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Distributed Relaxation Response for Two Classes of Material Temperature Behavior

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Expressions for the transient and frequency response of materials showing exponential distributions of transition rates are summarized and related to recent work in the field. Responses arising from temperature-independent distributions (class I) are contrasted to those that depend in a simple way on temperature (class II). The distinction between dielectric and conducting systems is particularly emphasized, and the different temperature dependences of their frequency power-law exponents for class-I situations are discussed in detail. Besides presenting model frequency-response curves, it is shown that an exponential distribution of activation energies can lead to conductance frequency response very similar to that recently found by Lee et al. for two glasses and several ionically conducting single crystals.

Ausdrücke für das Transient- und Frequenzverhalten von Materialien, welche exponentielle Verteilungen von Übergangsraten zeigen, werden zusammengefaßt in Verbindung mit kürzlich erschienenen Arbeiten auf diesem Gebiet. Das Verhalten, welches von temperaturunabhängigen Verteilungen stammt (Klasse I), wird verglichen mit dem, welches in einfacher Weise von der Temperatur abhängt (Klasse II). Der Unterschied zwischen dielektrischen und leitenden Systemen wird besonders hervorgehoben, und die unterschiedlichen Temperaturabhängigkeiten ihrer Frequenz-Exponenten für Klasse-I Situationen werden ausführlich behandelt. Zusätzlich zu dem modellierten Frequenzverhalten wird gezeigt, daß eine exponentielle Verteilung von Aktivierungsenergien zu einem Frequenzverhalten der Leitfähigkeit führen kann, welches praktisch mit dem kürzlich von Lee et al. gefundenen für zwei Gläser und mehrere ionisch-leitende Einkristalle übereinstimmt.

1. Introduction and Background

At least since the work of Fricke [1], it has been known that the small-signal frequency response of nearly all dielectric and conducting systems contains one or more appreciable frequency ranges in which the response is closely proportional to $(i\omega)^{-n}$ or to $(i\omega)^{+m}$, where the exponents n and m fall in the interval [0, 1]; $\omega \equiv 2\pi f$ is the angular frequency; and $i \equiv \sqrt{-1}$. When both the real and imaginary parts of a complex conductance (admittance) are proportional to $(i\omega)^{+m}$, such power-law behavior has come to be called constant-phase-element (CPE) response [2 to 5]. Its universality has been particularly emphasized by Jonscher [6] (and references therein). Incidentally, it has become common to write such power-law response in terms of equations such as $\chi'(\phi) \sim \chi''(\omega) \sim \omega^{-n}$, where $\chi = \chi' + i\chi''$ is the dielectric susceptibility, but this usage is dimensionally inconsistent unless $\sim$ is replaced by the proportionality sign $\propto$.

For dielectric, polymer, and conductive materials, frequency and transient response frequently involve regions with two power-law exponents (regions of constant slope when the logarithm of response is plotted versus the logarithm of frequency or time). Such

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frequency response often involves exponents of different signs and can show a peak in the imaginary component of the response (e.g., ε'' in the dielectric response case), but regions involving n_1 and n_2 exponents ($n_1 \neq n_2$), often termed anomalous low frequency dispersion, are not uncommon [6, 7].

But whatever particular n and m regions appear, or whatever expression is used to describe such distributed response, if the frequency range is extended far enough toward high or low frequencies, the limiting response is associated with the smallest or largest relaxation time possible for the system, respectively [8]. Since these times are required by physical realizability to be finite and non-zero, response curves must reduce to single-time-constant behaviour in these limits, and therefore complex-plane plots must approach the real axis perpendicularly at their ends. Thus, theoretical response which only involves power-law exponents, such as that of the CPE alone, is non-physical; such response cannot continue to apply unaltered in the extreme high- and low-frequency limiting regions.

All these responses can be expressed in terms of a finite-extent discrete or continuous distribution of relaxation times (DRT) or transition rates (DTR), unlike simple Debye response which involves only a single relaxation time or transition rate. Many different processes may lead to a DTR, e.g. a distribution of activation energies (DAE), a distribution of trap depths or waiting times, or a distribution of hopping distances [9, 10, 11][2]). These possibilities may be related to fractal structures and fractal time processes [12]. Although the present work deals explicitly with DAEs, any of the above physical processes can lead to identical frequency and time response: the distribution is the key.

A very important distinction, not always clearly made in the DTR analysis of relaxation response, is that between a dielectric system (j = D), where lattice contributions and dc conduction, if present, are usually independent, and a conducting system (j = C), where dc conduction is the $\omega \to 0$ limit of the full response. In the former, which typically involves dipole rotation, the principal relaxing entities do not contribute to charge transport, while in the latter they do. Proper identification cannot be made on the basis of the absence or presence of dc conduction because a dielectric may be leaky and a conducting system may be measured with completely blocking electrodes or at insufficiently low frequencies. It is most appropriate to derive an expression for the response of a distributed D-system at the complex dielectric constant level ($\varepsilon = \varepsilon' - i\varepsilon''$), and that of a C-system at the impedance ($Z = Z' + iZ''$) or admittance level, although one can, of course, then use the results to calculate the response of a D-system at the impedance level or that of a C one at the complex dielectric constant level.

Although Kauzmann [13] discussed a Gaussian DAE as early as 1942, it does not lead to power-law response in frequency and time [14].[3]) In fact, only an exponential DAE (or its associated power-law DRT) can yield such response. Later, Fröhlich [15] considered the response of a dielectric material following from a uniform DAE of finite extent in energy (cut off at both high and low energies, the box distribution), but it was not until 1963 that the transient response of a D-system involving a double-exponential distribution of activation energies (DEDAE) was calculated [16]. In order for it to lead to the two slopes

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[2]) The value 0.497 in Table 3 of [9] should be replaced by 1.497, and the product sr in the numerator of (B8), should be replaced by s. In (17) of [10a] the exp $(-N_{i1}E)$ term should be replaced by exp $(-\eta_{i1}E)$, and in (24) the $\pm$ sign should be replaced by an equality sign. The numerators of (5) and (7) of [10b] should be considered to be the effective DAE or DRT for normalization purposes, as in the present work.

