Linear relaxation: Distributions, thermal activation, structure, and ambiguity

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The equations governing the small-signal response of relaxing, nonresonant systems which may be described by a distribution of relaxation times (DRT) and/or a distribution of activation energies (DAE) are summarized and generalized and their implications discussed for several popular distributions. Much past work, both experimental and theoretical, associated with these distributions is discussed. A distinction is made between physically realistic distributions, which involve finite shortest and longest relaxation times, and the usual mathematical approaches which involve limiting zero and infinite relaxation times. The Lévy DRT, which is of the latter character and which leads to the popular stretched exponential (SE) time and Williams–Watts (WW) frequency responses, is inconsistent with a temperature-independent DAE, reducing its range of applicability for a thermally activated situation. The SE-WW response has been termed universal; it is not, both because of the above facts and also because it does not lead to the often found symmetrical log-frequency response. Both Gaussian and exponential DAEs can lead to both symmetrical and skewed results, and can involve either temperature-dependent or temperature-independent DAEs. However, the Gaussian DAE does not yield fractional power-law time or frequency response over a finite, nonzero range, behavior found in nearly all distributed data. However, all DAEs involving exponential probability densities do lead to such behavior and provide, as well, an explanation of the temperature dependence of power-law exponents. In addition, it appears that the response of systems involving an exponential DAE can fit that of virtually all previous models, including the SE-WW, and thus can fit all data for thermally activated systems which have been fitted by these models. Problems in data fitting and many sources and types of ambiguity and their resolution are discussed. Special attention is devoted to the distinction between parallel, sequential, and hierarchical microscopic-model structure and response, and the various different, but, surprisingly, equivalent ways the overall response can be represented mathematically or by means of equivalent circuits of different connectivity.

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I. INTRODUCTION

The measurement and analysis of the small-signal electrical (or mechanical) relaxation of a dielectric or conducting material has a long history and has proven valuable in elucidating and even quantifying the physical processes in the material associated with the relaxation. Measurements may be made in either the time (transient response) or frequency (frequency response) domain. For small-signal measurements, where the response is linear, the same information is contained in either type of result if they cover equivalent time-frequency spans. Nevertheless, for both experimental and analysis reasons, it is often more convenient to measure in one domain rather than the other. When both techniques are available, the total response span covered can usually be extended by combining results from both domains.

Analysis of relaxation results has often employed empirical response functions such as those Cole and Cole[1] and Davidson and Cole[2] introduced for analysis of dielectric relaxation frequency domain data. All reasonable response functions, empirical or not, may be associated with a continuous or discontinuous distribution of relaxation times (DRT) (a list of acronym definitions is provided at the end of this paper) function,[3] say $G(\tau)$, where τ is the relaxation time for an elemental process in the material. This association may only be a mathematical transform of no obvious physical significance, or it may be associated with actual physical processes leading to such relaxation times. When the apparent DRT found from analyzing small-signal data is very wide and temperature dependent, as it often is, the DRT is likely to arise from a distribution of activation energies (DAE). When the relaxation process response is thermally activated (Arrhenius temperature response of the τ's), the response may be analyzed in terms of a distribution of barrier heights, generally termed a distribution of activation energies,[4,5] although usually the distribution actually considered is that of the Gibbs free energy and enthalpies.[4,6]

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We shall be primarily concerned here with the structure more than the direct physical content of various approaches to analyzing linear relaxation processes in the relatively low-frequency region. The reason is that many different physical theories can lead to virtually the same kind of response, an ambiguity which usually requires more data to allow resolution than that present in single-temperature frequency response, no matter how wide. Although we shall not consider these microscopic-model to macroscopic-model theories in detail, they will be referred to in pertinent places throughout the paper, allowing the reader to follow up on those of particular interest. In addition, much relevant experimental work will also be mentioned. Although it is not a requirement of physical realizability that a DAE be temperature independent, it is a likely and plausible first assumption to use unless disproved by experimental results. It turns out[7] that while all temperature-independent DAEs may be associated with a DRT, not all DRTs lead to a temperature-independent DAE. In fact, the DRTs of most of the empirical relaxation fitting functions used in the past are inconsistent with such a DAE, although much of the data analyzed with them did involve thermal activation. In the present work, several such inconsistent and consistent response functions will be discussed, various important ambiguities pointed out, and the distinctions between different types of model structure and response brought out and emphasized. We begin by generalizing some standard continuum response equations in two ways so they apply to either dielectric or conductive systems, and include possible thermal activation effects associated with energy storage as well as with dissipation. Next, various important distribution functions—Pareto, Gaussian, Lévy, and exponential—are introduced and compared in terms of their associated response functions and fitting ambiguities. Finally, various kinds of microscopic-model structures are discussed and compared to connectivities, structures, and mathematical approaches commonly employed in analyzing distributed-property materials.

II. DISTRIBUTIONS AND RESPONSE

A. General

For added generality, it proves useful[8,9] to represent the relaxation frequency response associated with a single, possibly distributed, dispersion region of either dielectric or conductive systems by means of a single, normalized, dimensionless response function $I_j(\omega)$, where ω is the angular frequency. To do so, first let us introduce the subscript j which can take on the values ϵ (dielectric response) or Z (conductive response). Then let $U_j(\omega)$ represent either such kind of response. Specifically then $U_z(\omega) \equiv Z(\omega)$, the impedance of a conductive system, and $U_\epsilon(\omega) \equiv \epsilon(\omega)$, the complex dielectric constant. The definition of $I_j(\omega)$ is then

$$I_j(\omega) = I_j'(\omega) + iI_j''(\omega) \equiv [U_j(\omega) - U_{j\infty}]/(U_{j0} - U_{j\infty}). \quad (1)$$

Here $U_{j0} \equiv U_j(0)$ and $U_{j\infty} \equiv U_j(\infty)$, and $\omega \to \infty$ indicates a frequency region where the relaxation processes of interest are too slow to follow a sinusoidal input in this frequency range, not actual infinite frequency. Equation (1) is intended to represent the response of a single, usually distributed, relaxation process. When many such separate processes occur in different frequency ranges for a given system, several $I_j(\omega)$ functions must be used, with the $U_{j\infty}$ of the lowest-frequency one equal to the U_{j0} of the adjoining process, etc. Such response may involve ionic, dipolar, and/or electronic processes or a combination thereof. Here we shall be generally concerned with a relaxation frequency response range of, say, 10^{-4}–10^{7} Hz and primarily with a single dispersion region.

Now a relaxing system must both store and dissipate energy. These processes at an elemental level may be conceptually represented in the electrical case by an elemental capacitor C and an elemental resistor R, respectively. The corresponding elemental relaxation time is $\tau = RC$; for it to be thermally activated R, C, or both must be thermally activated. It is conventional to assume that only R is activated, but there are instances where C may also be.[9] To include all these possibilities, we may write in the thermally activated case[9]

$$R_j = R_{aj} \exp(\alpha_j E/kT) \quad (2)$$

and

$$C_j = C_{aj} \exp(\beta_j E/kT), \quad (3)$$

so

$$\tau_j = R_{aj} C_{aj} \exp[(\alpha_j + \beta_j)E/kT] \equiv \tau_{aj} \exp(\gamma_j E/kT). \quad (4)$$

Here R_{aj} and C_{aj} are temperature-independent quantities, E is the barrier height or activation energy variable, α_j and β_j are strength parameters which may possibly be temperature dependent, β_j may possibly be negative, and $\gamma_j \equiv \alpha_j + \beta_j$. In the conventional thermally activated case, one takes $\alpha_j = 1$ and $\beta_j = 0$, the situation where R is thermally activated and C is not. In the absence of thermal activation, $\alpha_j = \beta_j = 0$, so this case is included as well in the following.

