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The response of systems with exponential distributions of activation energies for two classes of material temperature behavior

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Methods for calculating the small-signal ac frequency and temperature responses of thermally activated materials arising from the presence of a distribution of transition rates are discussed. The specific case of a double-exponential distribution of activation energies (DEDAE), of great importance as a data-analysis model, is discussed in detail for distributed dielectric and intrinsically conducting materials, and important differences in the proper analyses of these systems are particularly emphasized. For both dielectric and conducting distributed systems, two different and important types of temperature response are described and related to earlier work. Model calculations are presented to illustrate frequency and temperature response possibilities for such thermally activated, distributed systems. Various errors in earlier work are corrected, particularly the near-universal identification of theoretical slope parameters appearing in the analysis of exponentially distributed systems with actual measured slopes and power-law exponents. The quite different experimental temperature dependences of the power-law exponents of many dielectric and conductive materials agree qualitatively and often quantitatively with the predictions of the DEDAE response model. Finally, the behavior is briefly discussed of systems which can exhibit wide-range dispersive results simultaneously in both their conductive and dielectric responses.

1. Introduction and background

1.1. Dielectric and conducting systems

Recently Wang and Bates [1] have discussed non-Debye dielectric frequency response associated with an exponential distribution of activation energies (EDAE) [#1]. Here we discuss and compare the small-signal response of thermally activated dielectric and conducting systems with DAEs. The distinction between an ideal dielectric system, which can conduct only by displacement currents, and an ideal conducting system, where charges can percolate through the entire material, is particularly important in the Impedance Spectroscopy area. A list of abbreviations and definitions is included at the end of this work.

The above distinction between the different non-Debye responses of real systems has not always been clearly made in the analysis of experimental relaxation response. Proper system identification cannot be established just on the basis of the absence or presence of dc conduction in a single experiment. A leaky dielectric, one with a very small amount of dc conduction, is still primarily a dielectric system, albeit a non-ideal one, according to the present definition, because the broad response in the frequency domain, the signature of non-Debye behavior, arises from dipolar effects in the bulk dielectric material (See, however, the discussion in Section 4.). Similarly, a broad-response conducting system (such as

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

Na-β-Al_2O_3) which always involves mobile charges, may be measured with completely blocking electrodes so no dc can flow. Nevertheless, it remains a conducting system.

Debye frequency response of either a dielectric or conductive system involves the presence of only a single relaxation time in the frequency domain (a narrow loss peak). But the great majority of actual materials show non-Debye behavior involving a broad loss peak, response which can be described by means of a distribution of relaxation times (DRT) or, correspondingly, DAEs [2,3]. Although non-Debye behavior, where the relaxation slows as it progresses, has been more frequently associated with a dielectric system than with a conducting one, the description of broad-peak conducting-system response by means of a DRT or DAE has been discussed since at least 1956 [2–4], and it is common to describe the broad frequency response of conducting systems as characteristic of non-Debye behavior [5]. The transient response of a non-Debye dielectric system with a general double exponential DAE (DEDAE) was first calculated in 1963 [6], and the responses of both dielectric and conducting systems with EDAEs were calculated in 1985 [3] [#2]. Further, at about the same time an independent treatment of conducting-system response with a discrete DRT/DAE was presented [7].

We may think of a continuous DRT for a dielectric system as associated with the limit as $N \to \infty$ of N parallel branches, each made up of a non-conducting combination of a differential resistor and a differential capacitance (dissipative element and energy storage element, respectively) in series. Each such series combination defines a specific relaxation time. For the conducting system, the dual applies: N resistor–capacitor combinations in series, each made up of a resistor and capacitance in parallel and thus defining individual C-system relaxation times. But it is important to note that these structures are not unique for either finite or infinite N; thus other connections can lead to the same frequency response over the entire frequency range [8] [#3]. What is unique is that an ideal conducting system allows dc to pass and an ideal dielectric system does not.

When a DAE is present, it is most appropriate to derive an expression for the response of a D-system at the complex dielectric constant level ($\epsilon = \epsilon' - i\epsilon''$), and that of a C-system at the impedance level ($Z = Z' + iZ''$), 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. In addition, there are likely to be more than a few situations which exhibit both C- and D-system non-Debye behavior simultaneously (See Section 4). Then, the broad response of the dielectric part of the overall behavior and that of the conducting-system part may each be described by DRT/DAEs which will generally be quite different. We may expect that in thermally activated situations, the relative importance of these two effects will often vary strongly with temperature, with conductive-system response dominating at high temperatures and dielectric-system response dominant at sufficiently low temperatures. Thus, at intermediate temperatures both processes may contribute significantly to the overall response. Such combined C–D behavior will be discussed in subsequent work.

Particularly in the past, it has been common to assume that the complex conductance (the admittance) of a material system exhibiting dc conduction can be well represented by the combination of the response of the broad-band behavior of a pure dielectric and an entirely independent, frequency-independent dc conductive path, i.e., a leaky dielectric [9,10]. But the alternative, analysis in terms of a broad-band conductive system, where the dc path is an integral part of the non-Debye conductive response, may often be more appropriate. When a loss peak is present at the complex dielectric level or at the impedance level and C–D behavior is not present, the choice is clear, but such a peak is often absent within the available frequency range. Then, knowledge of the physical characteristics of the material measured can often help in the choice, as can nonlinear complex least squares (CNLS) fitting of

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[#2] The value 0.497 in table III should be replaced by 1.497, and the product sr in the numerator of eq. (B8) should be replaced by s.

[#3] The numerators of eqs. (5) and (7) should be considered to be the effective DAE or DRT for normalization purposes, as in the present work.

the data [11,12] to a combined C–D model.

1.2. Exponential distributions of activation energies

In the present work, we explore some important consequences of the distinction between conductive ($j=\mathrm{C}$) and dielectric ($j=\mathrm{D}$) system behavior, and, in addition, compare the predictions of a DEDAE for two different types of temperature response, both of great experimental importance. The two classes of EDAE temperature response are Class I, where the EDAE is itself an intrinsic temperature-independent property of the material and the shape of the frequency response following from it depends on temperature [3,8,13] [#4], and Class II, particularly explored by Wang and Bates [1], where the temperature dependences of the distribution and its frequency response are just the opposite.

