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# SOME SMALL-SIGNAL RELAXATION RESPONSE MODELS AND THEIR LIMITING RESPONSES

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This paper is concerned with the small-signal time and frequency response of anomalous dispersion and distributed circuit elements in either conductive or dielectric systems. In the course of responding to recently published comments and criticisms of Dissado and Hill, a detailed discussion is presented of high and low frequency limiting response possibilities, with a special consideration of such response for a single broad dispersion region. For such a region the Dissado–Hill criticisms are shown to be either incorrect, inappropriate or irrelevant. The usefulness of distribution of relaxation and distribution of activation energy approaches is demonstrated and the response of a general exponential-distribution-of-activation-energies model is compared with that of a relaxation response function which was derived by Dissado and Hill in two different ways, with the two approaches based on different physical assumptions. It is concluded that the Dissado–Hill response function does not lead to the necessary low and high frequency limiting response for a single broad dispersion region, is essentially limited to dielectric materials and cannot describe intrinsically conductive ones which can pass DC, and is severely limited in its temperature dependence possibilities. By comparison, these limitations and restrictions do not apply to the distribution of activation energy model, one which has been shown capable of fitting a great variety of conductive and dielectric system experimental data for thermally activated situations.

## 1. Introduction

It is a truth universally acknowledged, that nothing is forever. Likewise, nothing is instantaneous. Between these two infinities lies the all. Much of this paper is about the small part of the all concerned with the form of the limiting long and short time small-signal electrical response of material systems which involve a single broad relaxation region. I wish to particularly acknowledge the work of Drs. Dissado and Hill [1] who have recently criticized some of my earlier statements [2] concerning the present subject. By doing so they afforded me the present opportunity to try to clarify certain aspects of the subject and to correct some misapprehensions.

It is worth mentioning that although my paper [2] was primarily concerned with the small-signal frequency response of *conducting* systems, a point explicitly recognized by Dissado and Hill at the beginning of their work, and was published in a journal devoted to ionically conducting materials, the Dissado–Hill (DH hereafter) discussion is nearly entirely devoted to dipoles in non-conducting dielectric materials, situations and theories. Much the largest part of their discussion, in fact, deals with the DH cluster model (CM) of dielectric response [3–5] (see section 6). A list of acronyms used herein is given at the end of section 6.

It is important to note at the outset of the present paper that while the limiting response matters discussed by DH and below are of theoretical importance, they often may be of little or no practical significance, particularly for conducting systems, the field of my earlier paper [2]. This difference arises because of measurement limitations inherent in real experimental situations. Such limitations are associated with practical limits on measurements at very high or low frequencies (or short or long times) and on residual noise and stability levels. For example, even when apparatus and techniques are available which allow measurements to be carried out at extremely low frequencies, there is usually no point in taking such data if the basic characteristics of the material change appreciably during the measurement time and/or if the intrinsic noise level of the experiment has already been reached at higher mea-

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surement frequencies. Thus, the common practice of the theorist of discussing $\omega = 0$ and $\omega = \infty$ response limits, or even asymptotic response, must be treated with caution when applied to practical situations. Here $\omega$ is the angular frequency.

Before getting into details, two disparities need to be mentioned. First, the DH criticisms deal directly with topics discussed in only one paragraph of my short paper. Second, although many of the points actually raised by DH are based on matters not discussed in my paer, I shall nevertheless respond to them as appropriate. An important distinction, not made clear by the DH discussion, is that I, and most other writers concerned with the small-signal ac response of conductive (and even dielectric) systems, deal only with *relaxation* processes, not with resonant ones. Thus, inertial properties and effects of electrons, ions or dipoles, which usually manifest themselves at very high frequencies, are excluded from the theoretical analysis, and it applies only for times longer than that required for the kinetic energy to reach equilibrium, the Smolochowski limit. Therefore, high-frequency limiting behavior is taken to be that of a relaxing system, an idealization certainly, but one of little or no importance in the usual frequency response range of impedance spectroscopy [6] (acronym: IS), say $10^{-4}$ to $10^{8}$ Hz, or possibly even higher.

Further, it should be emphasized that the theoretical analysis developed and discussed in my work [2,6–11] always deals with a single, usually broad, dispersion (relaxation) region. In many experimental situations, one finds two or more such regions, often considerably overlapping [6]. Clearly, in the overlap region of two dispersions the approach to asymptotic low frequency response of one such region is obscured by the overlap with the high frequency response of the other. Thus, one is precluded from accurately determining either of these limiting responses experimentally as long as such overlap is present. Complex nonlinear least squares (CNLS) fitting [12] can aid greatly in resolving, parameterizing and characterizing two such overlapping responses, but even it usually cannot help identify the forms of limiting responses in an overlap region unambiguously.

## 2. Dissado–Hill specific criticisms

DH have stated [1] that my work [2] is based on the following assumptions and that none of them is valid or can be validated. In addition, they have implied that they are not based on "sound physical phenomena."

(a) The limiting low and high frequency asymptotic behavior of immittance loss peaks involve $\omega^{+1}$ and $\omega^{-1}$ response, respectively.

(b) All immittance behavior can be represented physically in terms of parallel summations of Debye-like relaxation elements whose relaxation times are gives by series resistance/capacitance time constants, with the individual resistances and capacitances being the microscopical responses of the fundamental elements within the system.

They have also asserted that

(c) "The assumption of a parallel summation of relaxing elements, the distribution of relaxation times approach, is ... no more than a mathematical transformation of experimental data."

A statement related to assumption (a) is indeed mentioned in my paper, but assumption (b) or anything like it does not appear there and is not a basis for my work. Statement (c) will be discussed in section 5.1. Finally, DH state that I suggested (in another paper [9]) that their CM is "a zero temperature theory." In fact, I said "its range of applicability may be only for very low temperatures," a different statement. All the above matters and ones related to them will be discussed in some detail below.