[3]) The numerator of (5) should be considered to be the effective DAE for normalization purposes, as was actually done.

usually seen in the time response, two distinct regions of exponential dependence were required in this DAE, and they were cut off at high and low energies to ensure physical realizability. Detailed frequency response for the single-exponential DAE ($EDAE_1$) [9] and the DEDAE [10, 14] were presented later, and it was found that DEDAE response could fit very well those of all of the conventional empirical response functions [4, 5], including that of Havriliak and Negami [17] and stretched exponential response. Since the DEDAE can fit all data previously fit by these functions, further discussion of its temperature dependence possibilities is therefore warranted.

2. Thermal Activation and Physical Ranges

Most distributed response is thermally activated. Although both energy storage and energy dissipation processes may be separately thermally activated [9], the conventional approach for dielectrics is to consider only the activation of relaxation times, τ, which depend on both processes. Then, we may write

$$\tau = \tau_a \exp(E/kT), \tag{1}$$

where τ_a is a characteristic property of the material, E is an activation energy, k is the Boltzmann constant, and T is the absolute temperature.

The more general treatment, where both processes may be separately thermally activated, is particularly needed for C-systems [9]. Let us therefore assume that the activated dissipation process involves $\exp(\alpha E/kT)$ and the activated storage process involves $\exp(\beta E/kT)$. Then the generalization of (1) becomes

$$\tau = \tau_a \exp(\gamma E/kT), \tag{2}$$

where α and β are temperature independent constants and $\gamma \equiv \alpha + \beta$. Next, define $\mu_C \equiv \alpha$ for C-systems and $\mu_D \equiv \beta$ for D ones and use μ_j in general. Although we shall actually illustrate results for the usual choices $\mu_D = 0$ and $\mu_C = 1$, so that $\gamma = 1$, for generality, frequency-response formulas will be presented in terms of μ_j and γ.

Let us define τ_L (>0) and τ_H ($<\infty$) as the minimum and maximum relaxation times, respectively, which are possible for the system. Then the corresponding limiting E's are $E_L \equiv (kT/\gamma)\ln(\tau_L/\tau_a)$ and $E_H \equiv (kT/\gamma)\ln(\tau_H/\tau_a)$. When the frequency response of the system involves two fractional exponents, it is useful to define a further more or less central, τ, τ_0, where $\tau_0 \equiv \tau_a \exp(\gamma E_0/kT)$ and $E_L \leqq E_0 \leqq E_H$. Finally, the normalized quantity $\mathscr{E} \equiv E/kT$ will often be useful.

Since negative activation energies are meaningless, the smallest physically realizable value of E is zero; then $\tau_L = \tau_a$. Further, since $\tau_H < \infty$, it is unphysical to consider the range of E to be $-\infty \leqq E \leqq \infty$ as Wang and Bates (WB) [18][4]) recently did. The quantity τ_a may be expressed in terms of the entropy, S, of the thermally activated process [16, 19]; then E is essentially the corresponding enthalpy. Although negative entropy values have been found in some experiments [16], the minimum value of the entropy for a physically realizable system cannot reach $-\infty$, the value necessary to make τ_a zero.

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[4]) In (13) a factor of $(kT)^{-1}$ has been omitted. In (15) the β in the term $\exp[\beta(1-\alpha)\ldots]$ should be replaced by $-\beta$. The reference to Fig. 8b above (20) should be to Fig. 7b. The reference to (7) at the top of p. 84 should be to (17).

3. The Double-Exponential DAE for Classes I and II

3.1 The DEDAE for dielectric and conductive systems

If we define the DEDAE as $F_j(\mathscr{E})$, it follows from earlier work [9, 10, 14] that $F_j(\mathscr{E}) = 0$ for $\mathscr{E} < \mathscr{E}_L$ and $\mathscr{E} > \mathscr{E}_H$ and, otherwise.

$$F_j(\mathscr{E}) = \begin{cases} N \exp\left[(\mu_j - \lambda_1)\,\mathscr{E}\right]; & \mathscr{E}_L \leqq \mathscr{E} \leqq \mathscr{E}_0, \\ N \exp\left[(\lambda_2 - \lambda_1)\,\mathscr{E}_0 + (\mu_j - \lambda_2)\,\mathscr{E}\right]; & \mathscr{E}_0 \leqq \mathscr{E} \leqq \mathscr{E}_H, \end{cases} \tag{3}$$

where

$$\lambda_k \equiv kT\eta_k, \tag{4}$$

with $k = 1, 2$, and N is a normalization factor. Here λ_k and η_k are parameters of the distribution and are discussed in detail later. It is convenient to define

$$x \equiv \gamma(\mathscr{E} - \mathscr{E}_0), \tag{5}$$

$$x_L \equiv \gamma(\mathscr{E}_0 - \mathscr{E}_L), \tag{6}$$

$$x_H \equiv \gamma(\mathscr{E}_H - \mathscr{E}_0), \tag{7}$$

and the following important slope-related quantities,

$$\varphi_k \equiv (\mu_j - \lambda_k), \tag{8}$$

where $-\infty < \varphi < \infty$. We omit the j subscript from φ since its value will be clear from the context.

3.2 Class I and class II temperature dependences

When the DEDAE was first introduced [16], the two ηs were taken temperature independent on the basis that a EDAE, when present, might often be expected to be a basic property of the structure of the dielectric or conductive system and so might most plausibly be entirely independent of temperature (for at least a limited range not too close to the temperature of a phase change). Although the first detailed analysis of the frequency response of an EDAE system with a single η of arbitrary value [9] did not initially specify the temperature dependence of η, it was eventually taken temperature independent, and this choice has been generally followed in the subsequent work of the author in this area [10, 14].

Recent work of Kliem and Arlt (KA) [20], which deals very similarly with DEDAE time and frequency response for D-systems but does not reference any earlier work in the EDAE field, also involves the temperature-independent choice for η_k. It is this temperature independence of the EDAE which defines class-I behavior. It leads to frequency response whose shape on a log–log plot is dependent on temperature.

Another choice, which leads to quite different temperature dependence of $F(E)$ and $\varepsilon(\omega)$, is to set $\eta E = \lambda(E/kT)$ and take $\lambda \equiv kT\eta$ temperature independent. Such a choice has recently been discussed by WB [18] for D-systems and leads to class-II behavior. It yields a temperature dependent $F(E)$ and corresponding $\varepsilon(\omega)$ response whose shape is independent of temperature. Such behavior, where a universal frequency-response curve can be constructed by shifting curves for different temperatures along the frequency axis until they superimpose, is also consistent with the well-known time–temperature superposition law

[21], and has been illustrated for a variety of materials by Jonscher [6]. Although much small-signal frequency-response data are consistent with the predictions of either a class-I or of a class-II DEDAE model, once one allows η_1 and/or η_2 to be temperature dependent an infinity of possible types of response becomes possible. Here, attention will be restricted to only class I or II situations, the most important ones.