An EDAE is itself particularly important because for a thermally activated system it is the only form of DAE which can lead to exact power-law frequency response over a finite frequency range [3,8,13]. The most common example of such response is that of the constant phase element (CPE) [14–18], which seems to appear in the vast majority of all small-signal ac frequency-response measurements of either D- or C-type.

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 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 or Z'' in the $j=\mathrm{C}$ case), but regions involving n_1 and n_2 exponents ($n_1 \neq n_2$) of the same sign, often termed anomalous low frequency dispersion, are not uncommon [9,19].

All these responses can be expressed in terms of a finite-extent discrete or continuous distribution of relaxation times (DRT) or distribution of transition rates (DTR), unlike simple Debye response which involves only a single transition rate. Many different processes may lead to a DTR, e.g. a distribution of activation energies, a distribution of trap depths or waiting times, or a distribution of hopping distances [3,8,13,20]. These possibilities may be related to fractal structures and fractal time processes [21]. 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. Further, it should be clear that frequency-response models based on some form of a DTR, such as all those discussed herein, can apply not only for bulk response, but they can also be used to describe electrode contributions to the overall response, especially when the electrode impedance shows evidence of fractal-like behavior.

The near universality of CPE response has been particularly emphasized by Jonscher [9]. Incidentally, it has become common [e.g., 1,21] to write such power-law response in terms of equations such as $\chi'(\omega)\sim\chi''(\omega)\sim\omega^{-n}$, where $\chi=\chi'-\mathrm{i}\chi''$ is the dielectric susceptibility and $0\leqslant n\leqslant 1$, but this usage is dimensionally inconsistent unless $\sim$ is replaced by $\propto$, the proportionality symbol. Probably the first appearance of a DEDAE was in 1963 when it was introduced in the calculation of the transient response of a Class-I D-system [6]. In order for the DEDAE to lead to the two slopes 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 [22]. Detailed frequency response for the single-exponential DAE (EDAE$_1$) [3] and the more general DEDAE [8,13,23] were presented later, and it was found that DEDAE response could fit very well those of all of the conventional empirical response functions [17,18], including that of Havriliak and Negami [24] and stretched exponential response. Thus since the DEDAE can fit all data previously fit by these functions, it is an important fitting model, and further discussion of its frequency and temperature dependence possibilities is worthwhile.

2. Thermal activation and the DEDAE

2.1. Thermally activated response

Most distributed (non-Debye) responses are thermally activated. Although both energy storage and

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[#4] In eq. (17) the $\exp(-N_{i1}E)$ term should be replaced by $\exp(-\eta_{i1}E)$, and in eq. (24) the ± sign should be replaced by an equality sign.

energy dissipation processes may be separately thermally activated [3], the conventional approach for dielectrics is to consider only the activation of the overall relaxation time, τ, without attention to which of the above quantities is thermally activated. For C-systems, this distinction is particularly important. Let us therefore assume that the dissipation process (typically involving differential resistance for either a D- or C-system) is activated as $\exp(\alpha E/kT)$, and the energy storage process (typically involving differential capacitance) is activated as $\exp(\beta E/kT)$, where α and β are temperature-independent constants. Then the relaxation time for $j=$ D or C can be written as [3]

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

where $\gamma\equiv\alpha+\beta$; τ_a is a characteristic property of the material; E is an activation energy; k is Boltzmann's constant; and T is the absolute temperature. 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 [22]. Then the corresponding limiting Es 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 power-law exponents, it is useful to define a more or less central τ, τ_0, where $\tau_0\equiv\tau_a\exp(\gamma E_0/kT)$ and $E_L\leqslant E_0\leqslant E_H$. Finally, the normalized quantity $\mathscr{E}\equiv E/kT$ will often be used.

Since negative activation energies are meaningless, the smallest physically realizable value of E is zero; then $\tau_L=\tau_a$. Further, since $\tau_H<\infty$ [22], it is unphysical to consider the range of E to be $-\infty\leqslant E\leqslant\infty$ as Wang and Bates did [1]. The quantity τ_a may be expressed in terms of the entropy, S, of the thermally activated process; then E is essentially the corresponding enthalpy. Although negative entropy values have been found in some experiments (see refs. in [6]), the minimum value of the entropy for a physically realizable system cannot reach $-\infty$, the value necessary to make τ_a zero.

2.2. The DEDAE for dielectric and conductive systems

By using the subscript j, taken equal to C or D, we can express in a common form the general DEDAE for either type of system. Since there are two exponential- response regions for the general DEDAE, we express it in terms of a part for the region $\mathscr{E}_L\leqslant\mathscr{E}\leqslant\mathscr{E}_0$ and a second matching part for $\mathscr{E}_0\leqslant\mathscr{E}\leqslant\mathscr{E}_H$. If we now denote the DEDAE by $F_j(\mathscr{E})$, it follows from earlier work [3,4,6,8,13,23] that $F_j(\mathscr{E})=0$ for $\mathscr{E}<\mathscr{E}_L$ and for $\mathscr{E}>\mathscr{E}_H$ and, otherwise,

$$F_j(\mathscr{E}) = \begin{cases} N\exp[(\mu_j-\lambda_1)\mathscr{E}] & \mathscr{E}_L\leqslant\mathscr{E}\leqslant\mathscr{E}_0 , \\ N\exp[(\lambda_2-\lambda_1)\mathscr{E}_0+(\mu_j-\lambda_2)\mathscr{E}] & \mathscr{E}_0\leqslant\mathscr{E}\leqslant\mathscr{E}_H , \end{cases} \tag{2}$$

where the parameters λ_k and η_k, which set the strength of the exponential response, are connected by

$$\lambda_k=kT\eta_k , \tag{3}$$

with $k=1$, 2, and N is a normalization factor. By conservation of probability, we may write $F(\mathscr{E})\,d\mathscr{E}=F(E)\,dE$, and we shall use either $F(E)$ or $F(\mathscr{E})$ as appropriate. An equation equivalent to (2) for the $j=$ D dielectric situation with $\mu_D=\beta=0$, was later derived by Wang and Bates and will be discussed subsequently.