Now we wish to obtain an expression for $I_j(\omega)$ which is appropriate when both thermal activation and a distribution of activation energies may be present simultaneously in either a dielectric or conductive situation. Simplification of earlier work[9] leads to

$$J_j(\omega) = \int_0^\infty \frac{\exp(\chi_j \mathscr{E}) F(\mathscr{E}) d\mathscr{E}}{1 + i\omega\tau_j} \quad (5)$$

and

$$I_j(\omega) \equiv J_j(\omega)/J_j(0). \quad (6)$$

Here $\chi_\epsilon \equiv \beta_\epsilon, \chi_Z \equiv \alpha_Z$, and $\mathscr{E} \equiv E/kT$. The quantity $F(\mathscr{E})$ is a DAE function or probability density. Physically plausible $F(\mathscr{E})$ functions should be normalizable. But note that all finite-size linear systems with time-invariant physical properties should have a minimum relaxation time, τ_0, greater than zero, and a maximum relaxation time, τ_∞, less than infinite.[9,10] Thus, we may take the realistic range of $\mathscr{E}$ in the thermally activated situation as $\mathscr{E}_0 < \mathscr{E} < \mathscr{E}_\infty$, where $\mathscr{E}_0 \geqslant 0$ and $\mathscr{E}_\infty < \infty$. Outside this range $F(\mathscr{E})$ will be zero. Many conventional response functions used in the past do not satisfy these conditions[9] although their response may not be well distinguished from that of functions which do when comparison is made, as it usually is, over a rather limited fre-

quency or time range. It should be emphasized that the actual $\mathscr{E}_0$ and $\mathscr{E}_\infty$ quantities applying to a given dispersion region and the τ_0 and τ_∞ associated with them through Eq. (4) are not necessarily the absolute minimum τ_0 and maximum τ_∞ possible for the system but those that define a given dispersion region, as in Eq. (1). Note that a zero value of $\mathscr{E}_0$ does not yield a nonphysical zero τ_0 (zero response time). It is, of course, implausible to take $\mathscr{E}_\infty$ infinite since no real finite-size system requires infinite energy for even dissolution. Although the use of sharp cutoff values of $\mathscr{E}_0$ and $\mathscr{E}_\infty$ (and thus of τ_0 and τ_∞) is likely to be only an approximation in most real systems, it is certainly a good one in the frequency range considered here (no inertial effects included), and is more realistic than the procedure often used in DRT or DAE calculations of taking $\tau_0 = 0$ and $\tau_\infty = \infty$, and/or $\mathscr{E}_0 = 0$ and $\mathscr{E}_\infty = \infty$. Thus, the resulting DRTs often have a finite relaxation time probability density for arbitrarily large and/or small τ.[11]

Now by conservation of probability, we may set $G(\tau)|d\tau| = F(\mathscr{E})|d\mathscr{E}|$, and convert the DAE expression in Eq. (5) to the new DRT result

$$J_j(\omega) = \int_0^\infty \frac{\tau_j^{\theta_j} G(\tau_j)\, d\tau_j}{1 + i\omega\tau_j}, \tag{7}$$

where $\theta_j \equiv \chi_j/\gamma_j$. Although both dielectric and conductive response are included in Eqs. (5) and (7), it is important to underline the basic difference in the two responses, particularly when $\beta_j = 0$ and there is then no thermal activation of the energy storage process, the usual situation. Because θ_j involves α_Z in the $j = Z$ conducting situation, and β_ϵ in the $j = \epsilon$ dielectric case, even when $\beta_j = 0$ the value of θ_j in Eq. (7) is different for the two cases, leading to important differences in response. For example, notice that θ_j is zero in the absence of thermal activation and also in the special dielectric case when $j = \epsilon$ and β_ϵ is taken zero. This is the usual dielectric situation (only R thermally activated) and the author knows of no experimental results in this area for which it would be necessary to assume that C is thermally activated, thus leading to $\beta_\epsilon \neq 0$. For the conducting system ($j = Z$) situation, on the other hand, thermal activation of R alone leads to a nonzero $\chi_Z = \alpha_Z$ thus $\theta_Z \neq 0$ even though $\beta_Z = 0$. Experimental results for the temperature dependence of the fractional frequency exponents usually found to be present in small-signal frequency response data for conducting systems usually require $\alpha_Z \neq 0$, consistent with thermal activation of the dissipative processes present,[9] a natural requirement. Fractional-exponent temperature response is further discussed in Sec. II E.

By taking a Laplace transform of $I_j(\omega)$, one readily finds that the transient response, $A_j(t)$, of the system to a step-function stimulus applied at $t = 0$ may be written in normalized form as[3]

$$A_j(t)/A_j(0) = K_j(t)/K_j(0+), \tag{8}$$

where

$$K_j(t) \equiv u_0(t) \int_0^\infty \tau_j^{\theta_j - 1} G(\tau_j) \exp(-t/\tau_j)\, d\tau_j, \tag{9}$$

and $u_0(t)$ is the Heaviside unit step function. This equation may be transformed so that it involves $\mathscr{E}$ and $F(\mathscr{E})$ in the same way that we passed from (5) to (7). The "j" subscript will be omitted for simplicity from now on with the understanding that results can apply to either dielectric or conductive systems. Note that if $F(\mathscr{E})$ is a temperature-independent probability density, as is often likely, there is always a plausible DRT associated with it, $G(\tau)$, in the thermally activated case.[7] When $\beta_j \equiv 0$ in Eqs. (7) and (9), standard results[3] are recovered and the response may or may not be associated with a DAE.

It is sometimes suggested that the distribution functions $G(\tau)$ or $F(\mathscr{E})$ be derived from specific data rather than deriving them from analysis at the microscopic level, or by using a form associated with a convenient and useful empirical response function such as that of Cole and Cole,[1] or by assuming a DRT or DAE *ab initio*. There are two main reasons why such an approach is generally impractical. First, a functional form of $G(\tau)$ involving only a few parameters is easier to use than a many-point numerical definition. More importantly, the deconvolution of an equation such as (9) to obtain $G(\tau)$ involves the inversion of the Laplace transform, a notoriously unstable process.[12] The problem is not particularly helped by deriving $G(\tau)$ through inversion of an equation such as (7) instead. It is well known that transient or frequency response calculated using a $G(\tau)$ is extremely insensitive to the details of the $G(\tau)$. Examples are given in Refs. 11 and 13. Thus, the problem of obtaining $G(\tau)$ even when "many measurements are taken at very closely spaced frequencies over a very large range of frequencies" is a recalcitrant one since it "greatly magnifies the inevitable experimental errors."[14] Three different approaches to the problem have been recently published,[14–16] but it seems generally impossible to obtain a unique or closely defined $G(\tau)$ from ordinary experimental data. A corollary is that quite different $G(\tau)$'s can often lead to the same time or frequency response within normal experimental error. We shall discuss specific examples below.