3.3 General frequency-response expressions

It is useful to write the normalized frequency response, $I_j(\omega)$, of either a C-system or of a D-system in terms of a single equation [9]. Let $U_j(\omega)$ be either the part of the impedance associated with relaxation for an intrinsically conducting system (j = C), or the part of the complex dielectric constant associated with pure dielectric relaxation (j = D), and define

$$I_j(\omega) \equiv [(U_j(\omega) - U_{j\infty})/(U_{j0} - U_{j\infty})], \tag{9}$$

where U_{j0} and $U_{j\infty}$ are the limiting low and high frequency values, respectively, of $U_j(\omega)$ for a single distributed process. For j = D, for example, $U_{D0} = \varepsilon_0$ and $U_{D\infty} = \varepsilon_\infty$.

The general expression for $I_j(\omega)$ when a DAE, $F_j(E)$, is present may be written [9, 10]

$$I_j(\omega/\omega_0) = \int_{-\infty}^{+\infty} \frac{F_j(E)\,\mathrm{d}E}{1 + i(\omega/\omega_0)(\tau/\tau_0)}, \tag{10}$$

where $\omega_0\tau_0 \equiv 1$ and τ is given by (2). For $\omega = 0$, (10) reduces to just the $F(E)$ normalization condition. Now after using $F(E)\,\mathrm{d}E = F(\mathscr{E})\,\mathrm{d}\mathscr{E}$, equ. (3), and evaluating N, one may write the normalized frequency response as [14]

$$I_j(\omega/\omega_0) \equiv J_j(\omega/\omega_0)/J_j(0), \tag{11}$$

where

$$J_j(\omega/\omega_0) \equiv \int_{-x_L}^{0} \frac{\exp(\varphi_1 x)\,\mathrm{d}x}{1 + i(\omega/\omega_0)\exp(x)} + \int_{0}^{x_H} \frac{\exp(\varphi_2 x)\,\mathrm{d}x}{1 + i(\omega/\omega_0)\exp(x)}, \tag{12}$$

and

$$J_j(0) = \varphi_1^{-1}[1 - \exp(-\varphi_1 x_L)] + \varphi_2^{-1}[\exp(\varphi_2 x_L) - 1] \tag{13}$$

for φ_1 and φ_2 both nonzero. When they are both zero, $J_j(0) = x_L + x_H = \gamma(\mathscr{E}_H - \mathscr{E}_L)$.

For numerical work it is straightforward to evaluate the integrals of (12) directly by numerical quadrature, although closed forms are available for certain integral and fractional values of φ [9] (see Appendix B). Since 1985, the complex nonlinear least squares (CNLS) impedance spectroscopy fitting program, LEVM, has included both transient and frequency response DEDAE fitting and simulation capabilities and has been used in the present work. It incorporates a great many more possibilities as well [22] and is available at nominal, nonprofit cost from the author's department.

Equation (11) to (13) define the general frequency response for the DEDAE. When the data show only a single power-law response region, one need only set $\varphi \equiv \varphi_1$, $\varphi_2 = 0$, and $x_H = 0$ in (12) to obtain the single-slope $EDAE_1$. It leads to asymmetrical peaked loss near the low frequency end of a complex-plane plot of $I_j(\omega)$.

How then can one tell the frequency response of the DEDAE and the $EDAE_1$ apart when they both show peaks? The best way to obtain quantitative results is to fit the data by CNLS to each model. But usually a log–log graph of $I_j''(\omega)$ versus ω will allow discrimination. Because cut offs lead to limiting $I_j''(\omega)$ response with power-law exponents of ± 1, and DEDAE slopes near a central peak will involve exponents appreciably less than unity in magnitude for a broad DRT or DAE, it is straightforward to distinguish between the two possibilities provided the measured frequency range is sufficiently large. In the $EDAE_1$ case, the left slope will asymptotically approach 1, while at the right of the peak a negative slope of magnitude less than 1, associated with the single φ, will be followed by a limiting slope of -1.

3.4 Dielectric-system transient response

Once an expression for a DAE is available, it is straightforward to calculate the corresponding time- and frequency-response predictions using well-known integral transforms. In particular, the transient response of a D-system, $A_D(t)$, is given by a Laplace transform as [23]

$$A_D(t) = \int_0^\infty [\xi^{-1} F_D(\xi^{-1})] \exp(-t\xi)\, d\xi\,, \tag{14}$$

where $\xi \equiv \tau^{-1}$. This integral was evaluated in closed form for the $F(\mathscr{E})$ of (3) with $\mu_D = 0$, and although the result involves the incomplete γ-function, it can yield response for $A_D(t)$ with appreciable regions closely proportional to $t^{-(1+\lambda_1)}$ and $t^{-(1+\lambda_2)}$, where λ_k may be proportional to T (class I) or independent of T (class II). The original calculation [16] envisaged a situation where both entropy and enthalpy could be simultaneously distributed. Here, it has been simplified for the case where only E is distributed. Apparently unaware of the earlier work [16], KA independently derived a form of (14) and calculated the associated time and frequency response by numerical integration [20]. Since [16] contains much more extensive results and discussion of EDAE transient response possibilities than that of KA, only frequency response will be considered in the following.

4. Specifics of EDAE response

4.1 Illustrative examples of response possibilities

Fig. 1a shows a typical relaxation DEDAE for a class-I dielectric system. The slopes are defined as $S \equiv d[\ln\{F(E)\}]/dE$. The formulas for the DEDAE slopes and the actual values used here are presented in the top part of Table 1. The values selected for illustrative purposes were chosen to yield response of the same general character as those of WB [18] and KA [20]. We have purposely picked a somewhat asymmetric distribution here. Thus, the complex-plane response shown in Fig. 1b is correspondingly asymmetric.