## 3. Some simple response functions

In order to provide a concrete basis for later discussion and comparison, it is useful to consider first two simple immittance response functions, the Debye model and the empirical ZC model. With usual dimensionless normalization [6,8–10], one deals with the normalized immittance frequency response function $I(\omega)$, a quantity which approaches unity at sufficiently low frequencies and approaches zero at sufficiently high frequencies. It can represent either the response of a conductive system (one containing mobile charge carriers) at the impedance level or the response of an ideal dielectric system (no mobile

charges present) at the complex dielectric constant immittance level. For example, for a conducting system considered at the impedance level, $I_Z \equiv (Z-R_\infty)/(R_0-R_\infty)$, where $Z=Z'+iZ''$ is the impedance response and $R_0$ and $R_\infty$ are the low and high frequency limiting values of $Z'$ for a single dispersion region. With such normalization, the Debye model leads to

$$I(s)=[1+is]^{-1}, \tag{1}$$

where $s$ is a normalized frequency defined as $\omega\tau_D$. Here $\tau_D$ is the Debye relaxation time of the system, a quantity which may formally be written as a time constant, the product of a resistance $R$ and a capacitance $C$. Note that these elements, whose significance will be discussed later, are required to be in parallel for a conductive system and in series for a dielectric one. For a conducting system in which $R$ and $C$ describe bulk effects, $R$ would be the bulk resistance of the sample and $C$ its geometric capacitance.

Now let $I(s)=I'(s)+iI''(s)$, so that $I^*(s)=I'(s)-iI''(s)$. Then one readily finds from eq. (1) that for large $s$, $I''$ approaches $s^{-1}$ behavior, and for sufficiently small $s$ it approaches $s^{+1}$ behavior. In addition, eq. (1) leads to

$$S_I \equiv -dI''/dI' = 0.5(s-s^{-1}). \tag{2}$$

When the imaginary and real parts of eq. (1) are plotted in the usual $I^*$ complex plane for the full span of frequencies from 0 to $\infty$, a semicircle with its center on the real axis is obtained. Eq. (2) shows that as $s\to 0$ the slope $S_I$ approaches $-\infty$ and for $s\to\infty$ $S_I$ approaches $\infty$. In other words, the arc approaches the real axis vertically at both extremes. Such bulk (as opposed to surface) semicircles have been found for many conductive (see e.g. ref. [13]) and dielectric (see e.g. ref. [14]) liquid and solid systems. Thus Debye response does exist even for condensed matter. For such simple Debeye response, assumption (a) of section 2 is indeed well satisfied for all practical purposes (such as characterization of the material in the single relaxation region considered). It is thus both valid and validated by experiment for such situations. Since Debye frequency response implies simple exponential time decay in the linear response regime [15], such response can also be observed over a wide time span for relaxing systems.

Although single-time-constant Debye behavior is not very rare, especially for conductive systems, experiment very often yields a broader relaxation region, particularly for liquids, glasses, polycrystalline and amorphous materials. When such results are plotted in the complex plane, they often again yield a symmetrical arc of a circle, but one for which the circle center lies below the real axis. This is termed Cole–Cole response for dielectric situations [6,14], ZARC response for conductive ones [2,8], and has been denoted as ZC response when both situations are considered together [2,9]. The general $I(s)$ function for the ZC is

$$I(s)=[1+(is)^n]^{-1}, \tag{3}$$

where here $s=\omega\tau_C$ and $\tau_C$ is a characteristic relaxation time whose inverse is equal to the angular frequency at the peak of $-I''(s)$, $\omega_p$. The quantity $n$ satifies $0\leqslant n\leqslant 1$, and of course ZC response degenerates to Debye response when $n=1$. As $n$ decreases from unity, the dispersion region becomes broader and broader.

Eq. (3) shows that as $s\to 0$, $I'\to 1$ and $I''\to -s^n\sin(\theta)$, where $\theta\equiv n\pi/2$. On the other hand, when $s\to\infty$ $I(s)\to(is)^{-n}$, constant-phase-element (CPE) response [2,8–10,15–17], that where the phase angle is frequency independent. CPE behavior has sometimes been taken as a separate type of response, applying over all frequencies. As we shall see later, such response over the full frequency domain is physically unrealistic and cutoffs are needed at both frequency extremes. Nevertheless, CPE response over a limited frequency region is very common indeed and may often be observed to apply over many decades of frequency [6]. The $s\to\infty$ asymptotic ZC response, i.e. CPE response, yields $I'\to s^{-n}\cos(\theta)$ and $I''\to -s^{-n}\sin(\theta)$ behavior. The ratio of these two quantities is frequency independent: constant phase behavior. Finally, one can show that eq. (3) leads to $s\to 0$ and $s\to\infty$ $S_I$ limits of $-\tan(\theta)$ and $\tan(\theta)$, respectively. Unless $n=1$ the ZC arc thus does not approach the real axis vertically at either extreme of frequency. Since the ZC approximates CPE behavior for large $s$, it too is physically unrealistic in the limit of high frequencies.

## 4. Limiting response within the relaxation regime – general considerations

Response of a physical system will always be limited at the high frequency end by finite-speed-of-light considerations associated with the time required for subsystems to communicate and for a signal to travel from the input to the output [18]. Further, if the system involves the motion of microsocpic elements with mass, as those under consideration here do, inertial effects will limit the high frequency response even further.

There are other effects which can lead of cutoffs. For example, it has recently been shown [19] that fractal roughness properties of electrodes can lead to surface-associated CPE response behavior. But it is clear that such fractal structure is limited on the small-size end by the dimensions of electrode atoms and on the large-size end by the finite size of any possible experimental sample/electrode system. These cutoffs of fractal structure will be reflected in deviations of the frequency response from otherwise ideal CPE behavior over the entire frequency spectrum and they render the resulting response physically realizable. If the full unlimited fractal spatial behavior is expressed in terms of a distribution of relaxation times (DRT), always mathematically possible, the resulting DRT will be the Pareto distribution [8,11,20], a fractional power law in $\tau$, the relaxation time variable. Now necessary cutoffs of the fractal spatial distribution will lead to corresponding low $\tau$ and high $\tau$ cutoffs of the associated DRT. In turn, these cutoffs, beyond which the DRT function is zero, will lead to transitions from CPE to Debye behavior at the frequency extremes [8,9,17]. Such cutoffs will be discussed in more detail below, but it is worth emphasizing that whether or not one is considering fractal structure, relaxation behavior will be largely determined for sufficiently long times or low frequencies by the cutoff associated with finite sample size if no other cutoff occurs at higher frequencies. Some other cutoff processes have been mentioned by DH [5].

Although DH discuss very high frequency intertial effects in some detail [1,3–5], they seem to do so without explicitly introducing the masses or moments of inertia of the relaxing elements of their system. But this is not important in the present discussion for the following reason. Insofar as possible, it is desirable to discuss my relaxation approaches and relaxation response functions (RRF) for the same conditions for which those derived by DH for a CM apply. My work under discussion is solely concerned with a single broad relaxation region and thus includes no oscillatory inertial resonance effects. Therefore, inertial and speed of light limitations and effects are not germane to this approach since they are only important at frequencies far above the region of interest for a single relaxation process of the kinds considered. I am at fault for not always having made this point clear in my work. Although DH discuss inertial effects in their various papers, their actual theoretical response functions (e.g. eqs. (7a) and (7b) of ref. [1]), those that they have compared with experiment and claim to be widely applicable, do not directly include such effects. Therefore, their final relaxation functions, like mine, also seem to apply for a single relaxation, not relaxation and resonance, region. Thus $\omega \to 0$ and $\omega \to \infty$ asymptotic response should apply only for such a single relaxation region, though this has not always been made clear.