B. Pareto distribution and CPE response

The usual Pareto DRT[17] may be written $G(\tau) = (\tau/\tau_p)^{-\nu}$, with $0 < \nu < 1$, τ_p a scaling factor, and $G(\tau) = 0$ for $\tau < \tau_p$. When one considers the above $G(\tau)$ with such truncation, or without truncation, over the above full τ range, it is non-normalizable[3,9] but leads to transient response proportional to $(t/\tau_p)^{-\nu}$ and to frequency response, at the impedance level for a conductive system and at the complex dielectric constant level for a dielectric system, of the form $(i\omega\tau_p)^{\nu-1}$. Since the $t \to 0$ and $\omega \to \infty$ limits do not exist, the normalized response functions $I(\omega)$ and $A(t)/A(0)$ cannot be given for this response. Nevertheless, it is of great importance because very nearly all small-signal data which involve more than a single relaxation time (i.e., nearly all small-signal data) show a finite-length region of $t^{-\nu}$ and/or $\omega^{\nu-1}$ response. One form of such response in the frequency domain has been termed that of a constant phase element (CPE), a circuit element which is associated with some kind of property distribution which leads to the above $G(\tau)$ form. The name CPE follows because the phase angle is independent of frequency as long as $(i\omega\tau_p)^{\nu-1}$ response holds.[9,10,18]

Some recent theoretical work leading to CPE response appears in Refs. 19–22 and in the reference cited in the present Ref. 9. However, many treatments do not limit CPE response to a finite frequency range, necessary for physical realizability. It is not well known that Schrama[23] long ago showed that the CPE with $\nu = 0.5$ could be related to an infinite ladder network (see later discussion) with all the R's and C's the same. He then demonstrated that in the continuum limit the response was completely analogous to that of an infinite-length uniform transmission line, equivalent to uniform diffusion in a right half-space. Similarly, for $\nu \neq 0.5$ he first derived a discrete lattice network approximation and then showed that in the continuum limit the response was that of a specific nonuniform transmission line, or nonuniform diffusion. When $\nu \neq 0.5$, the resistors and capacitors in the ladder network approximation show scaling behavior for successive R's and C's, with the R's increasing when $\nu > 0.5$ and decreasing for $\nu < 0.5$. The successive C's show opposite behavior. Still, another different model for the CPE was developed independently of Schrama's work by Scheider.[24] He found that a CPE response could be modeled by various kinds of branched (hierarchical) infinite ladder networks with constant series resistance and parallel capacitance elements per unit length. In one type of network he replaced each elemental parallel capacitance of the ladder network by another branched ladder network. He also discussed branching of these first-order branches as well. He found that the admittance of such systems involved CPE-like behavior with discrete values of ν for the range $0 < \nu \leqslant 0.5$.

As already mentioned, it is physically unrealistic for the CPE response to extend to the extremes of time or frequency. This problem may be avoided by defining a Pareto $G(\tau)$ as nonzero only over the physically plausible range $0 < \tau_0 \leqslant \tau \leqslant \tau_\infty < \infty$. Such a doubly truncated distribution corresponds directly to a type of exponential DAE (EDAE) when thermal activation is present, one which is discussed in Sec. II E. We shall further discuss the physical/statistical rationale for these associated distributions in that section.

C. Gaussian distribution

The use of a Gaussian distribution for $G(\tau)$ involving the variable $\ln(\tau/\tau_G)$, often called the Wagner distribution, goes back a long time.[25] So also does the corresponding Gaussian DAE,[4,7] but it has been independently employed recently[26–31] with the implicit or explicit assumptions $\theta_j = 0$ and $0 \leqslant \tau \leqslant \infty$ or $0 < \tau \leqslant \infty$. Note that a Gaussian distribution has finite moments of all orders. Although the use of a full Gaussian distribution in Eq. (5) formally requires the limits $-\infty$ and ∞ for $\mathscr{E}$, it is actually only necessary for the lower and upper limits of $\mathscr{E}$ to be sufficiently smaller and larger, respectively, than some central $\mathscr{E} = \mathscr{E}_C (> 0)$ that the Gaussian function be negligible outside the resulting range. Thus, when we speak subsequently of a Gaussian distribution it should be understood to mean such a truncated function with limits of $\mathscr{E}$ between and including 0 and ∞ or a lesser finite range. Because of the use of a logarithmic variable in the Wagner distribution, a temperature-independent $F(\mathscr{E})$ of Gaussian form leads to the Wagner $G(\tau)$, also of Gaussian form. But note that a Gaussian DAE (GDAE) may either be temperature independent or temperature dependent.

A Gaussian distribution describes the behavior of a sum of very many independent, identically distributed random quantities. One physical model appropriate for the GDAE situation is that where there is a Gaussian distribution of barrier heights and the specific barrier seen by a particular relaxor at a given instant arises from the sum of random contributions from neighbors of the given relaxing entity, these contributions are taken to be independent and thus uncorrelated. Clearly, these assumptions will not always be physically plausible for either dielectric or conductive systems. However, it is worth mentioning that Van Weperen *et al.*[32] presented a theory in 1977 of dipole-dipole interactions which predicted a very nearly Gaussian distribution of activation energies.

Since the present author has recently published a paper[33] where the predictions of a Gaussian $F(\mathscr{E})$, along with a θ_j parameter possibly not zero, together with a finite extent for the Gaussian distribution, are explored in detail (general GDAE), compared with corresponding predictions of a general exponential distribution of activation energies situation (EDAE), and also used to analyze experimental data, only a few general results will be mentioned here. It is found that even when $\theta = 0$, response results for $-I''(\omega)$ vs $I'(\omega)$ or vs $\log(\omega)$ may be unsymmetrical when the distribution is itself unsymmetrical (limits not symmetrical about $\mathscr{E}_C$). Much actual response data are indeed found to be unsymmetrical, a result which does not generally follow from Eq. (5) with a Gaussian $F(\mathscr{E})$ in the conventional approach in which $\mathscr{E}_0$ is taken zero and $\mathscr{E}_\infty$ infinite. Further, and quite surprising, it is found that even when $\theta_j \neq 0$, exactly the same kind of unsymmetrical response obtained with $\theta_j = 0$ is found but, nevertheless, this parameter may be estimated from response data.

Finally, it should be pointed out that a Gaussian distribution can never lead to power-law $(t/\tau_P)^{-\nu}$ and $(i\omega\tau_P)^{\nu-1}$ behavior over a t or ω range of finite length, even when $\theta_j \neq 0$, except, of course, at the extremes of frequency where single-time-constant behavior dominates. Nevertheless, as shown elsewhere,[33] the GDAE model can approximate power-law behavior for a limited frequency range and thus Gaussian distributions should certainly not be eliminated from consideration when fitting new data.

D. Levy distribution and SE-WW response

1. General

The Lévy α-stable DRT (which involves a parameter ν, here again restricted to $0 < \nu < 1$), like the Gaussian distribution, also describes the behavior of a sum of independent, identically distributed random variables.[34–36] But unlike the Gaussian distribution, the Lévy distribution defined over the range $0 \leqslant \tau \leqslant \infty$ has no finite moments, an impossibility for processes occurring in a material of finite size. In addition, this distribution is inconsistent with a temperature-independent DAE, thus limiting its range of applicability. Incidentally, the $\tau \to 0$ asymptotic form of the Lévy distribution is just the Pareto distribution. The Lévy DRT probability den-

sity has been derived[11] for $\nu = 0.5$, and, in the present notation, the corresponding normalized[3] $G(\tau)$ is $(4\pi\tau_L\tau)^{-1/2}\exp(-\tau/4\tau_L)$, where τ_L is a constant relaxation time and $0 \leqslant \tau \leqslant \infty$.

In spite of the above anomalies of the Lévy distribution from a physical point of view, it, and the response associated with it, have been of great interest for analyzing small-signal transient and frequency response in recent years. In this section we shall take θ_j identically zero since no response has been calculated thus far using the Lévy distribution with $\theta_j \neq 0$.

The transient response associated with the Lévy DRT (LDRT) is readily obtained and turns out to be of the form of a stretched exponential (SE),

$$q(t) = q_0 \exp[-(t/\tau_L)^{\nu}], \tag{10}$$

where $q(t)$ might describe the decay of electric polarization of a charged dielectric material when it is shorted. An expression of the form of Eq. (10) was suggested in the mechanical relaxation area very long ago by Kohlrausch.[37] The derivative of Eq. (10), proportional to a current, is just

$$A(t) = -\nu(q_0/\tau_L)(t/\tau_L)^{-(1-\nu)}\exp[-(t/\tau_L)^{\nu}], \tag{11}$$

yielding Pareto-type $(t/\tau_L)^{-(1-\nu)}$ response for $t \ll \tau_L$. Thus, the short-time (not long-time) tail of the response is a power law. Note that $A(0)$ does not exist, indicative of one of the problems of the LDRT without cutoff. An interesting comparison has recently been given[38] of three theories for disordered systems involving quite different physical mechanisms but all leading, at least under some conditions, to SE or nearly SE response.