Here λ_k and η_k are parameters which help determine the shape of the distribution; they may or may not be temperature dependent, as discussed in detail in the next section. It is also convenient to define the logarithmic energy variables

$$x\equiv\gamma(\mathscr{E}-\mathscr{E}_0) , \tag{4}$$

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

$$x_H\equiv\gamma(\mathscr{E}_H-\mathscr{E}_0) , \tag{6}$$

and the following important slope-related quantities,

$$\phi_k\equiv(\mu_j-\lambda_k)\equiv(\mu_j-kT\eta_k) , \tag{7}$$

where $-\infty<\phi_k<\infty$. We omit the j subscript from ϕ since its value will be clear from the context. Since the range of ϕ is not limited to 0 to 1, it is not an ordinary frequency power-law exponent [3,4], but it is closely related to such an exponent, as also discussed later.

Note particularly that with the usual choices $\mu_D = \beta = 0$ and $\mu_C = \alpha = 1$, there are important differences between the DEDAEs of D-systems and C-systems. They arise because the activation of energy storage and dissipative processes must be taken into account separately from that of τ in considering D and C response and in determining the appropriate $F(\mathscr{E})$ for these systems. When only dissipation is activated, the usual case, only the resulting activation of τ need be considered in determining a DRT or a corresponding DAE for D-systems. But the activated dissipation plays a separate role for C-systems and leads to the appearance of $\mu_C = \alpha$ in the above results.

2.3. Class I and class II temperature dependences

When the DEDAE was first introduced [6], 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 taken 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 (the EDAE$_1$) did not initially specify the temperature dependence of η [3], it was eventually taken temperature independent, thereby inducing temperature dependence in ϕ as in eq. (7) and figs. 1 and 2, and this choice has been generally followed in subsequent work of the first author in this area [13,23]. EDAE$_1$ response is of particular interest when $\eta \geqslant 0$. For $\eta > 0$ one deals with an exponentially decreasing distribution, frequently seen experimentally in semiconductors ($j = C$) as an exponential band tail [25].

Recent work of Kliem and Arlt [26] is very similar to earlier analyses of DEDAE time and frequency response for D-systems, but it does not reference any earlier work in the EDAE field, and it 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 depends on temperature.

Another choice, which leads to quite different temperature dependence of $F_j(E)$ and of $\epsilon(\omega)$ or $Z(\omega)$, is to set $\eta E = \lambda(E/kT)$ and take $\lambda \equiv kT\eta$ temperature independent. Such a choice has recently been discussed by Wang and Bates [1] for D-systems and leads to Class-II behavior. It yields a temperature dependent $F(E)$ and corresponding $\epsilon(\omega)$ response whose shape is independent of temperature. Such behavior, where a master frequency-response curve can be constructed by shifting curves for different temperatures along the frequency axis (and y-axis also if necessary) until they superimpose, is also consistent with the well-known time-temperature superposition law [27], and has been illustrated for a variety of materials by Jonscher [9]. 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.

In order to clarify theoretical predictions, the results of several model calculations for different temperatures will be presented. To maintain some continuity with the work of Wang and Bates, we start by choosing the same numerical values of ϕ_k at $T = 200$ K as those used by Wang and Bates (appropriate for any temperature for Class II), namely $\phi_1 = 0.4$ (the quantity a in Wang and Bates) and $\phi_2 = -0.66$ ($-b$ in Wang and Bates). We shall use these values for both D- and C-systems and consider response at $T = 100$, 200 and 400 K.

Fig. 1 shows typical relaxation DEDAEs, expressed as normalized $F(E)$s, for a Class-I dielectric system. Their slopes are defined as $S \equiv \mathrm{d}[\ln\{F(E)\}]/\mathrm{d}E$, and the corresponding η_k values, consistent with the above ϕ_k choices, are shown in table 1, along with slope and η_k relationships in the top part of table 2. Note that the temperature-dependent values of η_k shown in table 1 apply for Class II. Fig. 2 shows the corresponding DEDAEs for a conductive system, peaked only at $E = E_L$. For Class-II behavior, the $T = 200$ K DEDAEs of the figures apply at all temperatures.

Although it is reasonable to take the DEDAE E_L, E_0, and E_H values temperature-independent for either response class, the dimensionless cutoff parameters x_L and x_H are then temperature dependent, and their values follow from $x_L = 0.14/kT$ and $x_H = 0.24/kT$ for the DEDAEs of figs. 1 and 2. The arbitrary values

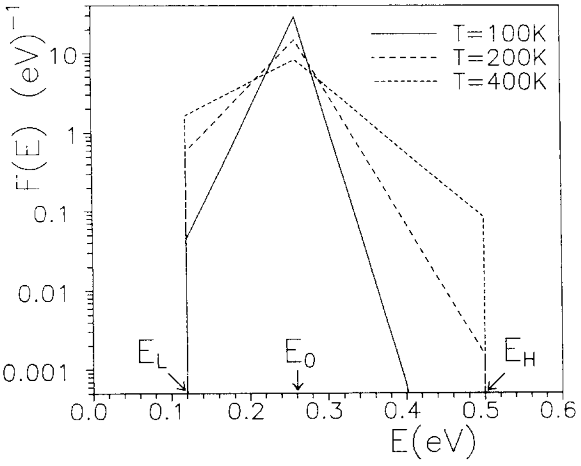

Fig. 1. Double-exponential distributions of activation energies (DEDAE), for the three temperatures listed, for Class-I dielectric situations. For Class-II dielectric-system behavior, the curve for $T=200$ K is applicable for all temperatures.

Table 1
Values of η_1 and η_2 in $(\mathrm{eV})^{-1}$ for Class-II response with $\phi_1=0.4$ and $\phi_2=-0.66$ at $T=200$ K for dielectric and conductive systems.

T(K)	Dielectric		Conductive	
	η_1	η_2	η_1	η_2
100	−46.42	75.59	69.63	192.63
200	−23.21	38.30	34.81	96.32
400	−11.61	19.15	17.41	48.16

0.14 and 0.24 eV have been used for illustration in figs. 1 and 2; in practice they can be estimated using CNLS fitting of sufficiently wide-range frequency response data. The abrupt cut-offs shown in the figures are appropriate for discrete distributions since they reflect the finite values of the longest and shortest relaxation times of the system. For continuous distributions, the actual transitions might be somewhat smoother and less abrupt, but this would nevertheless lead to no appreciable effect on the frequency or transient response.

2.4. 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 [3]. Let $U_j(\omega)$ be either the part of the impedance associated with relaxation-dispersion for an intrinsically conducting system ($j=\mathrm{C}$), or the part of the complex dielectric constant associated with pure dielectric relaxation ($j=\mathrm{D}$), and define

$$I_j(\omega)\equiv[(U_j(\omega)-U_{j\infty})/(U_{j0}-U_{j\infty})]\,, \tag{8}$$

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 $j=\mathrm{D}$, for example, $U_{\mathrm{D}_0}\equiv\epsilon_0$ and $U_{\mathrm{D}_\infty}\equiv\epsilon_\infty$.