In Fig. 1b the low frequency limit is at the right and the high frequency one is at the left. This complex-plane response was calculated using $x_L = 0.14/kT$ and $x_H = 0.24/kT$ (solid lines in Fig. 1b) and with "infinite range" (IR) values of these quantities (dashed lines) added for comparison. To obtain such infinite-range response, it is only necessary that x_L and x_H be sufficiently large that further increasing their values results in negligible change of the response within the frequency window considered. For the present range,

Table 1

Exact slopes, S_1 and S_2, for the DEDAE and approximate slopes for the corresponding relaxation-situation frequency response. The DEDAE slope values inside square brackets apply to conductive systems (j = C) and all other DEDAE results to dielectric systems (j = D). For the illustration, $\mu_D = 0$, $\mu_C = 1$, and at $T = 200$ K: $\lambda_1 = -0.4$ and $\lambda_2 = 0.66$ for j = D and $\lambda_1 = 0.6$, $\lambda_2 = 1.66$ for j = C

situation		general	class I η_1, η_2 and EDAE temperature independent	class II λ_1, λ_2 and $I_j(\omega/\omega_0)$ temperature independent	illustrative values at $T = 200$ K
quantity	**region**				
DEDAE	$E_L \leqq E \leqq E_0$	$-\eta_1$	$\lambda_1/kT = -\eta_1$	λ_1/kT	23.209 [−38.814] (eV^{-1})
	$E_0 \leqq E \leqq E_H$	$-\eta_2$	$\lambda_1/kT = -\eta_2$	$-\lambda_2/kT$	−38.295 [−96.317] (eV^{-1})
I''_j	$\omega < \omega_0$	$-\varphi_2$	$-\mu_j + kT\eta_2$	$-\mu_j + \lambda_2$	0.66
	$\omega > \omega_0$	$-\varphi_1$	$-\mu_j + kT\eta_1$	$-\mu_j + \lambda_1$	−0.4
Y''_D	$\omega < \omega_0$	$1 - \varphi_2$	$1 + kT\eta_2$	$1 + \lambda_2$	(1.66) → 1
	$\omega > \omega_0$	$1 - \varphi_1$	$1 + kT\eta_1$	$1 + \lambda_1$	0.6
Y''_C	$\omega < \omega_0$	$-\varphi_2$	$-1 + kT\eta_2$	$-1 + \lambda_2$	0.66
	$\omega > \omega_0$	φ_1	$1 - kT\eta_1$	$1 - \lambda_1$	0.4

values greater than 10 or so are sufficient. Fig. 2 shows the corresponding lg $[I_j(\omega/\omega_0)]$ versus lg $[\omega/\omega_0]$ response curves. For the present choices, the IR criterion is well met for the $T = 100$ K curves and is nearly met for the $\omega < \omega_0$ part of the $T = 400$ K curve, where $x_H \approx 7$.

The $T = 200$ K results of Fig. 1b and Fig. 2 apply to either a j = D or a j = C situation because the φ_k values have been taken the same for these two conditions at this temperature. But because of the dependence of the φ's on μ_j, the actual DEDAE shape which leads to this response is different in the two cases. As the values listed in the first part of Table 1 show, the temperature-independent, C-system DEDAE yielding these results is not centrally peaked but decreases with two negative slopes as E increases in the range from E_L to E_H. Also, because the values of μ_D and μ_C are different, the present equality of the actual values of the φ's at $T = 200$ K leads to different class-I values of the j = D and j = C φ values at other temperatures, producing C-system curve shapes different from those shown for the present D-system.

Further, only the differences $E_0 - E_L$ and $E_H - E_0$ affect the results plotted in Fig. 1b and 2. Thus, such normalized plots are independent of the actual value of E_0 present. But since ω_0 depends on E_0, the latter can be estimated if values of ω_0 for several temperatures are available. By fitting the DEDAE model to frequency-response data for different temperatures using, for example, the LEVM fitting program, estimates may be obtained of ω_0, τ_a, E_0 and some or all of φ_1, φ_2, x_L, x_H, U_0, and U_∞.

For frequency-response situations, we define "slope", s, to mean the slope obtained from a straight-line region of a log–log plot, such as that of Fig. 2. In such a region, it follows that $I''_j \propto \omega^{\pm n_I}$ and the slope is just $+n_I$ or $-n_I$ with $0 \leqq n_I \leqq 1$. If the full response is well approximated by the CPE, then $I'_j \propto \omega^{\pm n_I}$ as well, but for added generality let us take $I'_j \propto \omega^{\pm n_R}$, where $0 \leqq n_R \leqq 2$. The single-time-constant Debye curve of this figure applies when $E_H \to E_L$, and its limiting left and right slope values are $s_l = n_{Il} = +1$ and $s_r = -n_{Ir}$

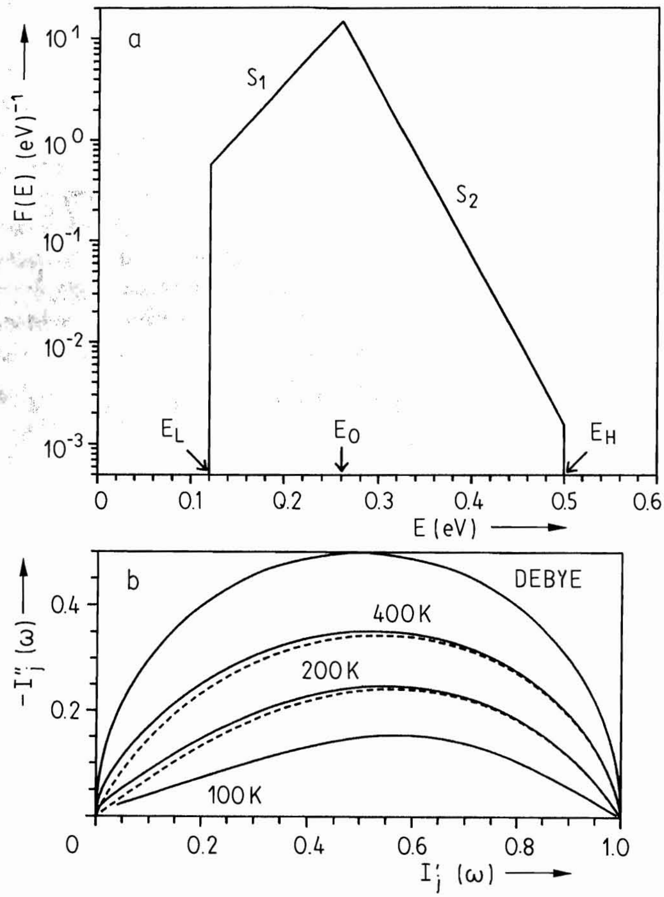

Fig. 1. a) Double-exponential distribution of activation energies (DEDAE) used at all temperatures for class I j = D frequency-response calculations. b) Complex-plane plot of the normalized frequency response for three temperatures. I_j is a normalized impedance for conductive systems (j = C) and a normalized complex dielectric constant for dielectric systems (j = D). The dashed curves were calculated without the cut-offs shown in Fig. 1a. Here, j = D or C for the T = 200 K curve, and j = D for the others