Although, as we have seen, the LDRT transient response, the SE, is simple in form, it turns out that the associated $I(\omega)$ response is not. It can be expressed in terms of slowly converging series or as difficult integrals whose integrands oscillate very rapidly for some ranges of interest. Thus, it has been generally impractical to obtain accurate values of the LDRT $I(\omega)$ function for arbitrary ν, τ_L, and ω values for fitting to experimental frequency response data. However, use of approximate $I(\omega)$ results for such fitting was first carried out by Williams and Watts[39] (WW) some time ago. Thus, we shall use the acronym WW to refer to the LDRT frequency response and shall use SE for the corresponding time response. Recently, accurate tables of WW response have been published,[40] but they alone still do not allow accurate small-signal frequency response fitting to be carried out. Of course, without the availability of a means of accurate fitting, one cannot make a sensible decision as to whether a particular set of data is best fit by WW or by some other type of response. We shall return to this important matter and its solution for WW response a little later.

2. Fitting, limitations, and ambiguity

The SE-WW response functions have been used for the analysis of data from a remarkable range of materials involving mechanical,[37,41–43] dielectric,[39,44] NMR,[45] dynamic light scattering,[46] and spin-glass remanent magnetization[47,48] experiments. This is an illustrative but not inclusive listing. Much of the experimental work has dealt with amorphous materials, e.g., polymers and spin glasses. Unfortunately, however, it is fair to say that none of the fitting carried out thus far has been definitive, either because the data extended over too narrow a range and/or because no alternative fitting models were considered. Furthermore, much of the fitting has been carried out for thermally activated systems which are likely to have a temperature-independent DAE, even though SE-WW response is formally inconsistent with such a DAE. Although fitting of temporal data to Eq. (10) can be readily achieved using a weighted nonlinear least-squares procedure, it is essential to verify that Eq. (10) is more appropriate than other possible choices. If one makes the reasonable assumption that the $q(t)$ range covered should be at least $0.01 \leqslant q(t)/q_0 \leqslant 0.99$, one finds that the data must cover somewhat more than five decades of time for $\nu = 0.5$ and more than 13 for $\nu = 0.2$!

It is always desirable to fit putative SE data to more than one fitting equation, not just to Eq. (10). The problem is well illustrated by results of Lindsey and Patterson[49] who compared $q(t)$ response for two models by least-squares fitting the SE equation to Davidson–Cole[2] (DC) $q(t)$ results. They found that although the DRTs themselves are very different for the two models, the $q(t)$ curves for them were nearly indistinguishable, especially for $\nu > 0.4$. Thus, only with very accurate data can one hope to distinguish between the two such fitting equations and be able to choose the most appropriate one.

An example of fitting ambiguity in the time domain arising from too narrow a range of measurement time for adequate discrimination is afforded by recent work of Aharoni.[50] He showed that data[47] for the decay of remanent magnetism in a spin glass can be fitted very well by a function arising from the assumption of a gamma DRT. But the data fit a SE equally, as well. A range of only three decades of time was available and the above $q(t)/q_0$ conditions were very far from being satisfied since the ν used in the SE was only 0.175! Incidentally, it is worth noting, since it was not mentioned by Aharoni, that the gamma distribution in untruncated form, as employed in his work, has been used, or proposed for use, in the relaxation area much earlier,[51–53] and even earlier still in truncated (on the larger-τ side) form.[5,54,55] Further, these distributions are also inconsistent with a temperature-independent DAE.

Luckily, discrimination between WW and DC response is somewhat easier in the frequency domain, as shown by Lindsey and Patterson[49] and in Fig. 1. Here we have fitted accurate, normalized WW data[40] with the DC response function using complex nonlinear least squares (CNLS), a procedure which fits both real and imaginary parts simultaneously.[56] The results are shown plotted in the complex $I^* \equiv I' - iI''$ plane. The frequency response data clearly do not need to be as accurate as the transient data to allow adequate discrimination, at least in the present WW-DC situation. Here ψ_{WW} is the present ν, and ψ_{DC} is a corresponding exponent parameter appearing in the DC equation. The direction of increasing frequency is shown by the arrows.

One reason we have stated that no SE-WW fitting carried out so far has been definitive is that little or no such fitting has compared alternate model predictions, and be-

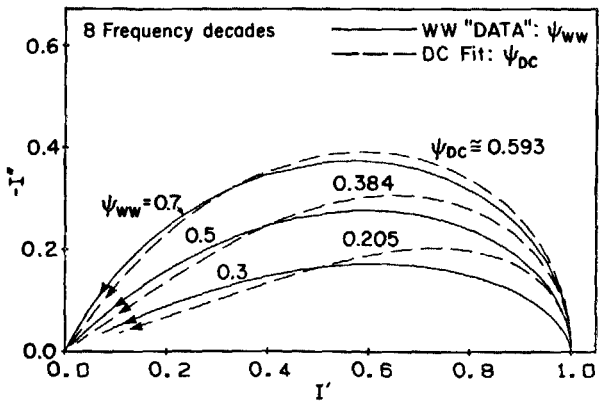

FIG. 1. Complex plane comparisons of accurate WW "data" with results obtained from CNLS fitting using the Davidson–Cole response model.

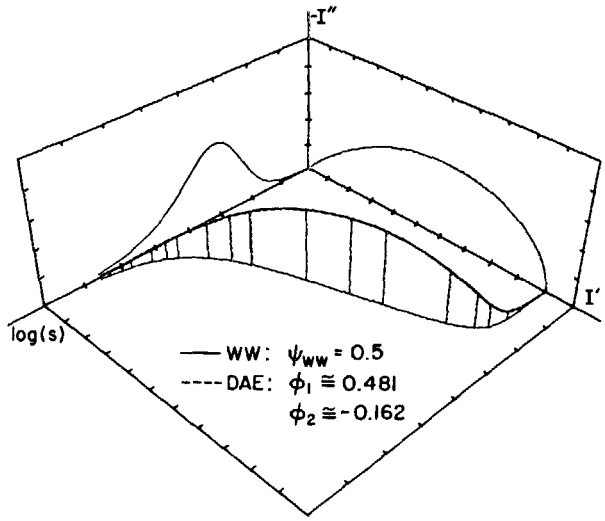

FIG. 3 Three-dimensional perspective plot showing the comparison of accurate WW response (solid lines) with response obtained by fitting the EDAE model to the data with CNLS (dashed lines). Here $s \equiv \omega\tau_0$ is a normalized frequency.

cause, until recently, accurate CNLS fitting of frequency response data to the WW model (LDRT) has been impractical. Usually, approximate fitting of $U''(\omega)$ vs ω alone has been carried out, e.g., see Refs. 27, 57, and 58. But this procedure may add even further ambiguity, even if the model can be evaluated quite accurately, because it is sometimes found that in fitting a model with several parameters to range-limited $U''(\omega)$ data alone, more than one set of different parameter values will yield a good fit, ambiguity which is eliminated when $U'(\omega)$ and $U''(\omega)$ are fitted by CNLS simultaneously to the same model over a considerable range of frequencies.

Although the WW and DC model predictions may be well discriminated in the frequency domain, other models can indeed mimic WW response closely. Figure 2 shows CNLS fit results of the general exponential distribution of activation energies (EDAE) model, discussed later, to accurate WW "data." Figure 3 shows some of the same fitting results plotted in 3D perspective form,[59] indicating the good fit in frequency obtained, as well as the complex-plane curve shape. Again discrimination of even excellent real data using CNLS would be most difficult even for the $\psi_{WW} = 0.3$ set of Fig. 2.