The general expression for $I_j(\omega)$ when a DAE, $F_j(E)$, is present may be written [3,13,23] as

$$I_j(\omega/\omega_0)=\int_{-\infty}^{+\infty}\frac{F_j(E)\,\mathrm{d}E}{1+\mathrm{i}(\omega/\omega_0)(\tau/\tau_0)}\,, \tag{9}$$

where $\omega_0\tau_0\equiv1$ and τ is given by eq. (1). This equation is consistent with the discussion given above of discrete and continuous distributions of relaxation times for $j=\mathrm{D}$ and C. We see that $F_j(E)$, which may be a discrete or continuous function, specifies the weighting of the $\tau(E)$ relaxation time involved in the response. When ω is taken zero, eq. (9) reduces to just the normalization condition for $F(E)$. Now transforming from E to $\mathscr{E}$, using eqs. (1) and (2), and evaluating N, one may write the normalized frequency-response as [23]

$$I_j(\omega/\omega_0)\equiv J_j(\omega/\omega_0)/J_j(0)\,, \tag{10}$$

where

$$J_j(\omega/\omega_0)\equiv\int_{-x_\mathrm{L}}^{0}\frac{\exp(\phi_1x)\,\mathrm{d}x}{1+\mathrm{i}(\omega/\omega_0)\exp(x)}+\int_{0}^{x_\mathrm{H}}\frac{\exp(\phi_2x)\,\mathrm{d}x}{1+\mathrm{i}(\omega/\omega_0)\exp(x)}\,, \tag{11}$$

and

$$J_j(0)=\phi_1^{-1}[1-\exp(-\phi_1x_\mathrm{L})]+\phi_2^{-1}[\exp(\phi_2x_\mathrm{H})-1]\,, \tag{12}$$

for ϕ_1 and ϕ_2 both nonzero. When they are both zero, $J_j(0)=x_\mathrm{L}+x_\mathrm{H}=\gamma(\mathscr{E}_\mathrm{H}-\mathscr{E}_\mathrm{L})$.

For numerical work it is straightforward to evaluate the integrals of eq. (11) by numerical quadrature, although for certain integral and fractional values of ϕ simple closed forms are available (see

Table 2
Exact slopes, S_1 and S_2, for the DEDAE and approximate slope relations for the corresponding relaxation-situation frequency response. 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	Class II	Illustrative values (at $T=200$ K)
quantity	region		η_1, η_2 and EDAE temp. independent	λ_1, λ_2 and $I_j(\omega/\omega_0)$ temp. independent	
DEDAE	$E_L \leqslant E \leqslant E_0$	$-\eta_1$	$\lambda_1/kT=-\eta_1$	λ_1/kT	23.209 (eV)$^{-1}$
	$E_0 \leqslant E \leqslant E_H$	$-\eta_2$	$\lambda_1/kT=-\eta_2$	$-\lambda_2/kT$	-38.295 (eV)$^{-1}$
I''_j	$\omega<\omega_0$	$-\phi_2$	$-\mu_j+kT\eta_2$	$-\mu_j+\lambda_2$	0.66
	$\omega>\omega_0$	$-\phi_1$	$-\mu_j+kT\eta_1$	$-\mu_j+\lambda_1$	-0.4
Y''_D	$\omega<\omega_0$	$1-\phi_2$	$1+kT\eta_2$	$1+\lambda_2$	$(1.66)\rightarrow 1$
	$\omega>\omega_0$	$1-\phi_1$	$1+kT\eta_1$	$1+\lambda_1$	0.6
Y''_C	$\omega<\omega_0$	$-\phi_2$	$-1+kT\eta_2$	$-1+\lambda_2$	0.66
	$\omega>\omega_0$	ϕ_1	$1-kT\eta_1$	$1-\lambda_1$	0.4

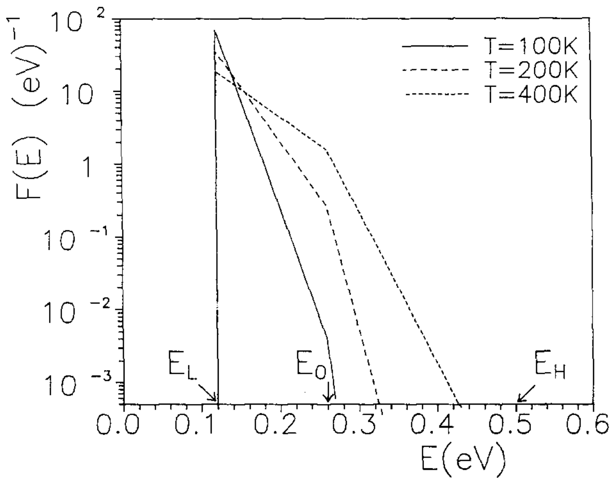

Fig. 2. Double-exponential distributions of activation energies, for three temperatures, for Class-I conductive-system situations. For Class-II conductive-system behavior, the curve for $T=200$ K is applicable for all temperatures.

Appendix B of [3]). Incidentally, the D-system transient response associated with the DEDAE has been expressed in closed form and can lead to appreciable regions of power-law time behavior [6]. Apparently unaware of this work, Kliem and Arlt [26] recently gave the transient response only in quadrature form and evaluated it numerically.

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 [11,12] and is available at nominal, nonprofit cost from the first author's Department.

Eqs. (10)–(12) define the general frequency response for the DEDAE. When the data show only a single power-law response region, one need only set $\phi \equiv \phi_1$, $\phi_2=0$, and $x_H=0$ in eq. (11) to obtain the single-slope EDAE$_1$. It leads to asymmetrical peaked loss in the frequency domain but to response generally different from that of the DEDAE.