In connection with their RRF, DH have discussed asymptotic behavior at short and long times [1,3,4], asymptotic behavior at the limits of high and low frequency [4], "instantaneous steady state distribution(s)" [3], the "zero time region" [1,5], and infinite time response [21]. But of course neither zero nor infinite time is attainable, even if the entire system response over all frequencies were only that of a single relaxation region. In the limits of high and low frequency, DH state that their response function involves loss (susceptibility: $\chi''$) proportional to $\omega^{n-1}$ for $\omega > \omega_p$ and to $\omega^m$ for $\omega < \omega_p$, where we can set $\omega_p$, the frequency at which the loss is maximum, equal to $\tau_p^{-1}$, where $\tau_p$ is a relaxation time. Here the fractional exponents satisfy [4] $0 < n < 1$ and $0 < m < 1$. But the above $\omega > \omega_p$ asymptotic behavior is inconsistent with the presence of inertial effects. Although DH were aware of the need of cutoffs at frequency extremes, they evidently did not incorporate them into the analysis which led to their susceptibilty function. Thus their response functions are applicable only for a frequency range where neither inertial nor any other limiting effects are important. It is therefore worth emphasizing that their "asymp-

totic" expressions "at the limits of high and low frequencies" only apply within a limited frequency range where such effects play no role, certainly not to actual zero and infinite frequencies.

## 5. Response to criticisms and general discussion

### 5.1. Distributions of relaxation times

Consider first assumptions (b) and (c) of section 2. Although neither of these statements, nor anything like them, appeared in paper [2] which DH criticize, some material related to them does appear in refs. [8–10], however, which are the basis of my recent work on response of systems with distributions of activation energies (DAE). I agree with DH that the DRT approach may be considered a mathematical transformation, not necessarily, however, just one of experimental *data*, as they state, but particularly a transformation of the form of linear response laws. The important point is surely one of whether such a transformation and approach is a useful one, not necessarily whether in every case considered there can be proved to be an objective physical reality to the relaxation times involved in such an approach. Because it is much easier to prove a negative statement than a positive one, however, a more realistic question, consonant with the usual practice of expressing physical laws in negative terms (e.g., material bodies cannot travel at the speed of light), would be to ask, "can one prove that there is no actual physical distribution of relaxation times in any given situation?" Since probaly hundreds of papers are published every year which use the DRT approach, and have been for many years, it appears that many people continue to find it useful. Further, I shall show below, in terms of some of DH's own examples, that it has proven useful even in situations where a "parallel summation of Debye-like relaxation elements" is not present in the physical situation.

DH have stated [1], "only when a distribution can be determined by a *different* physical investigation can it be associated with the material under study. Until this is done, and to our knowledge it has never been done, the assumption (of a DRT) remains unverified." In fact, such alternate determinations of the presence of a DRT have indeed been carried out. For example, for dielectric systems the effects of a DRT or DAE can often be observed by small-signal ac measurements, by nuclear magnetic resonance measurements, and by thermally stimulated current (ITC) measurements. The presence of a DAE, (discrete or continuous) for example, is clearly necessary to explain many ITC results. It has been found that, as the concentration increases of the dipolar impurities in a solid which lead to the electrical response, the response broadens because of the interactions between dipoles which are at various distances from each other. Such interactions and their distance distribution have been shown [22] to lead approximately to a Gaussian DAE. At sufficiently high concentrations, physical clustering has been invoked [23].

DH have severely criticized the entire DRT approach by saying [24]" ... the determination of such a distribution from the spectral response (i.e. the experimental data) [does] not add to our knowledge of the problem." In fact, the accurate determination of a DRT from typical experimental data is generally mathematically unsatisfactory [11,25] (ambiguous) and is usually not what one does in a DRT approach. Instead, one either derives or posits a theoretical time or frequency response function and calculates the associated DRT probability density, $G(\tau)d\tau$, associated with it, or instead, one assumes a particular form for $G(\tau)$ and investigates the response associated with it [6,8–10,15].

An approach closely related to the DRT one is that involving a DAE. Although a DAE implies a DRT and vice versa for thermally activated systems, it turns out [26] that most DRT $G(\tau)$ functions used in the past (e.g. that for the ZC) are inconsistent with a temperature-independent DAE, the most likely type. Two important DAE–DRTs where there need be no such inconsistency are discussed in ref. [10]. In spite of DH's broad assertion that the presence of DRTs has never been (microscopically) experimentally verified [1], enough data fitting results exist to make it clear that models based on DAEs yield the best available explanation of much data (e.g. exponential band tails and trap distributions in semiconductors [27–29]; see also the section 6 discussion). Thus, the likely existence of DAEs leads to the likely existence of the corresponding DRTs.

Contrary to DH's claim [1], my work [2,8–10] is

not based on the assumption that all immittance behavior can be represented physically in terms of parallel summations of Debye-like relaxation elements, each made up of a resistance and capacitance in *series*. First, the above description is that of the long known and much used ordinary DRT approach for a pure dielectric system. I have certainly never claimed that it is appropriate for *both* dielectric and conductive systems at all immittance levels [6,8,17] (complex modulus, impedance, admittance, and complex capacitance or dielectric constant). My own recent DAE work [8–10] for a dielectric system, for example, starts, with a slightly more general DRT expression than that described above (at the complex dielectric constant (or admittance) level), and transforms this to a DAE expression. I do not prejudge whether such physico-mathematical approaches are of particular value in representing experimental complex dielectric constant data physically. Rather, I let comparison with data and with the results of other theories speak to that matter (see section 6).

For impedance and complex modulus levels, appropriate for conducting systems, I start with a generalized DRT model which involves the *serial* summation (integration for continuous relaxation time distributions) of individual relaxation elements, each made up of a resistance and capacitance in *parallel*. Although I show that the same normalized DAE integral expression may be formally used for either purely dielectric systems (intrinsically nonconducting) and for intrinsically conducting systems, the general response expression has quite different physical content in the two disparate cases. Incidentally, it is worth noting that although the approach of a conducting-system DRT at the impedance or complex modulus level which involves series summation (or integration) over relaxation times associated with resistors and capacitors in parallel has been introduced independently by Murnaghan and coworkers in recent times [30], it may have been first suggested in the early linear system work of Macdonald and Brachman [15].