Then is all lost? No. If results are available for a range of temperatures as well as frequencies, one will generally be

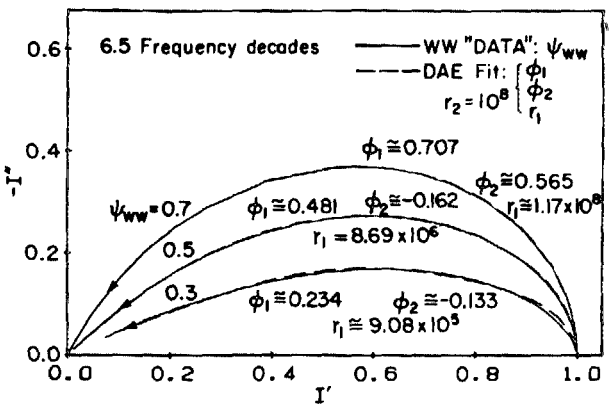

FIG. 2. Complex plane comparisons of accurate WW "data" with results obtained from CNLS fitting using the general EDAE model. Here ψ_{WW} is the ν of Eq. (10).

able to discriminate between ambiguous models such as the WW and EDAE on the basis of the temperature dependencies found for some of the parameters of the models (see Ref. 9 and Sec. II E below). Further, when distributed data are available over a sufficiently wide frequency range, one will expect to see the appearance of limiting single-time-constant response at sufficiently low and high frequencies (assuming that the distributed response of interest is well separated in frequency from any other response present). In such regions the finite-range distribution has run out of relaxation times. The transition to such response has actually been observed in some conductive systems.[60] But response functions such as those of Davidson and Cole and the WW response do not exhibit such behavior at both extremes, and thus will usually yield poorer CNLS fits than an allied "ambiguous" model such as the EDAE, one which does involve such limiting responses.

Perhaps in part because of the apparent good, but usually far from definitive, fitting success of the SE-WW in the time and frequency domains, there have been many theoretical statistical or semimicroscopic models proposed which lead to the SE, or to something close to it, for physical processes occurring in one to three dimensions.[61–73] Again, this is a representative but not exhaustive list. However, such theories do not usually lead to quantitative dependence of ν on temperature unless they involve a DAE. Nevertheless, as Shlesinger and Montroll[69] have pointed out, the (apparently) successful use of the SE-WW model by many investigators to fit their data has led to its establishment as "a 'universal' model for a wide class of materials, especially polymerics and glasses." However, since the fitting on which this conclusion is based has generally been inadequate, the conclusion is not necessarily well justified.

Thus, in spite of the undoubted usefulness of the SE-WW model, particularly for limited data ranges, and the current interest in it, it should not, in fact, be considered a "universal" model. There are several interrelated reasons.

First, and perhaps least important, is that it is associated with a nonphysical DRT, the LDRT. But this deficiency may be readily eliminated by restricting the range of τ over which the LDRT is nonzero to $0 < \tau_0 \leqslant \tau \leqslant \tau_\infty$, with τ_∞ possibly even infinite. Second, the LDRT is inherently inconsistent with a temperature-independent DAE, certainly a departure from "universality." More important, in spite of the lack of really definitive fitting of the SE-WW model to data, it is obvious that there is a great deal of real response data that this model can never fit. As shown by Figs. 1 and 2, WW response is inherently skewed to the right (for $0 < \nu < 1$), but much data lead to symmetric curves and even a little to left skewing.[9]

It is worthwhile to conclude this section with a brief discussion of recent developments in WW fitting techniques. Even though no useful, exact closed-form expressions for WW $I'(\omega)$ and $I''(\omega)$ response exist, it is now possible to use CNLS to analyze $U(\omega)$ data sufficiently well to yield direct $(U_0 - U_\infty)$, τ_L, and $\nu \equiv \psi_{WW}$ estimates accurate to about 0.1% for good data.

Recently, Weiss, Bendler, and Dishon[58] have used accurate WW tabular data[40] to develop an analysis method which uses only a few points of $U''(\omega)$ data to yield separate estimates of the above parameters sequentially. This is not a least-squares method, and it uses only a small part of the total data. Nevertheless, it can yield helpful initial parameter estimates for use in the following true CNLS approach.[74] It has been found that a simple addition to the empirical Havriliak–Negami[75] frequency response function allows the result (the HNC) to fit WW response exceedingly closely. Some results are shown in Fig. 4 and ones for a wider range of ψ_{WW} appear in the original paper.[74] By means of a reparametrization of the fitting model, its use with CNLS fitting yields very accurate direct estimates of the above parameters (and their estimated standard deviations). The CNLS program incorporating this fitting model, and many more, is available from the author. Only by comparing experimental results to predictions of several different theoretical models by some powerful procedure such as CNLS can one hope to establish which model is the more appropriate, and thus find the most plausible set of parameter estimates with which to characterize and interpret the response.

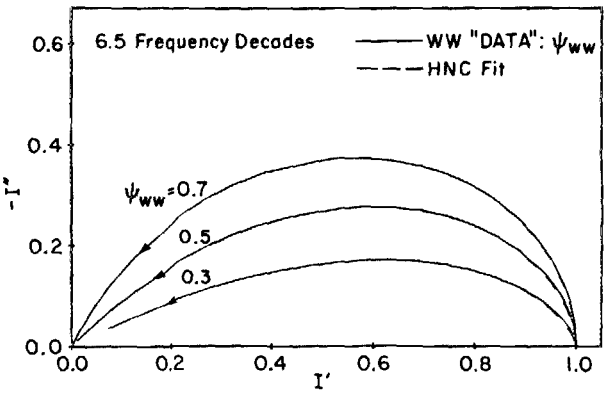

FIG. 4. Complex plane comparisons of accurate WW "data" with results obtained from CNLS fitting of a modified Havriliak–Negami response model (HNC).

E. Exponential distributions and response

1. General

Here we shall be concerned entirely with DAEs related to the doubly truncated Pareto power-law DRT discussed earlier. When the system is thermally activated and thus τ is given by an equation of the form of (4), then the DRT leads directly to a DAE; conversely, the assumption of a DAE with exponential probability density (EDAE) implies a Pareto-type DRT. Montroll and Shlesinger,[76] in a treatment of long-tail distributions, have shown that essentially the Pareto distribution follows from a log-normal distribution, one where overall "success" requires the execution of numerous independent subtasks, each of which must be successful for overall success to occur. Further, the Pareto distribution implies self-similar scale-invariant behavior over its range of applicability. Further rationale and theoretical work leading to an EDAE are discussed in Sec. II E 2 below.

Suppose we start with a single exponential DAE ($EDAE_1$) and take, for $\mathscr{E}_0 \leqslant \mathscr{E} \leqslant \mathscr{E}_\infty$,

$$F(\mathscr{E}) = N \exp(-\eta E) \equiv N \exp(-\lambda \mathscr{E}), \tag{12}$$

and $F(\mathscr{E}) = 0$ otherwise. Here $\lambda \equiv kT\eta$, N is a normalization constant, and η is a probability density strength parameter which must be temperature independent to yield a temperature-independent DAE. Then the relation $G(\tau)|d\tau| = F(\mathscr{E})|d\mathscr{E}|$ along with Eq. (4) for τ leads directly to the associated DRT

$$G(\tau) = N_1 \tau^{-(1+\gamma^{-1}\lambda)}, \tag{13}$$

where N_1 is a new normalization constant and comparison with the Pareto form of Sec. II B yields $\nu = (\gamma + \lambda)/\gamma$, certainly not a temperature-independent quantity, even when γ and η are, unless $\eta = 0$ (implying a constant probability density over a finite range).

