta(x)$  is the Dirac delta function. This expression for  $G(\tau)$  in (2) leads to simple Debye dispersion. From (1) and (4),

$$K_1(\tau) = (\tau/kT) \delta(\tau - \tau_0) = (\tau_0/kT) \delta(\tau - \tau_0), \quad (5)$$

and

$$\begin{aligned} K(E) &= (\tau_0/kT) \delta[B(T) \exp(E/kT) - B(T) \exp(E_0/kT)] \\ &= \delta(E - E_0), \end{aligned} \quad (6)$$

where the second equation follows from a delta-function relation of Gross and Pelzer.<sup>15</sup> It is clear that in this case  $K(E)$  is temperature independent as it should be.

A listing of a number of more complicated relaxation-time distribution functions which have been found useful has been given by Gross.<sup>3</sup> Included also are viscoelastic retardation-time functions, which correspond formally to dielectric relaxation-time functions. The Wagner distribution<sup>16,17</sup> is a Gaussian probability function and is symmetrical in the variable  $\ln(\tau/\tau_0)$ , where  $\tau_0$  is here the central and most probable time constant. The corresponding  $G(\tau)$  is

$$G(\tau) = (b\tau^{-1}/\pi^{\frac{1}{2}}) \exp[-\{b \ln(\tau/\tau_0)\}^2], \quad (7)$$

where  $b$  is a shape parameter. Equations (1), (4), and (7) lead directly to

$$K(E) = [1/\sigma(2\pi)^{\frac{1}{2}}] \exp[-\frac{1}{2}\{(E - E_0)/\sigma\}^2], \quad (8)$$

showing that in this case the function  $K(E)$  is also a normal probability distribution. Here, and in the succeeding distributions, for simplicity we have used the normalization appropriate for a range  $0 \leq \tau \leq \infty$ , which is inconsistent with the finite range required for an activated process. Since most distribution functions decrease rapidly on either side of a central relaxation time  $\tau_0$ , the use of infinite-range normalization will often be a good approximation.

The quantity  $\sigma$ , whose square is the variance of the distribution, is given by  $(kT/\sqrt{2}b)$ . For (8) to be temperature independent it is therefore necessary that  $b$  be directly proportional to absolute temperature. This conclusion is a direct consequence of the DAE assumed. There is little experimental evidence available on the temperature dependence of  $b$ , but Yager's<sup>17</sup> results on glycerol and vinsol indicate a slight decrease with increasing temperature over a narrow temperature range, suggesting that the DAE assumption is inapplicable here for these materials. On the other hand, the larger  $b$  the nearer the above  $G(\tau)$  distribution

<sup>16</sup> K. W. Wagner, Ann. Physik **40**, 817 (1913).

<sup>17</sup> W. A. Yager, Physics **7**, 434 (1936).

approximates that for a single relaxation time. Experimentally also, one finds that the  $\delta(\tau-\tau_0)$  distribution is approached when the temperature is sufficiently increased.

Another relaxation-time function which has been widely applied in the analysis of dielectric data is that of Cole and Cole.<sup>18</sup> The  $K_1(\tau)$  function corresponding to this distribution is

$$K_1(\tau) = \frac{1}{2\pi kT} \frac{\sin\pi m}{\cos\pi m + \cosh[\ln(\tau/\tau_0)^m]} \quad (9)$$

where  $m$  is a shape parameter such that  $0 < m \leq 1$ . If  $E_0$  is again the energy corresponding to  $\tau_0$ , then (1) and (9) lead to

$$K(E) = \frac{1}{2\pi kT} \frac{\sin\pi m}{\cos\pi m + \cosh[m(E-E_0)/kT]} \quad (10)$$

Because of the various functions in which  $T$  and  $m$  occur,  $K(E)$  can only be rendered approximately temperature independent in the range  $m\pi \ll 1$  by taking  $m$  directly proportional to  $T$ . In addition, however, since the Cole-Cole distribution degenerates to simple Debye dispersion for  $T \rightarrow \infty$  and  $m = 1$ , we can conclude that this distribution is only appropriate for a DAE case in the separate regions  $m \ll 1$  and  $(1-m) \ll 1$ . Lakshminarayana<sup>19</sup> has recently found for a number of liquids that in the intermediate range between the above regions  $m \cong 1 - Ae^{B/T}$ , where  $A$  and  $B$  are constants. Although this expression cannot apply well in the range  $m \ll 1$ , it agrees qualitatively with the DAE result that  $m$  must increase with increasing temperature when  $m$  is small.

Two other useful distributions have been suggested by Fuoss and Kirkwood<sup>20</sup> and by Davidson and Cole.<sup>21</sup> These distributions involve the shape factors  $\alpha$  and  $\beta$ , respectively, and analysis like that above shows that they are each only approximately consistent with a DAE when  $(1-\gamma) \ll 1$  and if  $\gamma$  is proportional to  $T$  for  $\gamma \ll 1$ , where  $\gamma$  is either  $\alpha$  or  $\beta$  depending on the function considered. In the Davidson-Cole case, approximate consistency with a DAE in the range  $\beta \ll 1$  also holds only when  $(E_0 - E)$  is considerably greater than  $kT$ . Fuoss and Kirkwood<sup>20</sup> have presented data for  $\alpha$  as a function of temperature for polyvinyl chloride-diphenyl systems which show an initial increase of  $\alpha$  with temperature and final saturation behavior at high temperatures. Final values of  $\alpha$  are less than unity, however, probably indicating the presence of other causes for a DRT in addition to a possible DAE. Glarum<sup>22</sup> has used the Davidson-Cole distribution to analyze dispersion data on isoamyl bromide and found

that Eq. (1) with  $E = E_0$  and  $B(T)$  apparently temperature independent was well satisfied in the range from  $-75^\circ\text{C}$  to  $+25^\circ\text{C}$ . He also found a virtually temperature-independent  $\beta$  of about 0.7 over this range. Since this value of  $\beta$  is in the intermediate range between  $\beta \ll 1$  and  $(1-\beta) \ll 1$  where the Davidson-Cole distribution is inapplicable to a DAE situation, it cannot be well related to the temperature dependence required by an activated process with a DAE.