DH also criticize the use of macroscopic quantities like resistance and capacitance to describe the response of microscopic systems [1]. It would certainly be best to use an accurate, fully microscopic n-body theory to derive the response of such a system without the introduction of any macroscopic concepts; unfortunately such a theory for either conducting or dielectric systems is currently unavailable. Certainly the DH CM is not such a theory (see section 6). An interesting approach towards such a theory, one concerned only with magnetic dipoles, is that of Sompolinsky and Zippelius [31]. Since it uses the mean field approximation, it is unlikely to be entirely accurate, however. In the present context, it is worth reminding the reader that "dielectric constant" is itself a macroscopic concept (representing an average over a region of macroscopic extent). It is thus necessary for even a fully microscopic theory to include such averaging to allow comparison with experiments which yield small-signal electrical response.

It seems to me that the conventional use of $R$'s and $C$'s in a DRT is not as serious a difficulty as DH seem to suggest [1] (though they themselves use the concepts of a dispersive capacitor and of a resistive element coupling their clusters), and it can, in fact, lead to useful results. First, in the usual continuous DRT approach these elements are elemental and differential [9–11]. Second, any relaxing system must involve the storage and dissipation of energy. These processes are crucial to the detailed response at a microscopic level. I have tried to modify the perception of the macroscopic character of elemental $R$'s and $C$'s by considering them as convenient ways of representing dissipation and storage of energy, respectively, at least at a semi-microscopic level [10,11]. Their use in a DRT or DAE may then be considered as an approximate method of taking account of the locally averaged kinetic and potential energy of the charges and/or rotators of the system and of the dynamic transformation (relaxation) of these energies to thermal energy (phonon generation). Again, it seems reasonable to ask how well such approaches can represent experimental data and can allow quantities which characterize the material being studied to be estimated. These matters will also be discussed in section 6.

As DH have mentioned [1], the series relaxation approach (see above discussion and refs. [8] and [15]) has recently been put forward by Palmer et al. [32] for processes involving many sequential, correlated activation steps. DH say [1] that this approach has a "sound physical basis from the

development, sequentially, of a hierarchy of responses." Although Palmer et al. do present such a plausible hierarchical physical model, DH may have overlooked that these authors have actually calculated their overall transient response by means of a sum or integral of elemental exponential responses, a typical DRT approach [15]. Further, the Palmer et al. approach actually leads to Williams–Watts response. But such response is intrinsically associated with the Levy $\alpha$-stable distribution, one like the Gaussian which involves a sum of independent, identically distributed random variables [11]. Thus the presence of a hierarchical, highly-correlated set of physical processes is not evident from the form of the overall response itself [11]. It seems that there is some inconsistency between DH's general castigation of the DRT approach and their strong espousal of the Palmer et al. theory, one whose results are actually calculated by means of DRT equations.

There is actually no problem (except that of ambiguity) raised by the calculation of hierarchical response by means of a parallel or series DRT approach. As I have pointed out elsewhere [8,11], a discrete or continuous DRT for a dielectric system may be expressed as a summation or integration of single-relaxation-time elements taken either in parallel, or hierarchically (ladder network, bifurcating array). Similarly, for an intrinsically conducting system, the response may be described by means of a summation or integration of single-relaxation-time elements taken in series or hierarchically. The situation is made clearer by fig. 1, which shows the two dielectric system possibilities in (a) and (b) and the conducting ones in (c) and (d). Here the circuit elements which define individual relaxation times may either be discrete and finite in number or differential and infinite in number, leading to a continuous distribution. The (hierarchical) response of the ladder network is naturally expressed in continued fraction form. There even exists a theorem which directly connects response given as an infinite continued fraction with an ordinary DRT integral [33]. The important point is that since either parallel or hierarchical (dielectric system) or series or hierarchical structure (conducting system) can fit data exactly as well as the other, *the form which one elects to use to fit the data by no means implies that the intrinsic processes in the material are independent* (parallel or serial form

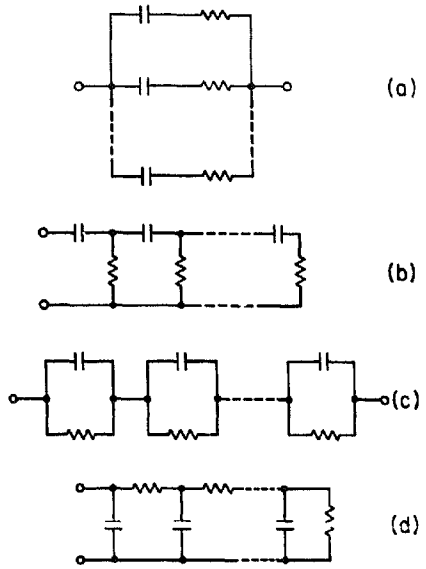


Fig. 1. Equivalent circuits with a finite or infinite number of elements which may have the same impedance over all frequencies. (a) and (b): pure dielectric system; (c) and (d): intrinsically conducting system.

where ordering is immaterial) *or highly interdependent* (hierarchical, ladder network, continued fraction form). Conversely, the particular mathematical form in which the theoretical response of a given system is presented or calculated does not necessarily prove that the model involves the independence or dependence inherent in that form. Instead, it is the microscopic physical processes present and their interactions which determine such matters. They cannot be established just from analysis of small-signal frequency or time response at a single temperature. Finally, in terms of the above definitions it is best to distinguish between series (or parallel) response (where the ordering of the elemental processes is immaterial to the overall response) and hierarchical response (ordering crucial).

### *5.2. Asymptotic behavior and limiting Debye response*

Let us now consider assumption (a) of section 2 in further detail. We have already discussed specific limiting frequency response and slope behavior of the Debye and ZC response functions in section 3 and have discussed limiting response of fractal sys-

tems in section 4. What more can be said in general? It seems likely that Schrama [34] was the first to point out that all response characterized by discrete relaxation time spectra must lead to complex plane plots with limiting high and low frequency curves perpendicular to the real axis (i.e. Debye limiting behavior, as in assumption (a) of section 2, applied, however, to a single dispersion region). In such a case it is obvious that the shortest or longest relaxation time present dominates in the extreme wings of the response. Schrama also pointed out that with a continuous DRT function which is non-zero only over a finite interval, $\tau_0 < \tau < \tau_\infty$, one will again obtain the Debye-like limiting vertical behavior. Here we can specify that $\tau_0 > 0$ and $\tau_\infty < \infty$. These requirements are obvious for the thermally activated exponential DAE situation, whose transient response was first discussed [20] in detail in 1963. Suppose we have, for example,

$$\tau = \tau_a \exp(\gamma E/kT) , \qquad (4)$$

where $\tau_a$ and $\gamma$ are usually temperature independent. Since negative activation energies are meaningless, the minimum possible $\tau$ is $\tau_a \equiv \tau_0$ when $E = 0$. Since no real, finite-sized material will have an infinite activation energy for a process of interest in the relaxation regime, we may set $E_{max} = E_\infty < \infty$; then $\tau_{max} \equiv \tau_\infty = \tau_a \exp(\gamma E_\infty/kT)$.