In order to achieve more generality than is possible with an EDAE with a single strength parameter η, the earliest work in this area, a transient response calculation[5] with (implictly) $\alpha = 1$ and $\beta = 0$, considered two joined exponential probability densities with parameters η_1 and η_2. One might ask why an EDAE should ever need to include more than the one exponential region of the $EDAE_1$. The reason is largely empirical for the present: the data often require two such regions[9,57] for adequate fitting, and in particular, two regions are needed to yield unskewed, symmetric response. Conversely, only two or less such regions seem to be required. The single $EDAE_1$ model leads to inherently asymmetrical response in the frequency domain, response involving a finite-length region of ω^p behavior with $p = 1$, followed at larger ω by a finite-length region of ω^{-n} response with $0 \leqslant n \leqslant 1$. But much data yield symmetric curves in the complex plane, ones for which $p = n \equiv m$ and $0 < m \leqslant 1$. Finally, considerable data involve response with regions for which $p \neq n$ and $p < 1$, as well as $n < 1$. Such general response is asymmetric like that of the $EDAE_1$ but cannot be well fitted by that simple model. Recently a detailed study of the frequency response predictions of the general EDAE has been carried out[9,33] without the above restrictions on α and β. Because of the existence of this work, we need only summarize a few results and conclusions here.

It turns out that, unlike the case for the Gaussian DAE, the θ parameters of the model combine directly to yield the two composite parameters

$$\phi_m \equiv \theta - \gamma^{-1}\eta_m kT \equiv (\chi - \lambda_m)/\gamma, \tag{14}$$

where $\lambda_m \equiv \eta_m kT$ and $m = 1,2$. These parameters are clearly different from ν, especially since it is found that their range is $-\infty < \phi_m < \infty$ rather than $0 < \nu < 1$. Such an unlimited range is important here. Even when α and β (and so γ), as well as the η_m's, are temperature independent, Eq. (14) shows that the ϕ's may depend linearly on absolute temperature and a $|\phi|$ may thus readily exceed unity. In the conventional $\beta_j = 0$ case (no thermal activation directly associated with energy storage processes), it turns out[9] that Eq. (14) can lead, under reasonable assumptions, to $\phi_m = BT$ for dielectric situations and to $\phi_m = A - BT$ for conductive ones. Here A and B are temperature-independent constants. These quite different responses are indeed found to be present in much data for these different kinds of systems (see, for example, Refs. 9 and 33, and references cited therein).

It further turns out that when $\phi_2 \geqslant 0$, meaningful response results are only obtained for the range $0 \leqslant \mathscr{E}_0 \leqslant \mathscr{E} \leqslant \mathscr{E}_\infty < \infty$ over which $F(\mathscr{E})$ is nonzero although it is mathematically unnecessary for $\mathscr{E}_\infty$ to be finite otherwise. For convenience, three EDAE response situations have been defined: the $EDAE_1$, where $\phi_1 = \phi_2 \equiv \phi$, a simple exponential distribution situation, the $EDAE_2$, where $\phi_1 = -\phi_2 = \phi \geqslant 0$ and a central $\mathscr{E}_C \equiv \mathscr{E}_1$ satisfies $(\mathscr{E}_\infty - \mathscr{E}_1) = (\mathscr{E}_1 - \mathscr{E}_0)$, or equivalently, $(\mathscr{E}_\infty - \mathscr{E}_0) = 2(\mathscr{E}_1 - \mathscr{E}_0)$, and finally the general EDAE where no restrictions are set on the ϕ's. The double exponential distribution of the $EDAE_2$ case is known as the Laplace distribution.[77] The DRT range parameters, r_1 and r_2, are given by $r_1 \equiv \tau_1/\tau_0 \equiv \exp[\gamma(\mathscr{E}_1 - \mathscr{E}_0)]$ and $r_2 \equiv \tau_\infty/\tau_0 \equiv \exp[\gamma(\mathscr{E}_\infty - \mathscr{E}_0)]$. For the $EDAE_2$, $r_1 = \sqrt{r_2}$, and one obtains fully symmetric response behavior. By contrast, the $EDAE_1$ yields[9] skewed curves in the complex plane, skewed to the right for $\phi > 0$ and to the left for $\phi < 0$. Furthermore, as $|\phi| \to \infty$, the response approaches single-time-constant Debye behavior. Incidentally, although closed-form analytical expressions can be given[9] for $EDAE_1$ and $EDAE_2$ frequency response for many specific values of ϕ, these expressions are useless for CNLS fitting; thus such fitting is carried out in the author's fitting program for both the EDAE and the GDAE using accurate numerical evaluation of their integral representations. On the other hand, closed-form analytical expressions for the corresponding EDAE transient response are available for any ϕ values.[5]

Although the earlier transient response calculation[5] for the EDAE involves the full composite $F(\mathscr{E})$ mentioned above, it does not include arbitrary θ values. But the presence of separate α and β values can be readily accounted for and only transforms the definitions of the slope parameters rather than changes the form of the response.

2. Fitting, ambiguity, and justification

Considerable transient and frequency domain responses for the EDAE have already been presented.[5,8,9] In addition, Figs. 2 and 3 show how well the general EDAE can simulate WW response. Figure 5 shows similar CNLS fits of the particular $EDAE_1$ model to accurate WW response. We see that, except for ψ_{WW} of 0.7 or greater, there is too much difference in the forms of the models to allow good fits. But the added degrees of freedom of the general EDAE model do allow good fits to be obtained.

The fitting ambiguity for the WW and EDAE models mentioned above and earlier is by no means unique. For symmetric frequency response data, it has been found[4,8,9,33,78] that the Cole–Cole,[1] Fuoss–Kirkwood,[79] and $EDAE_2$ models can all fit each other exceptionally well for usual experimental ranges of variation. In addition, the EDAE can fit GDAE data well.[33] Furthermore, for asymmetric curves, the $EDAE_1$ model can fit very well that of Davidson–Cole[2] and two asymmetric Jonscher "universal dielectric response" models.[9,57] Thus, for ordinary data there are a great deal of fitting ambiguities usually present. Although the presence of some fitting ambiguity has been known for a long time,[4,78] the amount and degree of ambiguity has been recently extended by CNLS fitting comparison of the predictions of the various models. Fitting ambiguity can be reduced or removed, using CNLS fitting comparisons, however, if one has available very accurate data extending over a very wide frequency range. It can also be greatly reduced or even eliminated, as already mentioned, if one carries out measurements for a range of different temperatures. If the data are found to be distributed, nearly always the case, one can next determine whether thermal activation is present. Furthermore, by examining curve shape and the possible temperature dependence of the n exponents in regions of $\omega^{\pm n}$ frequency response, one can usually determine whether only a DRT is present or, more likely, a DAE leading to a DRT. Then by CNLS fitting with several plausible models one can determine the most appropriate one and obtain its best-fit parameter estimates.