How then can one tell the frequency response of the DEDAE and the EDAE$_1$ apart since they both show peaks? The best way to obtain quantitative results is to fit the data by CNLS to each model. But a log–log graph of $I''_j(\omega)$ versus ω will usually allow such discrimination. Because cutoffs 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. Specifics of EDAE response

3.1. Illustrative examples of frequency-response possibilities

Fig. 3 shows the complex-plane responses of $I(\omega)$ which follow from the DEDAEs of figs. 1 and 2. In fig. 3 the low frequency limit is that the right and the high frequency one is at the left. The solid-line curves involve the cutoffs of figs. 1 and 2, and the dashed ones were calculated using "infinite range" (IR) values of x_L and x_H. To obtain such infinite-range response, it is merely 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, values greater than 10 or so are sufficient to meet this criterion.

In fig. 3 the curves involving circles are for C-system response, and the others apply for $j=\mathrm{D}$. In addition, the $T=200$ K responses apply for either D or C systems. For Class-I behavior, the temperature response is as shown, but for Class-II, the curves marked 200 K apply for all temperatures.

Fig. 4 shows the corresponding $\log[I_j''(\omega)/I_0'']$ versus $\log[\omega/\omega_0]$ response curves for D-system Class-I behavior. As before, the $T=200$ K curves also apply for C-systems, and for Class II only the curves identified by $T=200$ K are present and apply for all temperatures. 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 the determining cutoff parameter is $x_H \simeq 7$. Although no C-system $T=400$ K curve is shown here, it is broader than a Debye curve but has the same limiting slope values.

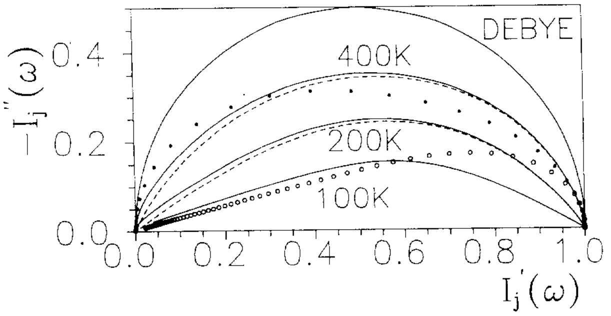

Fig. 3. Complex-plane plot of DEDAE normalized frequency response for three temperatures. $I_j(\omega)$ is a normalized impedance for conductive systems ($j=\mathrm{C}$) and a normalized complex dielectric constant for dielectric systems ($j=\mathrm{D}$). The dashed curves were calculated without the cutoffs shown in fig. 1. Here, $j=\mathrm{D}$ or C for the $T=200$ K curve, and $j=\mathrm{D}$ for the others except that the solid (400 K) and open (100 K) circles show corresponding $j=\mathrm{C}$ response.

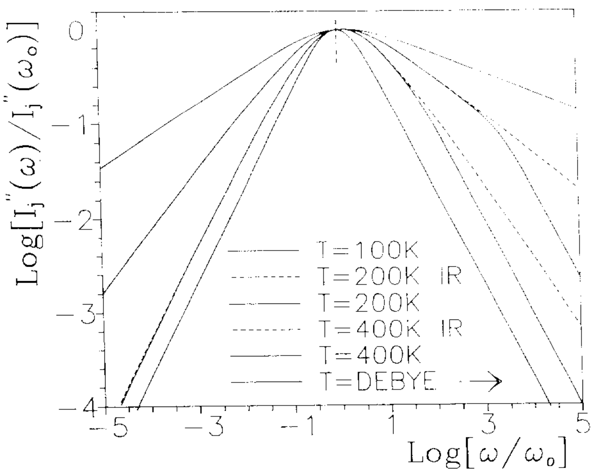

Fig. 4. Log-log plot of the normalized response quantity $[I_j''(\omega)/I_j''(\omega_0)]$ versus (ω/ω_0) for the three temperatures of fig. 1 ($j=\mathrm{D}$), for the identical $j=\mathrm{C}$ 200 K curve, and for single-time-constant Debye response. Here IR indicates that the effective range of the DEDAE is not cut off. The $T=100$ K curve is the one at the top here.

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. 4. Expressions for the approximate slopes of $I_j''(\omega)$ in the central regions of such a plot are presented in the middle part of table 2. In such constant-slope regions, one may write $I_j'' \propto \omega^{\pm n_{\mathrm{Im}}}$, and s is just $+n_{\mathrm{Im}}$ or $-n_{\mathrm{I}}$ with $0 \leqslant n_{\mathrm{Im}} \leqslant 1$. If the full response is well approximated by the CPE, then $I_j' \propto \omega^{\pm n_{\mathrm{Im}}}$ as well, but for added generality let us take $I_j' \propto \omega^{\pm n_{\mathrm{Re}}}$, where $0 \leqslant n_{\mathrm{Re}} \leqslant 2$.

The single-time-constant Debye curves of figs. 3 and 4 apply when $E_H \to E_L$, and the limiting left and right slope values of the Debye curve in fig. 4 are $s_l = n_{\mathrm{Il}} = +1$ and $s_r = n_{\mathrm{Ir}} = -1$. These same values are found for DEDAE response at frequencies beyond cutoff where only the lowest and highest relaxation times operative in the system dominate the response [3,8,13,22]. But in regions nearer ω_0, $I_j''(\omega/\omega_0)$ exhibits other slopes whose values are determined by those of ϕ_k, as presented in table 2. Table 3 shows actual j=D and j=C values of λ_k and ϕ_k for the Class-I responses presented in figs. 3 and 4. Incidentally, the more complicated temperature dependences of a ϕ arising from linearly related entropy and enthalpy distributions and/or from a glass-like transition have been considered [3,6] but are not incorporated in the present results.

It is worth emphasizing that only the differences $E_0 - E_L$ and $E_H - E_0$ affect the results plotted in figs. 3 and 4. 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_∞.

The T=100 K C-system DEDAE of fig. 2 would reduce to an EDAE$_1$ if its right slope approached $-\infty$. Since its magnitude is quite large here, its corresponding frequency response should be close to that of an EDAE$_1$, and the T=100 K curve of fig. 3 is similar to EDAE$_1$ response [3]. To test the matter, the actual DEDAE frequency-response data were fitted by CNLS to an EDAE$_1$ model. The standard deviation of the fit, obtained with optimized unity weighting [11], was about 1.5×10^{-3} and the EDAE$_1$ ϕ estimate was about (0.1722 ± 0.0002), close to the input DEDAE value of $\phi_2 = 0.17$. Thus, for this situation extremely accurate data would be required to allow adequate discrimination between DEDAE and EDAE$_1$ fitting models.