In the continuous distribution case, we cannot speak of dominance by a single largest relaxation time, $\tau_\infty$, since there will be other differential ones arbitrarily close to $\tau_\infty$. But Syed et al. [35] showed some time ago that for a DRT system with a normalizable $G(\tau)$ (note that $G(\tau)$ for the full CPE is non-normalizable [15]), one obtains $\omega \to 0$ limiting response of $I'$ proportional to $\omega$, and $S_I \to -\infty$, again perpendicular limiting behavior. Thus even in this case, limiting frequency response is governed by an effective single time constant and is of the Debye type. These authors also showed from general DRT considerations that for $\omega \to \infty$, $I''$ is indeed proportional to $\omega^{-1}$. Further, provided that $\langle \tau^{-1} \rangle$, the average inverse relaxation time over the relaxation time distribution, is finite (the usual situation for realistic distributions), they found that $S_I \to \infty$ in this limit, again single-time-constant Debye limiting response. In an actual system, of course, the $\omega \to \infty$ limiting response might not be measurable or, possibly, might be obscured by inertial or other effects.

The above arguments and results were the basis for the $\omega^{\pm 1}$ limiting response statement in my paper [2] which DH claim to be both invalid and not possible of validation [1]. Although the counter arguments above seem convincing, more can still be said. First, the above limiting behavior does not even need to depend on DRT considerations, even though it is mathematically possible to express any physically realizable response in terms of a DRT. Consider $\omega \to 0$ behavior, for example. It is only enough to posit that the material under investigation has various modes of relaxation response, call them relaxation times or not. Then because of the limited physical size of the experimental sample, if for no other reason, there must be either a longest response mode (involving a maximum, non-infinite correlation length), or if the modes form a continuum, a cutoff in the continuum at the long-time end. Then again the response well beyond the longest mode or cutoff point will approach limiting Debye frequency behavior.

Several response theories actually lead to broad relaxation regions with Debye limiting tails as above. In the frequency domain fractional power law response predicted by these theories transforms to limiting Debye response because the DRT and/or DAE involved is cut off at the extremes (yielding a finite-interval distribution in the Schrama sense). An example not directly involving a DRT or DAE is the conducting system model of Funke [36] which considers the forward and backward hops of charged defects and motion of the surrounding "defect cloud". As shown by fig. 2 it leads to the usual displaced circular arc response except at the extremes where Debye-like vertical behavior is evident. Other examples are the DAE models of the present author [8–10]. Here the limited DAE continuous spectrum automatically ensures such limiting frequency response. Had DH actually incorporated cutoffs in their own response models (assuming this to be practical), limiting $\omega^{\pm 1}$ behavior would likely have resulted.

Finally, we have already cited examples of simple Debye experimental response where the $\omega^{\pm 1}$ response rejected by DH appears. We have also shown how it can and should appear in physically realistic theories of wide dispersion regions. It thus only remains to show that it can be observed experimentally as well. Fig. 3, taken from ref. [35], shows that

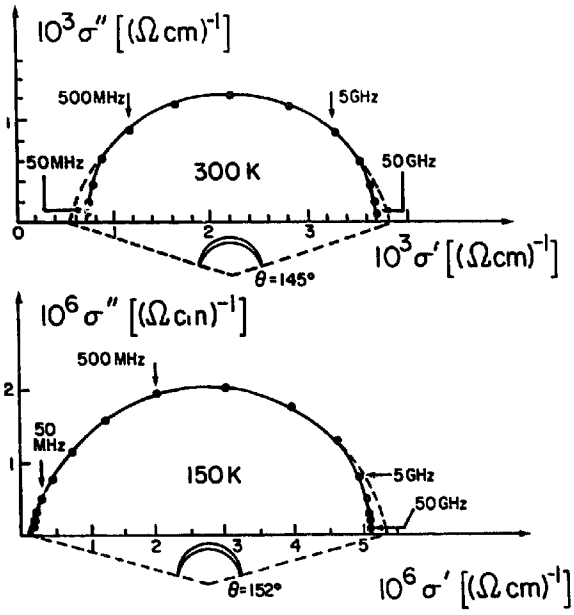


Fig. 2. Complex conductivity depressed arcs predicted by the hopping conductivity model of Funke [36] (solid lines).

it does indeed appear even in solids. The inserts in the figure clearly show the approach to final vertical behavior at both frequency extremes.

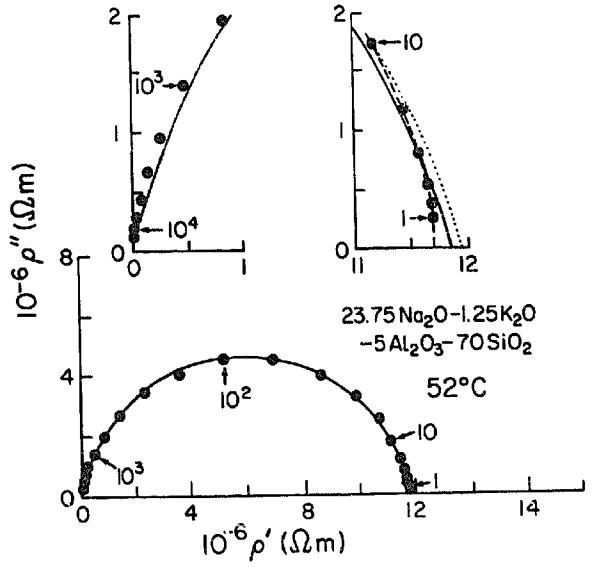


Fig. 3. Complex resistivity depressed arc and limiting behavior found by Syed et al. [35] for an ionically conducting glass at 53°C. Numbers near data points denote measurement frequencies in Hz.