As an example, we consider what information could be obtained from an EDAE fit to thermally activated, distributed frequency response data. Suppose the data are for a dielectric situation and are symmetric so the $EDAE_2$ may be used. A CNLS fit at a given temperature of a circuit involving a

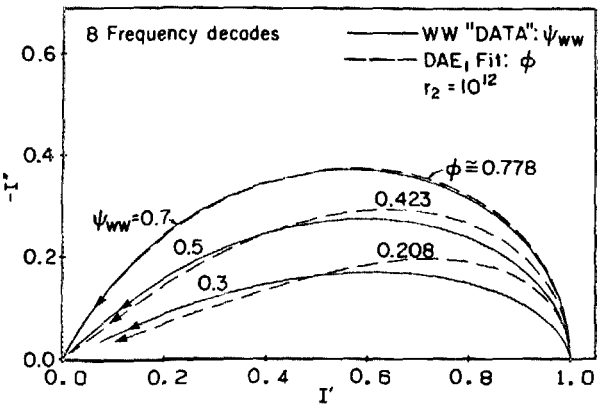

FIG. 5. Complex plane comparisons of accurate WW "data" with results obtained from CNLS fitting of the $EDAE_1$ model with the parameter $r_2 \equiv r = 10^{12}$ taken fixed.

geometric capacitor C_∞ and the $EDAE_2$ distributed model directly yields estimates of $(\epsilon_0 - \epsilon_\infty), \epsilon_\infty, \phi, X_S \equiv \ln(r_2) = \gamma(\mathscr{E}_\infty - \mathscr{E}_0) = 2\gamma(\mathscr{E}_1 - \mathscr{E}_0)$, and $\tau_1 \equiv \tau_a \exp(\gamma\mathscr{E}_1)$. From this one fit, one thus obtains estimates of $\epsilon_0, \epsilon_\infty, \phi, \gamma(E_\infty - E_0) = 2\gamma(E_1 - E_0)$, and τ_1. Now it has been shown[9] that in the $EDAE_2$ case, where $\phi_1 = -\phi_2 = \phi$, it is necessary to take $\eta = \eta_2 = -\eta_1 > 0$ to obtain a peaked (Laplace) probability density. Then $\phi = (\beta + kT\eta)/(\alpha + \beta)$ in the present case, increasing linearly with temperature (when α, β, and η are temperature independent), as is indeed usually found experimentally. Such behavior is an intrinsic, measurable prediction of an EDAE model and does not depend on the empirical assumptions required in other types of theories and models to obtain such dependence. It is thus one of the most important consequences of the model and can help greatly in identifying the presence of a DAE.

When results for more than one temperature are available, we can extract estimates of $\tau_a, \gamma E_0, \gamma E_1, \gamma E_\infty, (\beta/\gamma)$, and (η/γ), all of which, except possibly τ_a, might, in a complicated situation, be temperature dependent. But if we require that η be temperature independent, we can obtain the temperature dependence of γ, if any, instead of just that of η/λ. Temperature dependence of α and β is indeed possible if there is a glasslike transition in the material or the often found linear relation between activation entropy and enthalpy,[5,80] or both.[5,9,33] Next, analysis of the fitting results with or without temperature dependence of α and/or β will allow these quantities and γ to be determined within a scale factor. If this can be determined from measurements of another type on the material or by setting, say, $\alpha = 1$ in appropriate situations, one can obtain estimates of the important β, η, E_0, E_1, and E_∞ parameters of the material. Quantities such as η, E_0, E_1, and E_∞, which specify the strength, shape, and extent of the activation energy distribution, are important material parameters of the system, and their estimation in actual situations is a useful step towards the development of a fully microscopic theory leading to DAE-like response.

The DAE model does not require that E_0, E_1, and E_∞ be temperature independent, but if they and/or γ are not, τ_1 will not in general show simple Arrhenius behavior. It is indeed plausible in most cases to assume the E's are temperature independent and from the fitting results determine the temperature dependence, if any, of α and β. If they, in turn, are temperature dependent, we may be able to extract from their dependence the constant temperatures T_0 and/or T_∞ associated with the linear $\Delta S, \Delta H$ relation or with a glasslike transition, respectively. The above discussion shows that the parameter estimates which may be obtained from data fitting are a mixture of macro- and microscopic quantities. Nevertheless, they can shed much light on the possible physical processes occurring in the material.

Let us consider further the experimentally common, distributed, thermally activated situation. The most plausible explanation for a DRT will then be the presence of a DAE. The DAE might involve distributed state energies involved in hopping, trapping, spin flips, etc. But only the GDAE and EDAE models, of those considered here, yield temperature-independent DAEs, and only these models, of all those widely used in the past, such as those of Cole and Cole,[1] Davidson and Cole,[2] and Williams and Watts,[39] also yield plausible physically realizable response in both the high- and low-frequency limits of the single dispersion region considered. But although both the GDAE and EDAE models can yield either symmetric or skewed response, only the EDAE leads to the finite-length regions of t^{-n} and $\omega^{\pm n}$ response nearly always observed experimentally. Finally, it has been shown[8,9,33] that the EDAE model can very well simulate virtually all other empirical or semiempirical models which have been used in the past to fit small-signal data for an exceedingly wide variety of materials. Thus, it can fit the data as well, and in addition, leads to explicit temperature dependence of slope exponents such as the ϕ_m. Thus, it appears that the EDAE might well be considered the initial fitting model of choice, especially when a temperature-independent DAE is suspected, although alternative fitting with the GDAE is also worth trying when no appreciable $\omega^{\pm n}$ regions appear.

We have already seen what sort of parameters associated with a DAE may be derived from frequency-temperature data fitting of appropriate data. Since the EDAE is a semimacroscopic model, we cannot expect to use it to derive all the microscopic parameters of the system. In the present absence of an n-body microscopic-model solution which yields very similar overall response (necessary for agreement with experiment), the EDAE fills an important gap. Because of its importance and the presence in this model of features one would expect even in a microscopic model, it is worth giving some more discussion of the statistical and physical content of the model.

If one restricts attention to only the skewed $EDAE_1$ model, which involves a simple exponential density of states (EDOS), one finds considerably[80–90] less general but sometimes more microscopically based work than that in Refs. 5 and 9 (see also references in these papers). Different kinds of glass transitions have been predicted to yield either a Gaussian or an exponential DAE.[90] Although it has been stated that power-law transient decay (Pareto distribution in τ) is only consistent with an EDOS and is thus its signature, this is only true if the material is thermally activated. But tunnelling can yield approximate power-law dependence,[91] and various models can lead to power-law response without thermal activation. But when such activation is indeed present, one expects to find characteristic temperature dependence of the power-law exponents, yielding a way to distinguish between a DRT alone and a DAE and its associated DRT.

It is worth noting that Monroe and Kastner[92] have found very accurate power-law response for transient photocurrent measurements on As_2Se_3 over more than nine decades of time, involving a range parameter r_2 of nearly 10^5 and a temperature-dependent exponent less than unity. Considerable progress has been made recently in explaining the presence of an EDOS in disordered materials,[89,90] but further progress is needed for three-dimensional systems and to explain the $EDAE_2$ Laplace distribution.

One can also give some further statistical and stochastic underpinning for the use of an EDAE or Laplace distribution. For example, consider events occurring at random in

time and assume that the future lifetime, x, of an individual has the same distribution no matter what its current age. Then the probability density of x is an exponential distribution (see Ref. 17, p. 208). Furthermore, "if a system is modeled by a finite Markov chain which is ergodic, the passage time from some specified initial distribution over the state space to a subset B of the state space visited infrequently is often exponentially distributed to good approximation."[93] Finally, the more general Laplace distribution mentioned above and used in the $EDAE_2$ model may be considered to be the distribution of the difference of two independent random variables with identical exponential distributions.[77] These statements and their generalizations are certainly suggestive and should find places in future statistically and microscopically based treatments of dielectric and conductive systems.