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 cutoff effects in the frequency response may lead to a finite region of no well-defined constant slope (the actual case for the right-hand region of the T=400 K curve of fig. 4) or to one where $n_{\rm Re}$ and $n_{\rm Im}$ are not entirely equal even for $\omega > \omega_O$ [3,13]. Generally, cutoff effects are seen more often for C-system than for D-system response.

The second reason is even more important. The second and third parts of table 2 are appropriate for IR conditions. They indicate that the I_j'' slopes are approximately given by $-\phi_2$ and $-\phi_1$, 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 $|\phi|$ increases beyond 1, DEDAE response approaches simple Debye behavior. But the actual slopes must satisfy $|s_{\rm Im}| \leqslant 1$ and $|s_{\rm Re}| \leqslant 2$ [3,13,23]. Thus, the predicted approximate slope of 1.66 given in table 2 is actually limited to unity. Even when cutoff effects are negligible, the relations $n_{\rm Il} \simeq |\phi_2|$ and $n_{\rm Ir} \simeq |\phi_1|$ certainly cannot hold when $|\phi| > 1$ or when $\phi < 0$. Fig. 5 in ref. [23] illustrates how $n_{\rm Im}$ and $n_{\rm Re}$ approach their limiting values as ϕ exceeds 1 or 2.

The above restrictions were apparently not appreciated by Kliem and Arlt [26]. 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 [26], the present ϕ_k. Although Wang and Bates used actual temperature-independent $|\phi_k|$ values less than unity and so did not directly face the problem of the difference in the ranges of ϕ_k and s, they nevertheless also equated power-law exponents to theoretical slope parameters. It is of interest to note that it is the slope of the high-E right side of the DEDAE which determines

Table 3
Values of λ_1, λ_2, ϕ_1, and ϕ_2 for Class-I response with the same ϕ_1, and ϕ_2 values at T=200 K for dielectric and conductive systems.

T(K)	Dielectric				Conductive			
	λ_1	λ_2	ϕ_1	ϕ_2	λ_1	λ_2	ϕ_1	ϕ_2
100	−0.2	0.33	0.2	−0.33	0.3	0.83	0.7	0.17
200	−0.4	0.66	0.4	−0.66	0.6	1.66	0.4	−0.66
400	−0.8	1.32	0.8	−1.32	1.2	3.32	−0.2	−2.32

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 curves of fig. 4 are quite similar to some of those calculated by Kliem and Arlt and compared by them (but not fitted) to actual experimental data on polyethyl-methacrylate. The magnitudes of the experimental slopes *increase* with increasing temperature, consistent with earlier predictions for a Class-I D-system (see tables 2 and 3). Note, however, that the slopes of a Class-I C-system at the I_C level are of the approximate form $-1+kT\eta_k$. Thus for a positive η_k, the associated slope will be near -1 at low temperatures and will *decrease* in magnitude as the temperature increases, with ϕ_C reaching zero at $T=T_{0k}\equiv 1/k\eta_k$. For the present Class-I conductive case, it follows from the temperature-independent values of η_k in table 1 (those on the $T=200$ K line) that T_{0k} is about 333 K and 120 K for $k=1$ and 2, respectively. As the $j=\mathrm{C}$ ϕ_k values in table 3 show, the slope magnitudes initially decrease with increasing temperature, but as the $T=400$ K curve of fig. 3 demonstrates, as the ϕ_k go negative, Debye response is approached.

Finally, note that the peak loss of $I(\omega/\omega_0)$ curves similar to those of fig. 4 will only occur at $\omega/\omega_0\equiv\omega\tau_0=1$ when the condition $\phi_1=-\phi_2$ holds, yielding a symmetric curve (termed the EDAE$_2$ in earlier work [13,23]). Otherwise, the peak occurs to the left or right of the $\omega=\omega_0$ point, depending on whether $|\phi_1|>|\phi_2|$ 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 values of τ_0 at a given temperature from $1/\omega_p$ in the usual way, 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 Kliem and Arlt [26] 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 $1/\tau_0$.

3.2. Class-II frequency response

In the Class-II situation recently considered for dielectric materials by Wang and Bates [1], the λ_k are temperature independent and the shapes of the corresponding frequency-response curves are temperature independent in the IR approximation used by Wang and Bates. Thus the $T=200$ K curves of figs. 3 and 4 apply at all temperatures. But as T increases indefinitely for the realistic finite-range situation, $F(\mathscr{E})$ approaches a flat-top box distribution shape and x_L and x_H approach zero, yielding a δ-function in the limit so that again only simple Debye behavior remains. Nevertheless, if x_L and x_H are sufficiently large over the entire temperature range of measurement, frequency-response curves for different temperatures can be shifted in frequency, to account for the temperature dependence of τ, so that they all fall on a single master curve.

Although many experimental situations of this type are discussed by Jonscher [9], they need not necessarily be associated with a Class-II EDAE. Instead, for a thermally activated situation, it is sufficient that the pre-exponential factor in τ have a power-law (Pareto) distribution [6,8,13]. Unlike Class-I EDAE response, where the temperature dependences of the slopes are an important signal that an exponential DTR is present, there is no such indicator available which allows one to readily distinguish between Class-II EDAE response and a power-law distribution of the pre-exponential term.

3.3. Fitting of other response models

Fig. 3 curves are similar to ones presented by Kliem and Arlt [26], 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, Kliem and Arlt identify the shape of these curves as being of Cole–Davidson (CD) character. But it has long been known that the DEDAE without cutoffs can excellently fit Cole–Cole, CD, and other empirical response functions [3,13,23], and its response is in general very similar to that produced by the empirical Havriliak–Negami (HN) expression [24]

$$I(\omega/\omega_0)=\{1+[\mathrm{i}(\omega/\omega_0)(\tau/\tau_0)]^{1-\alpha}\}^{-\beta}, \qquad (13)$$

where the slope parameters satisfy $0\leqslant\alpha\leqslant 1$ and $0\leqslant\beta\leqslant 1$. 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 Kliem and Arlt most appropriate here?

As a test of model appropriateness, the $T=200$ K DEDAE $I(\omega/\omega_0)$ complex data of figs. 3 and 4 were fitted by LEVM to the CD and the HN expressions, using optimized function-proportional weighting [11]. The DEDAE data used were calculated for IR since this choice is appropriate for these empirical functions, which involve no cutoffs. 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 $s_l = n_{Il} = 0.656$ and $s_r = -n_{Ir} = -0.402$, 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.