### 5.3. Low frequency limiting diffusion effects

The limiting size effect is well illustrated in the diffusion case, where one need not invoke a DRT even though it is possible to do so if desired. DH state [5] that for a conducting-system diffusion situation at sufficiently low frequencies both $\chi'$ and $\chi''$ (or $I'$ and $I''$) will show $\omega^{-1/2}$ frequency dependence behavior, actually, though not referenced, that first calculated by Warburg [37] nearly a hundred years ago. DH set no lower frequency limit on the applicability of this response. But it was long ago shown [38–43] that in a sample of finite length such "infinite-length" Warburg response cannot continue indefinitely to lower and lower frequencies. For a sample with identical, plane, parallel electrodes a distance $l$ apart, it was demonstrated that when the diffusing particle reacts rapidly at the electrodes (conducting case, $Z$ level) or does not react there at all (dielectric case, complex dielectric constant level) one can write

$$I(s)=\tanh(\sqrt{is})/(\sqrt{is})\,, \qquad (5)$$

where $s\equiv l^2(\omega/D)$ and $D$ is the diffusion coefficient of the diffusing particle. Note that for $s\gg 1$, $I(s)$ approaches $(is)^{-1/2}$, CPE behavior with $n=1/2$. Physically, when $s\gg 1$ the effective diffusion length, $(D/\omega)^{1/2}$, is much smaller than $l$ and the finite size of the sample exerts no influence on the reponse. In the other extreme, when $s\ll 3$, the diffusion length becomes greater than $l$, and it has been shown that the low frequency limiting response following from eq. (5) is just that of a resistance and capacitance in parallel, i.e. single time constant $\omega^{+1}$ limiting response enforced by the finite size of the sample. It should finally be mentioned that this finite length modification is not just a theoretical result with little or no relevance to experiment. In fact, a great deal of data, particularly in the fields of liquid and solid electrolytes, can be very well fitted by response of the eq. (5) form, with data often extending well into the $s\ll 1$ region [6]. Here is another example where the DH rejection of assumption (a) of section 2 must itself be rejected. It is perhaps ironic that although DH strongly abjure [1] the possibility of $\omega\to 0$ asymptotic response proportional to $\omega^{+1}$, their own fitting of data of several materials with their CM RRF leads [4,21] to just such dependence (i.e. $m=1$ results; see section 6).

### 5.4. Asymptotic transient response

We have seen that there is good theoretical and experimental reason to expect $\omega^{\pm 1}$ limiting behavior at the extremes of a wide (or narrow) relaxation dispersion region. Note, however, that such limiting response may fall outside the range of measurement for a sufficiently wide dispersion region. For this reason it is often not observed and reported. Such limiting behavior is particularly evident in the theoretical exponential DAE (EDAE) work of the author, an approach which involves at the DRT level a doubly-truncated Pareto-relaxation-time fractional power law distribution [8–10,11,17]. For pure single-time-constant dielectric system Debye response, the associated charging or discharging transient current is of course of pure exponential form. But when $\omega^{\pm 1}$ behavior is present only as asymptotic response of a wide dispersion region, not as part of single-time-constant Debye behavior, it is possible that the asymptotic transient response may not be a pure exponential. For example, the above truncated Pareto distribution leads [20] to $t \to \infty$ limiting behavior of $t^{-1} \exp(-t/\tau_{max})$ form, even faster decaying than exponential and far faster than the $t^{-n}$ asymptotic response of the DH CM. On the other hand, a discrete DRT will always lead to limiting exponential response. In fact, it can readily be shown that a sharp cutoff of a continuous DRT probability density function (one which does not approach infinite density at the cutoff point) in such a way that it is zero beyond a value $\tau_{max}$ will always lead to $t \to \infty$ limiting behavior of the $t^{-1} \exp(-t/\tau_{max})$ form. Thus in all practical cases it appears that the limiting behavior will be either exponential or at least no faster than the quasi-exponential decay defined above.

Of course, to measure the intrinsic very-long-time discharge response of a dielectric material, it is necessary, if one wants to observe the full response of the system, to charge the sample for a time appreciably longer than the longest response mode and longer than any measurement discharge time. This is not always done. Further, one may not see the final exponential or quasi-exponential decay because earlier $t^{-n}$ decay may persist over a time longer than the longest convenient measurement time or until the current has decayed to the noise level. Failure to observe final exponential-like decay does not, therefore, prove that it does not exist at sufficiently long times. DH's statement [1] that "even an exponential decay takes an infinite time to reach equilibrium" is misleading. Although it certainly takes an infinite time for an exponential to decay to zero, this is both unnecessary and immaterial since it is only necessary for the process to decay to the thermal equilibrium noise level or measurement noise level, something that always happens in finite time for an undisturbed system with time-invariant material properties.

Although DH cite two references to justify their assertion [1] that exponential decay is unphysical at both long and short times, these references are not really germane to the point at issue. First, the start of exponential decay at sufficiently short times, which is associated with $\omega^{-1}$ response, is often masked by other processes such as the beginning of inertial effects. Of the two references cited by DH, one considered broad relaxation regions without cutoffs of the types discussed above. Thus it is not suprising that it did not involve exponential-like behavior at sufficiently long times. The other article was solely concerned with a decay theory of unstable quantum systems and dealt with radioactive decay – not at all the sort of relaxation we are concerned with here! Even this article reached the conclusion that "the experimentally observed non-decay probabilty law is exponential at all relevant times" [44].

## 6. Discussion of two response models

### 6.1. Introduction

Since the relaxation response functions (RRF) of DH and the EDAE of the present author have both been claimed to fit data very well for a wide variety of materials, it seems worthwhile to compare them and to point out some similarities and differences. DH have stated that the CM gives "an extremely good description of the different types of response shapes observed over a wide frequency/time range [and that] its claim to generality can therefore be held to be valid in detail" [4]. Similarly, I have stated [9], "a unified dielectric or conductive distribution of activation-energies (DAE) physical model is proposed whose predictions agree remarkably well with those

of all the Jonscher universal dielectric response equations as well as with many other common dielectric response equations." Can both these statements be correct? We shall see.

### 6.2. Similarities

First, what are some of the other similarities between these models?

(a) They each have somewhat microscopic and macroscopic elements; thus neither is a thoroughgoing microscopic theory.

(b) They can both yield two connected regions of fractional power law behavior in frequency or time. The parameters which control such behavior for $I''$ are denoted $n$ and $m$ (or $p$) in the CM and $\phi_1$ and $\phi_2$ (or $\phi$) in the JRM EDAE model. Since one or two such fractional slopes indeed appear in the vast majority of non-Debye (or anomalous dispersion) experimental results, any theory which purports to describe such data must include these possibilities.