Important conclusions discussed in this section are that experimental and theoretical DAEs have been widely used in the past; the EDAE can fit very well the response of nearly all earlier two- or three-parameter heuristic frequency response models and thus as well all thermally activated data they have been used to fit; and complex nonlinear least-squares data fitting should be much more used in fitting models to frequency data in order to obtain better resolution between competing models. Although DAE models, such as the GDAE and EDAE, are more complex than empirical models such as that of Cole and Cole or even William–Watts, they contain greater physical content and are more physically realizable. The price paid is the appearance of a larger number of parameters than present in the other approaches. But the DAE model parameters are related to real physical properties of the material associated with its DAE. For example, the empirical models usually contain no information about the temperature dependence of their fractional exponent parameters such as the ν of Eq. (10) or the ψ of the Cole–Cole response. Because of the limitation of these parameters to the range 0–1, they cannot depend directly or inversely on temperature over an appreciable temperature range. But the Eq. (14) ϕ_m parameters of the EDAE are not thus limited in range and can involve such frequently found experimental behavior.[8,9]

Most of the heuristic response models are not fully physical because they do not involve the physical limitations inherent in the present DAE models of requiring finite maximum and minimum relaxation times. In the absence of other limitations, a minimum relaxation time is set as usual by the finite speed of light and/or by inertial effects, and a maximum effective relaxation time by the finite size of the experimental sample or by the inherent noise level of the process considered. In thermally activated situations, the limitation of a maximum activation energy less than infinite (the model does not and need not consider energies which lead to other processes such as melting) also leads to a maximum finite relaxation time. Finally, a recent paper[33] compares the present GDAE and EDAE models in detail and uses them in analyzing $(KBr)_{0.5}(KCN)_{0.5}$ dielectric data.[27]

III. STRUCTURE AND RESPONSE

We have already discussed and illustrated some of the large amount of ambiguity generally present when one uses small-signal response data to attempt to distinguish between different distributions or between distributed response models (i.e., mathematical fitting expressions). Here I shall discuss another important kind of ambiguity which can occur in the relaxation area, that involving intrinsic model structure and the structure implied by the mathematical form of the equations, or equivalent circuits, used in fitting response data.

A microscopic model may exhibit one or several kinds (or combinations of kinds) of structure (connectivity) in space, time, and/or energy. Some possibilities are parallel, sequential, or hierarchical (i.e., sequential with branching) dynamics. In a parallel situation, the system might involve a collection of independent states such that the system is unconstrained and can pass from any overall possible configuration to any other. Its response could also represent the sum of many different processes acting independently. Alternatively, one could consider a nonbranching sequential (ordered serial) system where many states or processes are possible but the $(n+1)$th process cannot occur until the nth one is complete. Finally, consider hierarchically constrained dynamics, as in the recent work of Palmer, Stein, Abrahams, and Anderson[71] (PSAA). Here various abstract levels form a branching tree structure. A given level is defined to include processes with a common type (e.g., functional form) of constraint. Thus, the constraint tree has nodes at different levels, each level involving a different constraint situation. With the usual ordering, one can say that the system cannot relax at the $(n+1)$th level until it has relaxed at the nth level.

But it turns out that the structure of the theory does not usually constrain the way its overall response can be represented mathematically or by means of an equivalent circuit. For example, the response of the hierarchical PSAA model was actually calculated using Eq. (9), with no θ_j term. But Eqs. (7) and (9) formally represent the response of a continuously distributed parallel model, the sum of independent single-time-constant exponential processes in the continuum limit. Alternatively, one may consider a finite or infinite number of discrete time constants or relaxation times. The circuit of Fig. 6(a) shows a discrete representation of such parallel response, one involving energy storage elements (capacitors) and energy dissipating elements (resistors) for the PSAA dielectric system case. But it is well known that the same response (over all times or frequencies) as that of the Fig. 6(a) circuit can be produced by the Fig. 6(b) circuit with proper (different) values of the R's and C's. But this is a ladder network which represents sequential, not parallel, response! Furthermore, its response is of continued fraction form. That the same equality between parallel and sequential response representation holds in the continuum limit (infinite ladder network) with a sufficiently regular $G(\tau)$ follows from the asymptotic expansion theorem of the theory of continued fractions.[94] This is an important conclusion.

Since we have pointed out that the $I_j(\omega)$ form applies for either dielectric or conductive systems, we must be able to draw the same conclusions as above for a conductive system. The two circuits which apply in this case are presented in Figs. 6(c) and 6(d), one being an unordered series circuit

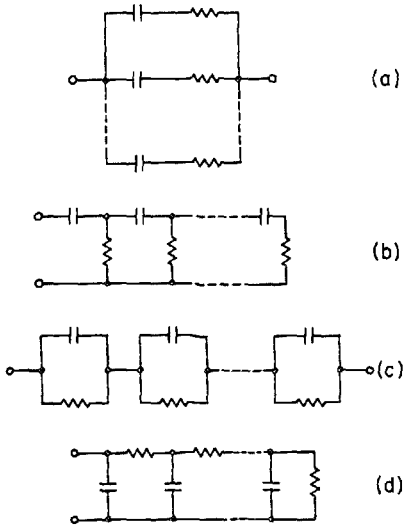

FIG. 6. Dielectric model circuits, (a) and (b), and conductive model circuits, (c) and (d). With proper component value choices, the parallel circuit of (a) and the hierarchical ladder network of (b) can exhibit the same impedance over all frequencies. Similarly, the series circuit of (c) can have the same impedance as the conducting ladder network shown in (d).

and the other a sequential ladder network.

We have already seen that the CPE/Pareto response can be represented by a DRT,[3] as in Eq. (7), by a continued fraction-ladder network,[23] or by a hierarchical circuit.[24] Yet CPE response over a finite or infinite time/frequency range is a common feature of many microscopic or semimicroscopic theoretical models, many of which involve continued fractions[19,63,95,96] at either the microscopic or overall response level. A recent example is afforded by the work of Liu.[97] He considered a fractal (self-similar) model of an interface in the conducting case and derived response in the form of a bifurcating hierarchical circuit with constant capacitances and scaled (increasing) resistance elements. Below a certain high frequency, the impedance of the Liu circuit in the limit of an infinite number of hierarchical levels is just that of the CPE. Furthermore, in this case, although it is not mentioned by Liu, the hierarchical circuit may be more simply represented as an infinite ladder network [Fig. 6(d)] whose impedance expression is thus of the form of an infinite continued fraction.

Complex least-squares fitting of appropriate data to either the Fig. 6(c) circuit or that of Fig. 6(d) (with the same number of discrete elements) will yield exactly the same fit and residuals, although the estimated parameter values will differ. But by varying controllable conditions such as sample thickness, temperature, pressure, etc., one can usually establish that one of the two circuits yields better determined parameters with less intercorrelation and less (or expected) dependence on the varied conditions. One can then conclude which approach is the more appropriate. As an example, the nested Fig. 6(d) circuit with six discrete elements was found to be much more appropriate than that of Fig. 6(c) with six elements for a detailed continuum model of the small-signal ac response of solids and liquids.[98]

In summary, virtually any physically reasonable response can be described by means of a DRT, a sum of independent elemental processes, even when the DRT itself is not physically meaningful and has no direct connection to the structure of a microscopic model. When the DRT is associated with and arises from a DAE in a thermally activated situation, its physical and information content is much higher, even though DAE behavior also leads to a response which can be represented by a circuit representing independent (parallel or series) processes or by a ladder network involving sequential (possibly hierarchical), infinite continued fraction response. The form of the fitting equation or circuit alone is insufficient to allow one to conclude that actual processes present in the material involve the same form/connectivity/constraints in time, space, or energy. The map is not the territory.

ACKNOWLEDGMENTS

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ACRONYM DEFINITIONS

CNLS:	Complex nonlinear least squares.
CPE:	Constant phase element.
DAE:	Distribution of activation energies.
DC:	Davidson–Cole.
DRT:	Distribution of relaxation times.
EDAE:	General exponential DAE.
$EDAE_1$:	Single exponential DAE.
$EDAE_2$:	Double exponential (symmetrical) DAE.
EDOS:	Exponential density of states.
GDAE:	Gaussian DAE.
HNC:	Havriliak–Negami capacitor.
LDRT:	Lévy DRT.
PSAA:	Palmer, Stern, Abrahams, and Anderson.
SE:	Stretched exponential.
WW:	William–Watts.

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