$= -1$. These same values are found for DEDAE response at frequencies beyond cut-off where only the lowest and highest relaxation times operative in the system dominate the response [8 to 10]. But in regions nearer ω_0, $I_j''(\omega/\omega_0)$ exhibits slopes whose values are determined by those of φ_k. Expressions for the approximate slopes in the central regions of such a plot as Fig. 2 are presented in the second part of Table 1. Incidentally, the effects on the temperature dependence of a φ arising from linearly related entropy and enthalpy distributions and/or from a glass-like transition have been considered [9, 16] but are not incorporated in the present results.

There are two reasons why we speak here of approximate rather than exact slopes in the frequency-response domain. First, in any physically realizable system there can be no non-zero DAE probability density outside of a finite region of E (E_L to E_H). The resulting cut-off effects in the frequency response may lead to a finite region of no well-defined

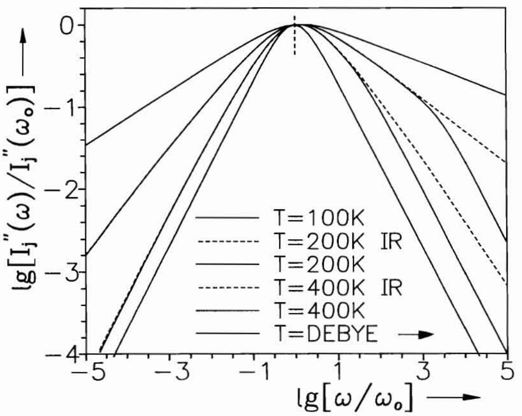

Fig. 2. Log–log plot of the normalized response quantity $I_j''(\omega/\omega_0)$ vs. (ω/ω_0) for the three temperatures of Fig. 1b (j = D), for the identical j = C 200 K curve, and for single-time-constant Debye response. Here IR indicates that the effective range of the DEDAE is not cut off. (The T = 100 K curve is that at the top here)

constant slope (the actual case for the right-hand region of the T = 400 K curve of Fig. 2) or to one where n_R and n_I are not entirely equal even in the $\omega/\omega_0 > 1$ region [9, 10].

The second reason is even more important. The second and third parts of Table 1 are appropriate for IR conditions. They indicate that the I_j'' slopes are approximately given by $-\varphi_2$ and $-\varphi_1$, respectively. But when η_1 and η_2 are non-zero, the magnitudes of φ_1 and φ_2 can increase indefinitely as T increases for class-I behavior, and as $|\varphi|$ increases beyond 1, DEDAE response approaches simple Debye behavior. But the actual slopes must satisfy $|s_I| \leqq 1$ and $|s_R| \leqq 2$ [9, 10]. Thus, the predicted approximate slope of 1.66 given in Table 1 is actually limited to unity. Even when cut-off effects are negligible, the relations $n_{Il} \approx |\varphi_2|$ and $n_{Ir} \approx |\varphi_1|$ certainly cannot hold when $|\varphi| > 1$ or when $\varphi < 0$. Fig. 5 in [14] illustrates how n_I and n_R approach their limiting values as φ exceeds 1 or 2.

The above restrictions were apparently not appreciated by KA. They dealt with a class-I dielectric response system and made the serious conceptual error of directly equating the actual frequency- and time-response power-law exponents to the DEDAE slope parameters [20], the present φ_k. It is of interest to note that it is the slope of the high-E right side of the DEDAE which determines the slope of the low-frequency left side of frequency-response curves (and vice versa), a result completely consonant with the presence of a thermally activated process which occurs more slowly the higher the energy barrier.

The Fig. 1b curves are similar to ones presented by KA, plotted by them in the χ complex plane. Although they did not specify that they were actually plotting χ''/χ_0 versus χ'/χ_0, they must have done so since the maximum value of all their χ's is unity. Further, KA identify the shape of these curves as being of Cole-Davidson (CD) chartacter. But it has long been known that the DEDAE without cut offs can excellently fit Cole-Cole, CD, and other empirical response functions [9, 10, 14], and its response is in general very similar to that produced by the empirical Havriliak-Negami (HN) expression [17]

$$I(\omega/\omega_0) = \left(1 + \left\{i\frac{\omega}{\omega_0}\frac{\tau}{\tau_0}\right\}^{1-\alpha}\right)^{-\beta}, \tag{15}$$

where the slope parameters satisfy $0 \leqq \alpha \leqq 1$ and $0 \leqq \beta \leqq 1$. This expression reduces to that of CD when $\alpha = 0$ and to that of Cole and Cole for $\beta = 1$. So is the CD identification made by KA most appropriate here?

As a test of model appropriateness, the $T = 200$ K DEDAE $I(\omega/\omega_0)$ complex data of Fig. 1b and 2 were fitted by LEVM to the CD and the HN expressions, using optimized function-proportional weighting [22]. The estimated standard deviation of the CD fit was found to be about 0.34, while that of the HN one was about 0.016, a far better fit. The values of α and β estimated from the HN fit were 0.344 ± 0.002 and 0.614 ± 0.002. These values correspond to asymptotic HN slopes of $s_l = n_{\text{Il}} = 0.656$ and $s_r = -n_{\text{Ir}} = -0.402$, satisfactorily close to the actual values of 0.66 and -0.4, respectively. On the other hand, the HN estimated value of τ_0 was about 55% too high, reflecting a systematic error arising from using a wrong fitting model for the data.