Wang and Bates [1] also compared HN DAE and DEDAE shapes, and corresponding frequency responses, for a choice of $T=500$ K and found agreement which appeared very close when plotted in log form. Their DEDAE comparison has been repeated by means of nonlinear least squares fitting of IR DEDAE data extending from $E=0.01$ to 1.89 eV, with weighting as above. First, following Wang and Bates, the HN α and β parameters were fixed at values which yielded the same asymptotic slopes as those of the DEDAE, and E_0 was left free to vary. Parameter values and the E_0 estimate, E'_0, are shown in fig. 5 and are consistent with the corresponding ones of Wang and Bates. Fig. 5 is a plot of the relative residuals of the fit, joined by a smooth curve. The fit results show that at $E=E_0$ there is about a 27% relative difference between the DEDAE and the HN fit and asymptotic relative differences of about 1% at low E and 5% at high E. Alternatively, when α, β, and E_0 were all free, a slightly better fit was obtained which yielded the α, β, and E_0 estimates 0.348, 0.617 and 1.197 eV, respectively. Clearly, there are appreciable differences between the DEDAE and the HN DAE, especially near their peaks.

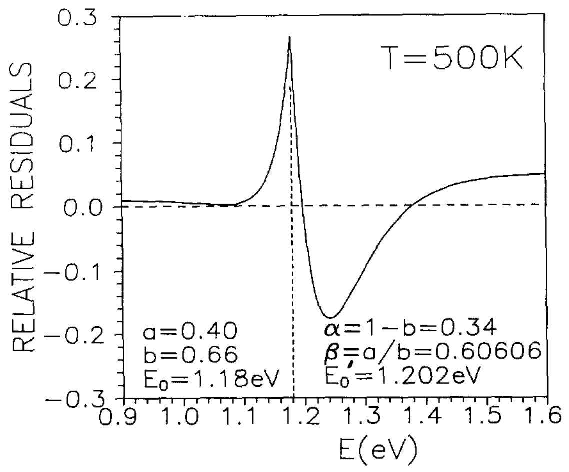

Fig. 5. Relative residuals versus E obtained from a nonlinear least squares fit of DEDAE data with negligible cutoffs to the Havriliak–Negami empirical response function for parameter choices used by Wang and Bates [1].

3.4. Comparison of dielectric and conductive system admittance responses

Not only is it of interest to compare the slope predictions of table 2 with actual slopes of I'_j and I''_j curves in the IR case, where cutoff effects are outside the range of measurement, but it is also instructive to compare full curve shapes for normalized admittances. We shall do so for the $T=200$ K data of figs. 3 and 4. For simplicity, we shall set $U_{j\infty}=0$ and $Y_D(0) \equiv G_{D0} = 0$ as well; some of the effects of these quantities, when they are not negligible, have been discussed elsewhere [4]. Then, it is appropriate to define for $j=\mathrm{C}$ the normalized admittance (complex conductivity) $Y_{NC} \equiv 1/I_C$, and for $j=\mathrm{D}$ the normalized admittance $Y_{ND} \equiv (i\omega/\omega_0) I_D$.

Because of our choice of the same ϕ_k values at $T=200$ K for both the $j=\mathrm{D}$ and the $j=\mathrm{C}$ situations, $I_j(\omega/\omega_0)$ curves will be the same for both $j=\mathrm{D}$ and C. But this will not be the case for the two $Y_{Nj}(\omega/\omega_0)$ responses since they arise from different response levels. In fig. 6, the frequency dependences of the above three different complex quantities are plotted. The limiting slopes of both real and imaginary quantities are equal for $\omega > \omega_0$ (CPE response) and are generally consistent with the values given in

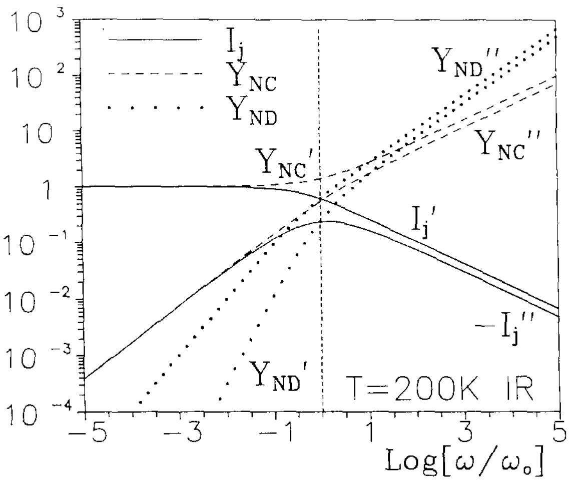

Fig. 6. DEDAE log–log frequency response of normalized response functions for the $T=200$ K DAE of fig. 1 without cutoffs. Here, the choice $I_C(\omega/\omega_0)=I_D(\omega/\omega_0)$ has been made and the corresponding normalized admittance responses are illustrated for $j=\mathrm{D}$ and $j=\mathrm{C}$.

the bottom part of table 2. 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 the $\omega>\omega_0$ region, notice in particular the difference in the slopes of the Y_{NC} components from those of Y_{ND}. Incidentally, $Y_C(\omega)$ response associated with a DTR or other processes has recently been discussed in detail [4,20], and $Y_C'(\omega)$ slopes of approximately Class-I form, $1-kT\eta$ with $\eta\geqslant 0$, have recently been reported by Lee et al. [28] [#5]. Some discussion of these results is presented elsewhere [29].

4. Discussion of some response models

Although there exist a great many theories which yield CPE-like response with one or more slopes (see [8,13,20], 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 and earlier EDAE approaches, rather 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 usually 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. Further, when one transforms experimental power-law exponents to corresponding ϕ values, the linear dependences of ϕ on temperature shown in table 2 are frequently found over an appreciable temperature range [13,28].

Wang and Bates [1] have recently proposed a semi-microscopic hopping model for polar materials which involves charged-particle activation in a potential double well. By restricting the motion of each ion present to the double potential well with which it is associated, Wang and Bates actually treat a non-conducting D-system rather than a C-system, although at sufficiently high temperatures one would expect that a fraction of the ions could percolate through the entire material, yielding some C-system response as well (C–D response). A good discussion of such C–D response involving ion pairs and ionic conductivity has been given by Johari and Pathmanathan [30].