(c) Both the DH CM and the JRM EDAE models lead to RRFs which may be expressed as (different) hypergeometric functions. In the CM case, calculations of the response from the hypergeometric function are carried out [4] using a series which is poorly convergent as $\omega/\omega_p \to 1$. The JRM EDAE RRF is expressed in intergral form and may be used, with the proper input and interpretation, for either dielectric or conducting systems. It has been incorporated as one of the many distributed circuit elements [17] available for direct use in the general CNLS fitting program [12] available from the author. In this program, the integral is evaluated numerically, both rapidly and accurately as needed for the least squares fitting.

### 6.3. Differences

Along with the above similarities, there are also many important differences between the models.

(a) Although they have some common features, the two models are largely based on different physical assumptions. The EDAE model [8–10] is applicable for a thermally activated system and assumes that an exponential distribution of activation energies, $E$, (distributed enthalpy and possibly entropy) having finite extent in $E$, is present in the material. Such a barrier-height distribution might arise from the presence of a distribution of the values of structural parameters of the material, as expected in an amorphous material. In the conducting case, for example, transport laws may depend exponentially on such parameters, leading to an EDAE. Further, exponential density of states are common in semiconductors [27–29], and a double-exponential density of states (such as that in the $EDAE_2$ model [9,10]) has been found from polycrystalline silicon data [29]. On the other hand, the DH RRF has been derived in two different ways: the first is based on a two-level system containing two types of decay mechanisms [21], (and it even contains a DAE assumption [24]!), and the second, the CM, which differs significantly from the first, involves a model of clusters of ions or molecules, each cluster having some local ordering with both inter and intra cluster interactions.

DH do not refer, in their derivations of the CM, to earlier work likely to be relevant, particularly the quantum many-body coupled-cluster method (see ref. [45] for background and references that go back to 1957), and possibly the free-volume model for dense liquids and glasses [46] which involves a DRT for finite and infinite clusters, and the Schlesinger–Montroll model [47] which involves self-similar bursts of hopping events with intervening clusters of pauses (intermittency).

Of course, the presence of two distinct, physically different derivations of the DH RRF means that its ability to provide a good description of some small-signal data does not allow one to decide which of the two models, if either, actually describe the physical processes present in the material. This point is not addressed by DH. Again it is much easier to prove a negative than a positive assertion.

(b) Although the DH and JTM RRFs lead to two fractional power law regions (which may or may not involve a peak in $-I''$ between the two regions), these regions continue indefinitely in frequency for the DH RRF but eventually show physically necessary transitions to $\omega^{\pm 1}$ behavior for the JRM RRF. Because of the presence of these transitions, the latter function involves the presence of one ($EDAE_1$ and $EDAE_2$ models) or two (general EDAE model) more parameters than does the DH RRF. These parameters determine where the transitions occur; of course

if the data do not include transition regions, these parameters need not be free.

(c) Although both models claim to lead to RRFs which apply for either pure dielectric or intrinsically conducting systems, there is a crucial difference between them. One form of the DH RRF applies when the inter-cluster interchanges carry charge, but it apparently does not involve the possibility of a true direct current, even with completely ohmic (unblocked) electrodes. Instead, as $\omega \to 0$, $\chi''$ increases indefinitely as $\omega^{-p}$, where the new fractional exponent $p$ satisfies $0<p<1$. Thus, the DH RRF cannot represent data for intrinsically conducting materials adequately. Certainly, a conducting-system small-signal response expression should be able to represent the behavior of such a system when its electrodes are not completely blocking; otherwise it is too severely limited to be of general utility. It is, of course, therefore to be expected that DH have applied this model only to the analysis of data with no apparent dc conductivity [5]. Except for the formal transformation of $m \to -p$ the DH RRF for dielectric systems and the one where charge is carried are exactly the same in form. Therefore it is not necessary to distinguish between them further here, and the DH RRF designation will include both.

The JRM RRF for a conductive system can, on the other hand, lead to fractional power law behavior for $\omega\tau_p<1$ of either the $\omega^{-p}$ or $\omega^{p}$ type (the latter giving a peak in the neighborhood of $\omega=\tau_p^{-1}$). But even the former type of dependence is eventually limited in this model by either a finite maximum value of $E$ or by sample-size effects; it then transforms into the usual $\omega^{+1}$ limiting behavior. Clearly, the maximum value of $E$ involved may be determined by the finite size of the sample if no other effect controls the low frequency limiting response. Thus for either the $\omega^{p}$ or $\omega^{-p}$ type of intermediate-frequency behavior, the model eventually yields a non-zero and non-infinite dc conductivity. Alternatively, the JRM RRF for a pure dielectric system leads to no such dc conductivity (assuming no extraneous leakage resistance is present) and is thus similar, in this sense, to both of the DH RRFs.

(d) Next, the temperature dependence of the DH and JRM RRFs is quite different. Although DH state [1] that the CM is not a zero temperature theory, it seems to be based on the presence of zero-point fluctuations and the production of virtual phonons (virtual displacement dilation modes), and none of the parameters of the corresponding RRF show temperature dependence arising from the theory itself. It appears that completely temperature independent fractional exponents, $n$ and $m$ (or $p$) are introduced into the CM in a rather ad hoc fashion [3] and interpreted qualitatively in an ex post facto manner. The $\omega_p$ parameter is, in turn, introduced as a damping factor, $\gamma_c$, with no direct temperature dependence specified [3]. In the fitting of actual data, however, DH take $\omega_p$ thermally activated whenever needed to fit the data, but this choice also seems separate from the main CM assumptions.

The situation is quite different for the EDAE approach. There, thermal activation is a natural part of the theory and connects the DAE involved with a corresponding DRT. Thus, $\tau_p \equiv \omega_p^{-1}$ is thermally activated and of the form of eq. (4), where, in certain cases, $\gamma$ may be temperature dependent. The $\phi_1$ and $\phi_2$ EDAE parameters determine the fractional power law exponents (see, e.g., fig. 5 of ref. [10]) but are not generally equal to these exponents. Let $n_r$ and $n_i$ be the actual fractional values for $I'$ and $-I''$, respectively. Then it turns out that $0<n_r<2$ and $0<n_i<1$ for a single CPE-like response region. But $\phi_1$ and $\phi_2$ fall in the range between $-\infty$ and $\infty$. Further, their temperature dependences are entirely determined by the assumptions of the EDAE model itself; no ad hoc quantities or assumptions are necessary. If $\gamma$ is temperature independent, the simplest case, and there is no DAE (the EDAE exponential probability strength parameter, $\eta$, is zero), then $\phi_1$ and $\phi_2$ (and $n_r$ and $n_i$) are temperature independent and only a DRT associated with a distribution of the pre-exponential factor in eq. (4) is present, perhaps arising from a distribution of configurational entropies. Thus this special case can yield results very much like those of the DH RRF.

