Paley–Wiener criterion for relaxation functions

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The conclusion [K. L. Ngai, A. K. Rajagopal, R. W. Rendell, and S. Teitler, Phys. Rev. B **28**, 6073 (1983)] that simple exponential decay is a nonviable model for electrical relaxation, because it fails to satisfy the fundamental Paley–Wiener Fourier transform criterion, is shown by direct analysis to be inapplicable to small-signal electrical relaxation situations. Thus, not only is exponential decay and its associated single-relaxation-time Debye frequency response a valid model for relaxation, but, by extension, all distributions of relaxations times and energies which use a superposition of simple exponentials or Debye functions are also acceptable descriptions of relaxation phenomena. Reasons why the earlier conclusion is nonviable in the present context are discussed. © *1997 American Institute of Physics.* [S0021-8979(97)05115-3]

I. INTRODUCTION

In 1983, Ngai *et al.*[1] published a paper with the above title in which it was shown that the Paley–Wiener criterion, a necessary and sufficient requirement for the existence of a Fourier transform of a given function, predicted that a relaxation function involving linear exponential decay was not acceptable. As these authors pointed out, this conclusion has far-reaching consequences. If a simple exponential relaxation function is invalid, then the superposition of such functions to produce a discrete[2] or continuous[3] distribution of relaxation times (DRT) cannot be ‘‘a viable description of relaxation phenomena.’’ Note that for a thermally activated process, a DRT can be readily cast in the form of a distribution of activation energies (DAE);[4–6] so these possibilities are also ruled out. The purpose of the present work is to demonstrate that the Paley–Wiener criterion does not, in fact, prohibit the existence of a simple exponential relaxation function as a viable model for small-signal relaxation.

Let us define the important stretched-exponential [Kohlrausch–Williams–Watts (KWW)] temporal relaxation response in conventional form[7,8] as

$$\phi_s(t/\tau_s)=\exp[-(t/\tau_s)^{\beta}], \tag{1}$$

where τ_s is a characteristic relaxation time and the exponent satisfies $0<\beta\leqslant 1$. For $\beta=1$, simple linear exponential response is obtained; for this case replace τ_s by τ_0 and ϕ_s by ϕ_0. In contrast to the $\beta=1$ situation, Ngai *et al.*[1] found that for $\beta<1$ the Paley–Wiener criterion was not violated.

Hundreds of papers are published each year which make use of a DRT or DAE, and many of them either directly involve a discrete or continuous (differential) superposition of simple exponentials, equivalent in the frequency domain to a superposition of simple one-relaxation-time Debye response functions (e.g., Refs. 2, 3, 6, and 9) or can be expressed in terms of such DRTs.[5,6,8,9] If the Ngai *et al.* results[1] are indeed applicable, these treatments must be rejected in principle, although in practice, it will usually be impossible to discriminate adequately between say $\beta=1$ and $\beta=0.9999$ situations.

Although there have been many theoretical treatments which indicate that simple exponential decay is an approximation (e.g., Refs. 10 and 11), the deviations from such a response may be vanishingly small in many cases of interest; the conclusion may not be applicable to the present situation; and, in addition, such theoretical analysis is itself idealized and approximate and cannot capture the full complexity of nature. Thus, although these considerations should not be sufficient to preclude the use of linear exponential decay in both theoretical and experimental treatments, it would be much more serious if the Paley–Wiener criterion indeed rejected the possibility of such a response. Since Ngai and associates[1] have used this criterion as the ‘‘touchstone’’ of their demonstration that $\phi_0(t/\tau_0)$ is not a valid relaxation function, it is worthwhile to examine the matter more carefully.

II. PALEY–WIENER ANALYSIS

Consider the standard form of the relationship between the normalized linear-system relaxation function, $\phi(t)$ [a causal function since $\phi(t)=0$ for $t<0$] and the associated complex system function, $I(\omega)$. Written as a Fourier transform, it is may be expressed as[6–9,12]

$$I(\omega)=\int_{-\infty}^{+\infty}\exp(-i\omega t)[-d\phi(t)/dt]dt. \tag{2}$$

For the dielectric response situation, $I(\omega)\equiv[\epsilon(\omega)-\epsilon(\infty)]/[\epsilon(0)-\epsilon(\infty)]$ and $-d\phi(t)/dt$ is the normalized transient current present when a fully charged relaxing system is short circuited at $t=0$. Thus, $\phi(t)$ is a step-function response function.[8,12] We take it to be nonnegative, nonzero,

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and square integrable. Although here we shall assume that it is nonzero over the entire range $0 \leq t < \infty$, it may alternatively be time limited and thus be zero above a particular value of t.