Several investigators who have used the Davidson-Cole distribution have found that  $\tau_0 = B(T) \exp[E_0/k(T - T_\infty)]$  for  $T > T_\infty$ . Some discussion of this equation, which cannot be directly related to rate theory, is given by Davidson and Cole.<sup>21</sup> When such an expression for  $\tau$  is used instead of that with  $T_\infty = 0$ , approximate temperature independence of the Davidson-Cole  $K(E)$  requires  $\beta$  to be proportional to  $(T - T_\infty)$  for  $\beta\pi \ll 1$ . Very little actual dependence of  $\beta$  on  $T$  is found, however, for propylene glycol in the range from  $-89^\circ$  to  $-45^\circ\text{C}$  where  $\beta$  is approximately 0.66. On the other hand, Denney<sup>23</sup> finds a somewhat greater than directly proportional dependence of  $\beta$  on  $T$  for *i*-butyl chloride over the range from 101.9°K to 113.5°K, which is probably considerably closer to  $T_\infty$  for this material than is the measurement range for propylene glycol above. In this range,  $\beta$  varies from 0.5 to 0.6.

Although the Wagner distribution may be made fully consistent with a DAE, it can only represent models which lead to a distribution symmetrical in  $\ln(\tau/\tau_0)$ . The description of considerable data requires an unsymmetrical distribution like the Davidson-Cole function, however, and even in symmetrical cases, where the Cole-Cole plot<sup>18</sup> is a circular arc, the Wagner distribution often fails to lead to close agreement between theoretical and experimental frequency-response results. Further, we have seen that the Cole-Cole, Davidson-Cole, and Fuoss-Kirkwood distributions cannot be made consistent with a DAE in the intermediate shape region where most of the experimental data falls.

In order to be able to determine whether a given experimental dispersion region is associated with and only with a DAE or not, it is desirable to have available a DRT which is fully consistent with a DAE for all temperatures, which can represent both symmetrical and asymmetrical situations, and which is sufficiently flexible to allow a good representation of dispersion data at a given temperature. Then comparison of data taken at various temperatures with that predicted from the distribution will allow a definite decision to be made. In a later paper, the transient, frequency, and temperature response will be investigated for a  $K(E)$  which is made up of terms of the form  $\exp(-\xi_i E)$ , where the  $\xi_i$ 's are temperature-independent constants. The  $G(\tau)$  which follows from such a  $K(E)$  meets the above conditions very well.

<sup>23</sup> D. J. Denney, J. Chem. Phys. **27**, 259 (1957).

<sup>18</sup> K. S. Cole and R. H. Cole, J. Chem. Phys. **9**, 341 (1941).

<sup>19</sup> B. Lakshminarayana, J. Sci. Ind. Research **20B**, 46 (1961).

<sup>20</sup> R. M. Fuoss and J. G. Kirkwood, J. Am. Chem. Soc. **63**, 385 (1941).

<sup>21</sup> D. W. Davidson and R. H. Cole, J. Chem. Phys. **19**, 1484 (1951).

<sup>22</sup> S. H. Glarum, J. Chem. Phys. **33**, 639 (1960).

In particular, when a single exponential term is used, the corresponding  $G(\tau)$  is of the form  $N\tau^{-(1+\rho)}$ , where  $N$  is temperature dependent and  $\rho = \xi kT$ . Outside the limits  $\tau_s$  to  $\tau_l$ ,  $G(\tau)$  is zero. This distribution is of interest because it can lead to symmetrical Cole-Cole plots for  $\rho=0$  and to asymmetrical curves with either right or left skew, dependent on the sign of  $\xi$ . The amount of skew also depends on the temperature-dependent ratio  $\tau_l/\tau_s$ . Debye dispersion is again obtained in the high temperature limit. This  $G(\tau)$  has been employed by Andrews<sup>24</sup> for  $\rho$  a positive integer only and for the range  $0 \leq \tau \leq \infty$  by Macdonald and Brachman.<sup>15</sup> Recently Vaughan, Lovell, and Smyth<sup>25</sup> have

found that their dispersion data for alkyl halides may be described by this distribution with at least approximately the above temperature dependence for  $\rho$ . Finally, a  $G(\tau)$  of the above form leads to transient response of the often-encountered form  $t^{-(1+\rho)}$  over a long time interval. For  $\rho=0$ , the corresponding distribution has been considered by a number of authors,<sup>3,7,26,27</sup> but neither for  $\rho=0$  nor  $\rho \neq 0$  has much attention been given to temperature dependence.

#### ACKNOWLEDGMENT

The helpful comments and suggestions of Dr. Robert Stratton are much appreciated.

<sup>24</sup> R. D. Andrews, *Ind. Eng. Chem.* **44**, 707 (1952).

<sup>25</sup> W. E. Vaughan, W. S. Lovell, and C. P. Smyth, *J. Chem. Phys.* (to be published). The author is grateful to Professor Vaughan for correspondence and for a preprint of this paper.

<sup>26</sup> R. Becker, *Z. Physik.* **33**, 192 (1925).

<sup>27</sup> C. G. Garton, *Trans. Faraday Soc.* **A42**, 76 (1946).