The curves of Fig. 2 are similar to some calculated by KA and compared by them (but not fitted) to actual experimental data on polyethylmethacrylate. The magnitudes of the experimental slopes increase with increasing temperature, consistent with earlier predictions for a class-I D-system. Note, however, that the slopes of a class-I C-system at the I_C level are of the form $-1 + kT\eta_k$. Thus for positive η_k, the associated slope will be near -1 at low temperatures and will decrease in magnitude as the temperature increases, reaching zero at $T = T_{0k} \equiv 1/k\eta_k$. For the present values of η_k, which are both positive in the present conductive case, T_{0k} is about 333 K and 120 K for $k = 1$ and 2, respectively.

Finally, note that the peak loss of $I(\omega/\omega_0)$ curves similar to those of Fig. 2 will only occur at $\omega/\omega_0 = \omega\tau_0 = 1$ when the condition $\varphi_1 = -\varphi_2$ holds, yielding a symmetric curve (termed the EDAE_2 in earlier work [10, 14]). Otherwise, the peak occurs to the left or right of the $\omega = \omega_0$ point, depending on whether $|\varphi_1| > |\varphi_2|$ or vice versa, respectively. This phenomenon, which does not require equality of x_L and x_H, implies that one should not generally determine the value of τ_0 at a given temperature from $1/\omega_p$, where ω_p is the frequency at the peak. Instead, CNLS fitting of the full data should be used to obtain an appropriate estimate of τ_0. Incidentally, although KA considered an asymmetric situation, their peaks all occur at $\omega = \omega_0$, contrary to the above expectation. The difference arises because they evidently implicitly defined ω_0 as ω_p, rather than as $1/\tau_0$.

4.2 Class-II frequency response

Table 1 shows slope expressions for the class-II situation where the λ_k are temperature independent, the case recently considered for dielectric materials by WB [18]. Then, the DEDAE is itself temperature dependent, as illustrated in Fig. 3 for the three temperatures considered here. But for this situation, the shapes of the frequency-response curves are now temperature independent in the IR approximation used by WB, and the $T = 200$ K curves of Fig. 1b and 2 apply at all temperatures. But as T increases indefinitely for the realistic finite-range situation, $F(E)$ approaches a flat-top box distribution shape and x_L and x_H approach zero. In the limit, again only simple Debye behavior remains. Nevertheless, if x_L and x_H remain sufficiently large over the entire temperature range of measurement, frequency-response curves for different temperatures can be shifted in frequency, to account for the temperatures dependence of τ, so that they all fall on a single universal curve. Many experimental situations of this type are discussed by Jonscher [6].

4.3 Comparison of dielectric and conductive system immittance responses

Not only is it of interest to compare the slope predictions of Table 1 with actual slopes of I'_j and I''_j curves in the IR case, where cut-off effects are outside the range of measurement, but it is also instructive to compare full curve shapes for normalized immittances

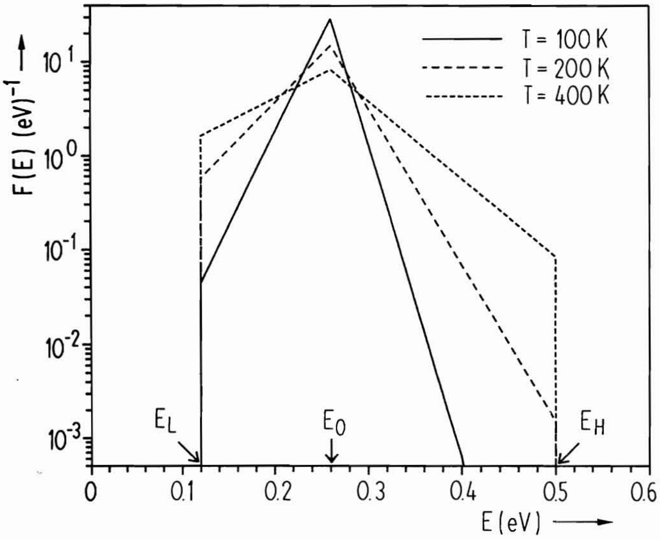

Fig. 3. The temperature-dependent DEDAE for class II and j = D at T = 100, 200, and 400 K

(impedances, admittances, and complex dielectric constant). We begin with a discussion of the transformation of unnormalized quantities for j = C and D. Since the measured system will always include a geometrical capacitance, C_∞, given by $C_\infty = \varepsilon_\infty C_c$, where C_c is the capacitance of the empty measuring cell, its electrical effect should be included in the analysis. Then the impedance of the C-system which involves a specific response function at the Z level, $U_C(\omega)$, can be written $Z_C(\omega) = U_C(\omega)/[1 + i\omega C_\infty U_C(\omega)]$, and it follows that $Y_C \equiv 1/Z_C$, and $\varepsilon_C \equiv Y_C/(i\omega C_c)$. Note that the dc conductance is $G_{C0} = Y_C(0)$.

Similarly, for a leaky dielectric with a dc conductance of G_{D0}, $\varepsilon_D(\omega) = U_D(\omega) + G_{D0}/(i\omega C_c)$, and Y_D and Z_D follow immediately. Since U_C and U_D describe different physical processes, we do not expect that $Y_C = Y_D$. For a C-system, where the dispersion is primarily associated with conductive rather than dielectric processes, one should clearly deal with Z_C rather than ε_C. In fact, concentration on ε_C, rather than on Z_C or Y_C, tends to obscure the actual relaxation process involved. Unless both dielectric and conductive relaxation processes are simultaneously present and important, one should therefore be concerned with conductive response functions for j = C rather than with dielectric ones.

For simplicity, we shall set $U_{j\infty} = 0$ and $G_{D0} = 0$ as well. Then, it is appropriate to define for j = C the normalized admittance (complex conductivity) $Y_{NC} \equiv 1/I_C$ and the associated normalized complex dielectric constant $\varepsilon_{NC} \equiv Y_{NC}/(i\omega/\omega_0)$. Similarly, when j = D, the normalized admittance is defined as $Y_{ND} \equiv (i\omega/\omega_0)\, I_D$ and the normalized impedance as $Z_{ND} \equiv 1/Y_{ND}$. With these choices, it follows that $Z_{ND} = \varepsilon_{NC}$ if I_C and I_D are taken the same.