But in the usual EDAE situtation there are non-zero values of $n_1$ and $n_2$ and many different temperature dependences of $\phi_1$ and $\phi_2$ are possible. Note particularly that since the ranges of the $\phi$'s are unlimited, they may depend linearly on temperature over an arbitrary range of that variable, unlike the exponents themselves, which fall between 0 and 1 or 2 and are thus unable to exhibit such behavior except over a limited temperature range.

In the simplest EDAE case, where the $\gamma$ parameter of eq. (4) is temperature independent, i.e. ordinary thermal activation, one finds [8–10] that $\phi$ *decreases* linearly with $T$ for a conductive system and *increases* linearly for a dielectric one. But the $T$ dependence possible is considerably more complicated if the material shows a glass-like transition and/or a linear relation between activation enthalpy and entropy [8,10,20] (the Meyer–Neldel rule [48]). In the dielectric case, for example, the presence of the latter relation leads, for the $EDAE_2$ model, to $\phi^{-1}$ proportional to $(T^{-1}-T_0^{-1})$, where $T_0$ is a constant relating entropy and enthalpy. Incidentally, work of Dyre [49] strongly suggests that there are two types of glass transition in glasses, resulting in a Gaussian or an exponential DAE, with Gaussian for a slow cooling rate and exponential for a fast rate. As another counter example to the DH rejection of DRTs, Dyre [49] states, "this may explain the ubiquitous appearance of gaussian and exponential barrier distributions ... in glassy solids," (four references cited).

Suppose one is dealing with a conducting system which follows the $EDAE_1$ model predictions and thus show A–BT dependence for $\phi$. If sufficiently high temperatures could be reached, $\phi$ would become zero and then negative. Is this case for alarm? DH [5] have criticized the EDAE work of Bernasconi and co-workers [50] because it leads to the fractional exponent $n$ going to zero at a finite temperature. But $n$ and $\phi$ are not exactly the same, as the more accurate EDAE work of the author [8–10] has shown. Similarly, Maglione et al. [51] have stated that when $n=0$ (which may also happen in the $T\to 0$ limit for dielectric systems), the associated DRT spreads to infinite width. Again, the predictions of the more exact and physically realistic JRM EDAE model show this not to be the case. Although the $\phi=0$ condition may indeed lead to $n_i=0$ over an appreciable range of frequency, that range is limited [8]. Further, as $\phi$ goes negative, the relevant $EDAE_1$ complex plane plot becomes asymmetric, with a CPE-like region at the low frequency side of the peak ($n_i<0$), rather than the more usual $\phi>0$ behavior where this region occurs at the high frequency side of the peak ($n_i>0$). Incidentally, as $|\phi|$ becomes larger than unity, ordinary simple Debye response is approached. This can happen, for example, when $T\to T_0$ for the $(T^{-1}-T_0^{-1})$ behavior of $\phi$ mentioned above. There are thus no problems over the entire available range of $\phi$: $-\infty<\phi<\infty$.

### 6.4. Comparison of model predictions

Two sorts of comparisons have been carried out for both the DH and JRM RRFs. First, both functions have been compared with other frequency response functions such as the Williams–Watts, Cole–Cole (ZC), Davidson–Cole, and Jonscher universal dielectric response functions. But the method of comparison used generally differed appreciably. DH have compared the response of their function with others by taking the asymptotic slopes the same, a procedure which usually shows up appreciable differences when the results are plotted in the complex plane [52]. Althoug I have also used such an approach (when the actual asymptotic $\omega^{\pm 1}$ regions are outside the range of interest), I have, more often, generated exact "data" from one response function and fitted it to other functions using CNLS. When unity weighting is used in such a fit, agreement is best near the peak of the response, at the expense of exact power-law-region agreement. Just the opposite behavior occurs with proportional weighting [12]. The general conclusion reached after much such fitting [7–10,17,53] is that the EDAE can fit exceptionally well all the other functions with which it has been compared. Thus it can, by extension, fit all the data which have been fitted by these other forms. Although no direct comparison has been made between the DH RRF and the EDAE, it appears likely that except for the final $\omega^{\pm 1}$ asymptotic regions of the EDAE and possibly near the peak (or where $\omega\sim\omega_p$ if there is no peak), good mutual fitting should be possible at a single temperature. Incidentally, Hill shows [52] symmetrical complex plane theoretical curves for the Williams–Watts and Davidson–Cole functions, but the response of these functions is inherently skewed and asymmetric. The origin of this discrepancy is unknown.

The second sort of comparison is that where two or more different RRFs are fitted to actual data. Considerable such fitting has been carried out by both DH [3,5,52] and JRM [10,54–56]. But the DH work does not use CNLS and thus does not provide least squares estimates of both fitting parameters and their estimated standard deviations. Further, as might be

expected, most of the DH fits are for dielectric systems and most of the JRM ones for conducting systems. The actual fits are generally good.

But the big problem is that DH have considered only a limited subset of all possible anomalous dispersion responses – that for which the $\omega^m$, $\omega^{-p}$, and $\omega^{n-1}$ responses involve only temperature independent exponents. But much data (e.g. see refs. [28,51,57,58]) involve *temperature dependent* exponents with dependence such as that predicted by the EDAE and discussed in the last section. In spite of the DH claim [4] of the generality and validity in detail of their RRF, we have seen that (a) it is physically unrealistic because it does not reduce to $\omega^{\pm 1}$ behavior at the frequency extremes (not usually a matter of much experimental importance); (b) it is inappropriate for fitting intrinsically conducting materials which can pass dc; and (c) it is limited to data for which the fractional power law exponents are temperature independent. None of these limitations apply to the EDAE, and thus the generality of the EDAE, but not the DH RRF, is upheld.

### 6.5. *List of acronyms*

CM: cluster model, CNLS: complex nonlinear least squares, CPE: constant phase element, DAE: distribution of activation energies, DH: Dissado–Hill, DRT: distribution of relaxation times, EDAE: exponential distribution of activation energies, IS: impedance spectroscopy, JRM: J.R. Macdonald, RRF: relaxation response function, ZC: ZARC/Cole–Cole depressed semicricle small-signal RRF.

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