In order to deal with dimensionless quantities, let $x \equiv \omega\tau_0$, where τ_0 is a nonzero characteristic relaxation time or scaling factor. Then, we may replace ωt by xT, where $T \equiv t/\tau_0$. Linear exponential decay may now be expressed as

$$\phi(T) = \phi_0(T) = \exp(-T). \tag{3}$$

When one substitutes Eq. (3) into Eq. (2), rewritten with dimensionless variables, and carries out the transform, the result, not surprisingly, is just

$$I_0(x) = 1/(1+ix), \tag{4}$$

simple the one-relaxation-time Debye response. Note that its associated distribution of relaxation times is $\delta(\tau-\tau_0)$ in unnormalized form.

Consider now a general $\phi(T)$, its associated $I(x)$, a complex function, and its amplitude $A(x) = |I(x)|$. $A(x)$ also must be nonzero, nonnegative, and $A(x) = A(-x)$. By Parseval's theorem, since $\phi(T)$ has been assumed square integrable, $A(x)$ is also square integrable and vice versa. Now, according to the Paley–Wiener criterion,[13–15] a necessary and sufficient condition that a given $\phi(T)$ exists is that

$$\int_{-\infty}^{+\infty} \frac{|\ln\{A(x)\}|dx}{1+x^2} < \infty. \tag{5}$$

We can now examine whether the Paley–Wiener criterion is satisfied for the exponential relaxation function $\phi_0(T)$ of Eq. (3). It follows from Eq. (4) that $A_0(x) = |I_0(x)| = [1+x^2]^{-1/2}$. On using this result in Eq. (5), one obtains

$$\int_{-\infty}^{+\infty} \frac{|\ln\{1+x^2\}^{-1/2}|dx}{1+x^2} = \int_0^{\infty} \frac{\ln(1+x^2)dx}{1+x^2}. \tag{6}$$

The actual value of this integral is just $\pi|\ln\{A_0(1)^2\}| = \pi\ln(2)$ (Ref. 15, p. 417), showing that the criterion is indeed satisfied for simple exponential decay. These results indicate, contrary to the conclusion of Ngai *et al.* that linear exponential decay is a valid relaxation function, and by extension, a superposition of such functions to form a discrete or continuous distribution of relaxations times is also a viable description of relaxation phenomena as far as the Paley–Wiener criterion is concerned. Finally, note that a distribution with $N < \infty$ discrete relaxation times automatically satisfies the physically based criterion that the response of a system involves a nonzero smallest relaxation time and a finite largest relaxation time.[16]

III. DISCUSSION

The conclusion that $\beta = 1$ simple exponential response is nonviable has been used to emphasize the importance of $\beta < 1$ stretched-exponential response (e.g., Refs. 1, 17, 18), an integral part of the Ngai coupling response theory.[17,19–22] Although stretched-exponential response is indeed important and has often been found to yield apparently good fits to experimental data (e.g., Refs. 18, 23–25), only recently has it been possible to accurately compare experimental frequency-response data with KWW-model predictions.[25] In addition, with the above rehabilitation of the simple exponential decay model, it can also be used where appropriate.

Why is the negative conclusion of Ngai *et al.* inapplicable to the usual relaxation situation defined herein? The difference arises from their use of definitions of an energy distribution function and its Fourier transform, a complex relaxing amplitude, $c(t)$, which are not immediately relevant to small-signal relaxation in conducting and dielectric systems. Much of the work of Ref. 1 is based on an earlier analysis of Khalfin,[26] which is most appropriate for the decay of an almost stationary state, as in radioactive decay. Thus, it should not be surprising if Paley–Wiener conclusions valid for such a system are inapplicable to the present situation.

Although the meaning and usage of the $c(t)$ complex function in the time domain was not fully discussed in Ref. 1, it was later considered in some detail in Ref. 17. There, the relaxation function $\phi(t)$ was identified as the positive-time part of a function $\Phi(t)$, even in the time variable and equal to the real part of the Fourier transform of the energy distribution function. Although $\Phi(t)$ was taken as causal,[17] it is only its positive-time part, $\phi(t)$, that is causal.

Ngai and associates[1] take their $|c(t)|$ as the $A(x)$ appropriate for use in Eq. (5), but, following the work of Khalfin, they define the x variable not as frequency, as is conventional in the electrical-relaxation field,[14,15] but as time, with the Paley–Wiener denominator term written as $1+t^2$ and t not dimensionless. On setting their $|c(t)|^2$ equal to a form of the KWW response function of Eq. (1), they conclude with Khalfin that the Paley–Wiener criterion is not satisfied for $\beta = 1$. A further measure of the difference between their analysis and conventional results is their expression for their energy distribution in the $\beta = 1$ case,

$$\rho_0(\epsilon) = \tau_s/[1+(\tau_s\epsilon)^2], \tag{7}$$

where ϵ is the energy (in $\hbar = 1$ units). In the conventional DAE case, by contrast, $\rho_0(\epsilon) = \delta(\epsilon-\epsilon_0)$, where ϵ_0 is the energy associated with thermal activation of τ_0.

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