The work of Wang and Bates leads to exactly the DEDAE of eq. (3) with $\mu_D=0$ and thus yields a loss peak in $\epsilon''(\omega)$, just as the relaxation of rotating permanent dipoles would do. Alternatively, if one applied their approach to ions in a C-system and did not assume that each ion was bound to a single double exponential well, one might obtain the $j=\mathrm{C}$ version of eq. (2), and the peak would then occur in $Z''(\omega)$, where such effects are commonly observed in ionic solids and liquids [3,8,23], not in $\epsilon''(\omega)$.

It is especially worth emphasizing that for a conductive system a peak in $Z''(\omega)$ versus ω does not lead to a peak in $\epsilon''(\omega)$. Also for a dielectric system, a peak in $\epsilon''(\omega)$ does not lead to one in $Z''(\omega)$. But the situation is more complicated for a C–D system. Then a peak can appear in either $Z''(\omega)$ or $\epsilon''(\omega)$,

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[#5] In this work, the authors associate power-law frequency response with stretched-exponential transient response, but this is only asymptotically true in the high-frequency region.

although none may be evident because of a limited available frequency range.

A simple example is provided by a resistance in parallel with a non-Debye $j=\mathrm{D}$ response function. Assume that at the dielectric constant level the latter alone yields a peak in $\epsilon''_{\mathrm{D}}(\omega)$, although none will appear in the corresponding $Z''_{\mathrm{D}}(\omega)$. But when a nonzero resistor is put in parallel with $Z_{\mathrm{D}}(\omega)$, the resulting overall impedance, $Z(\omega)$, will show a peak in $Z''(\omega)$ and the corresponding $\epsilon''(\omega)$ will not. Here the (frequency-independent) resistor may be taken to arise from an undispersed ohmic path between the electrodes and so is a limiting form of C-system behavior, and the combination of the two processes yields a (leaky-dielectric) type of C–D system response.

The other interesting limiting form of C–D response is that produced by a non-Debye C-system in parallel with a frequency-independent capacitance C_{g}, the geometric capacitance of the system, which is associated with ϵ_∞. In impedance spectroscopy experiments, the effect of C_{g} is often negligible in the available frequency range [18], but since it is always present in principle, one should strictly treat all C-system behavior as that of a C–D system.

The full expression at the impedance level for dispersive bulk C–D system response, which includes the above two limiting cases, may be written

$$\begin{aligned} Z(\omega) &= R_\infty + (R_0 - R_\infty) I_{\mathrm{C}} \\ &\quad \times \{1 + \mathrm{i}\omega\{[C_{\mathrm{g}} + (C_0 - C_{\mathrm{g}}) I_{\mathrm{D}}] \\ &\quad \times [R_\infty + (R_0 - R_\infty) I_{\mathrm{C}})]\}\}^{-1}, \end{aligned} \tag{14}$$

where $U_{\mathrm{C}0} \equiv R_0$ (the dc resistance) and $U_{\mathrm{C}\infty} \equiv R_\infty$. In actual situations, one usually needs to add an additional electrode impedance in series with the eq. (14) response, a contribution generally of most importance at low frequencies. These possibilities have all been incorporated in the LEVM fitting program and allow one to fit complex data to combined C–D response or to C- or D-system response separately. A closely related, but different approach to C–D data fitting has been presented earlier [30].

By somewhat arbitrarily assuming that $-\lambda_1$ (their "a") and λ_2 (their "b") are positive and by taking both quantities temperature independent, Wang and Bates arrive at Class-II peaked relaxation response but do not extend their work to include other possibilities, even though their own earlier work on Na β-alumina [31] is consistent with Class-I $\phi \simeq 1 - kT\eta$ electrode response with $\eta > 0$ (and temperature independent) over an appreciable temperature range. Instead of taking the λ_k temperature independent in order to obtain Class-II behavior, the alternate choice of taking the η_k temperature independent yields Class-I response instead.

In earlier work, Elliott [10,32] also considered hopping of charged particles (electrons) over a distributed barrier between two sites. Unlike Wang and Bates, however, he found a single Class-I Y'_{C} frequency power-law exponent of approximately $[1 - kT(6/W_{\mathrm{M}})]$, of exactly the form of the EDAE_1 result for ϕ, where the binding energy W_{M} was approximated by the energy gap of the material. This gives an explicit result for η, and others are also discussed for amorphous semiconductors [10,32]. 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 one- or two-slope dispersion data be explicable without the need for any ad hoc assumptions.

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ABBREVIATIONS AND DEFINITIONS

A. Acronyms

C	Conductive system
CD	Cole–Davidson response function
C–D	Conductive–dielectric system
CNLS	Complex nonlinear least squares
CPE	Constant phase element
D	Dielectric system
dc	Direct current
DAE	Distribution of activation energies
DEDAE	Double EDAE
DRT	Distribution of relaxation times
DTR	Distribution of transition rates
EDAE	Exponential DAE
HN	Havriliak–Negami response function

B. Subscripts

j	C or D
k	1 or 2
l	Left
H	Highest value
I	Imaginary
L	Lowest value
N	Indicates normalization
O	$A_L \le A_O \le A_H$; A arbitrary
r	Right
R	Real
0	Zero limit
∞	Infinite limit

C. Principal definitions

Class I	The EDAE is temperature independent; see section 2.3
Class II	The EDAE is temperature dependent; see section 2.3
E	Activation energy
$\mathcal{E}$	$E/\mathrm{k}T$
F	DEDAE distribution function: eq. (2)
I	Normalized frequency response function: eqs. (8) to (10)
J	Normalization factor: eqs. (11) and (12)
k	Boltzmann constant
n	Power law exponent
s	Log–log frequency response slope

S	EDAE slope
x	Logarithmic energy variable: eqs. (4) to (6)
Y	Admittance
Z	Impedance
α	Energy dissipation thermal activation parameter, or HN parameter
β	Energy storage thermal activation parameter, or HN parameter
γ	$\alpha+\beta$
ϵ	Complex dielectric constant
η	Parameter of $F(\mathscr{E})$: eq. (3); see also section 2.3
λ	Parameter of $F(\mathscr{E})$: eq. (3); see also section 2.3
μ	$\mu_C=\alpha$; $\mu_D=\beta$
τ	Relaxation time
ϕ	Slope-related parameter of $F(\mathscr{E})$: eqs. (7), (11), and (12)
χ	Dielectric susceptibility
ω	Angular frequency