In Fig. 4, the frequency dependences of the above quantities are plotted for j = D on the left and j = C on the right. These graphs are for the T = 200 K DEDAE situation considered in Section 4.1. The limiting slopes of both real and imaginary quantities are equal for $\omega > \omega_0$ and are generally consistent with the values given in Table 1. But although the low-frequency slope of Y''_{ND} is limited to unity, that of Y'_{ND} is not so limited and exhibits the expected value of 1.66. For $\omega < \omega_0$, the asymptotic slope of Z''_{ND} is just the negative of that of Y'_{ND}, as expected, and that of Z'_{ND} is equal to that of I'_D. For the right graph,

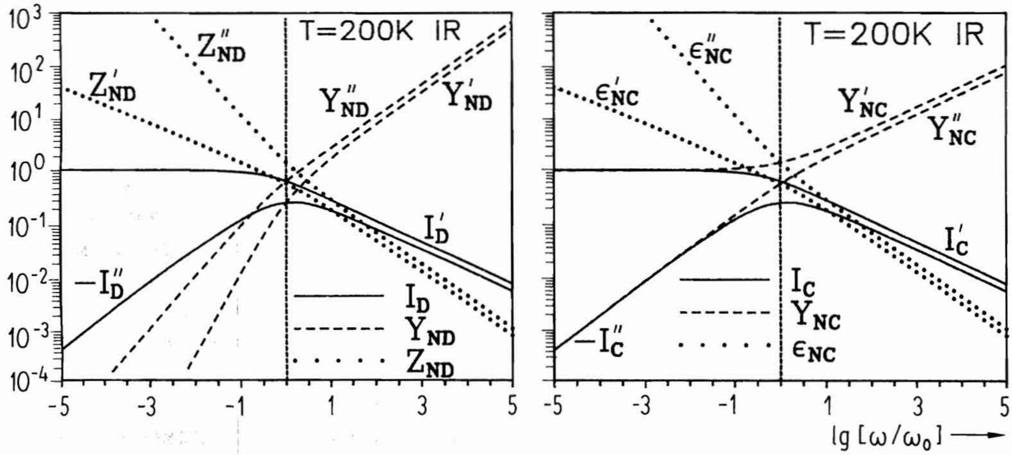

Fig. 4. Graphs illustrating the normalized frequency response at $T = 200$ K of the DEDAE of Fig. 1a without cut offs. The left part shows dielectric-system response at three immittance levels, while the right part compares conducting-system response for the condition that $I_C(\omega) = I_D(\omega)$

notice particularly the difference in the slopes of the Y_{NC} components from those of Y_{ND}. Further, the slope of the ε''_{NC} curve for $\omega < \omega_0$ is just -1, arising from the non-zero G_{C0} of the C-system.

As already mentioned, the $EDAE_1$ exhibits a single slope determined by $\eta = \eta_1$. It is of particular interest when $\eta \geqq 0$. Then, for $\eta > 0$ one deals with an exponentially decreasing distribution, frequently seen experimentally in semiconductors as an exponential band tail [24]. For $\eta = 0$, the slope is zero, and the DAE is then a box distribution with a flat top extending from E_L to $E_0 = E_H$. Fig. 5 shows responses for the $\varphi_C = \varphi_D = \varphi = 1$ choice; the corresponding values of λ_C and λ_D are 0 and -1, respectively.

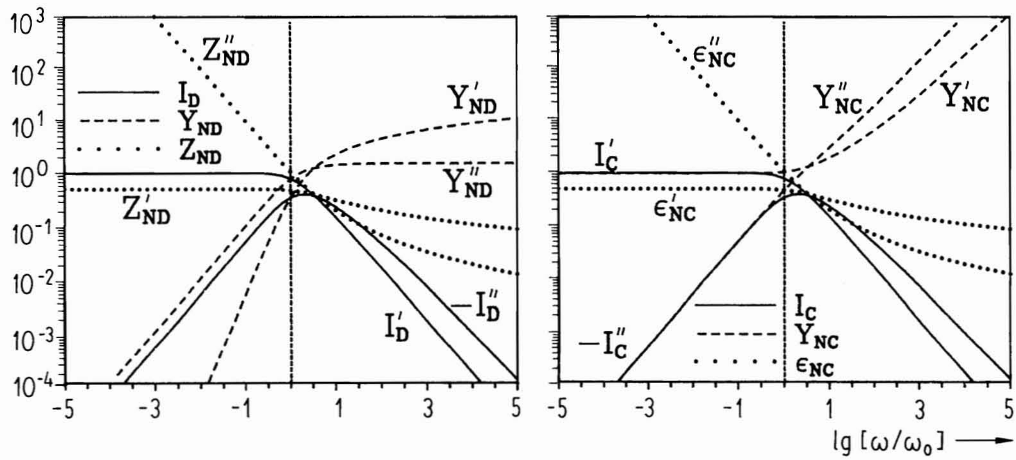

Fig. 5. Graphs of the same character as those of Fig. 4, but here response is for a single-exponential distribution of activation energies ($EDAE_1$) with $\varphi = \varphi_C = \varphi_D = 1$, using IR cut-off values of $x_L = 15$ (or greater) and $x_H = 0$

The $\omega < \omega_0$ slopes in Fig. 5 arise from the cut off at $E = E_L$, and we see that the left-side slope of Y'_{ND} has the limiting value of 2. For $\omega > \omega_0$, on the other hand, the slopes of the components of Y_{NC} asymptotically approach the value of unity predicted in Table 1, and those of I'_D and I'_C are properly -1. But the other slopes do not entirely agree with those predicted. For example, that of I''_C is algebraically greater than -1. Finally, note that since the slope of Y''_{NC} approaches unity for $\omega > \omega_0$, the associated capacitance (see the ε'_{NC} curve) approaches approximate frequency independence as well.

5. AC Conductance for a Conductive System

In recent work [11, 25], it has been pointed out that measurement of $Y'_C(\omega)$ alone is usually insufficient to allow unambiguous discrimination between different dispersion models, but that CNLS fitting of full $Y_C(\omega)$ data does permit such discrimination [25]. Macdonald [25] also discusses ways of analyzing $j = \mathrm{C}$ data when ε_∞ cannot be neglected. Interesting $Y'_C(\omega)$ data have recently been presented by Lee et al. [26][5]) which fall into two types: one in which the slope of the data is unity over a wide temperature range, and another in which s decreases linearly from unity down to a saturation value of 0.6 as the temperature is increased. Lee et al. propose that such limiting $s = 1$ behavior at low temperatures is a universal phenomenon.

Now since, for the EDAE$_1$ with class-I behavior, $\varphi = 1 - kT\eta$ when $\mu_C = 1$, Fig. 5 and the last line in Table 1 show that with $s \approx \varphi$ the above slope behaviors are approximately consistent with those predicted by an EDAE. When $s \approx 1$, it is merely necessary that $kT|\eta| \ll 1$ over the temperature range of measurement. Further, $j = \mathrm{C}$ data for numerous different materials are known to lead to s values which decrease approximately linearly over a range of increasing temperature, implying that $\eta > 0$. The high-T saturation value of exactly 0.60, which was observed for three different materials by Lee et al. may be an artifact of measurement arising from the difficulty of determining s when the maximum available frequency is limited and only a vanishingly small region of $Y'_C(\omega)$ response exhibits an approach to a constant slope value. Alternatively, it may signal a transition to a different dispersion process (e.g., that from class-I to class-II behavior).

Although Lee et al. rejected the hypothesis that their data imply the presence of a DAE because they believed that a wide uniform DAE is unlikely for the materials they measured, the temperature dependence of s they found is nevertheless evidence for the possible presence of such a distribution. Although their $s = 1$ data for NaCl:Zn^{2+} over the temperature range from 296 to 533 K were only available in graphical form, I used their value of 0.95 eV for the activation energy of G_{C0} and their published curves to obtain $G_{C0}(T)$ values well approximating theirs. Then with $\varphi = 1$ and an activation energy of 0.88 eV for τ_0, the EDAE$_1$ led to the curves of Fig. 6. The $j = \mathrm{C}$ ones are very similar to those of Lee et al., and the $j = \mathrm{D}$ one is included to show that the corresponding D-system EDAE$_1$ with $G_{D0}(T) = G_{C0}(T)$ and $\varphi = 0$ leads to a limiting slope of 2 rather than 1 and is thus inappropriate, as expected. Incidentally, the presence of a C_∞ with a value even much larger than likely affects $Y''_C(\omega)$ here but not $Y'_C(\omega)$. The minimum value of $(E_0 - E_L)$ found which led to negligible cut-off effects was 0.42 eV. Thus the EDAE$_1$ extended from about 0.46 eV, or less, to 0.88 eV.

[5]) In this work the authors associate power-law frequency response with stretched-exponential transient response, only true in the asymptotic $\omega \gg \omega_0$ limit.

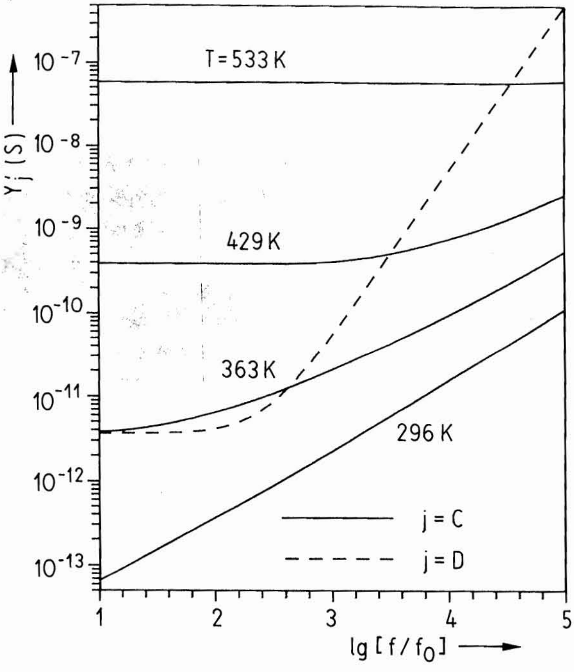

Fig. 6. Log–log plot of the real part of the $EDAE_1$ admittance, the conductance, vs. frequency, f, where f_0 is a scaling factor equal to 1 Hz. For $j = C$, $\varphi = 1$ and for $j = D$, $\varphi = 0$. Values of $Z(0)$ and τ_0 were selected to yield close agreement with similar curves of [26]

These results suggest that since the $j = C$ $EDAE_1$ model can fit the main features of the data of Lee et al., it may be appropriate after all, unless a more plausible model which can explain the slope temperature dependence is found. If the $EDAE_1$ is applicable, the $\varphi \approx s = 1$ value at low temperatures is not surprising and scarcely seems to merit elevation to universality.

6. Discussion of Response Models

Although there exist a plethora of theories which yield CPE-like response with one or more slopes (see [10, 11] and references therein), few of them predict slope temperature dependences and none predict such dependences from an *ab initio* many-body treatment. Thus, as in the present EDAE approach, arbitrary assumptions are generally made about such temperature dependences. Although these models are thus incomplete, when good agreement between EDAE predictions and measured frequency and temperature response is found, it is probable that there is a DTR present in the material–electrode system being investigated. Further, class-I and class-II responses together cover the majority of experimentally seen D- and C-system slope-temperature responses. For class-I response, it is often found that in the $\omega > \omega_0$ region the magnitude of the I_j slope increases with increasing temperature for D-systems and decreases for conducting ones for $\eta_1 > 0$, the usual $EDAE_1$ situation, consistent with the linear φ dependence of Table 1 when the difference between φ and actual slope exponents is recognized [9, 14].

Wang and Bates [18] have recently proposed a semi-microscopic hopping model for dielectric materials which involves charged-particle activation in a potential double well. It leads to exactly the DEDAE of (3) with $\mu_D = 0$. By somewhat arbitrarily assuming that $-\lambda_1$ (their "a") and λ_2 (their "b") are positive and by taking both quantities temperature independent, they arrive at class-II peaked relaxation response but do not extend their work to include other possibilities. With the alternate assumption that η_1 and η_2 are temperature independent, however, class-I response results. The WB work is discussed in detail elsewhere [27].

In an earlier work, Elliott [28] also considered hopping of charged particles (electrons) over a barrier between two sites. Unlike WB, however, he found a single class-I Y'_C frequency power-law exponent of approximately $[1 - kT(6/W_M)]$, where the binding energy W_M was approximated by the energy gap of the material. Although these results confirm that hopping can lead to class-I behavior, the world still awaits the availability of full microscopic theories for dielectric and conducting systems which lead at the macroscopic level to good approximations to DEDAE class I and II response, since only then will two-slope dispersion data be fully explicable without the need for any *ad hoc* assumptions.

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