Analysis of dielectric or conductive system frequency response data using the Williams–Watts function

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The electrical, optical, and mechanical behavior of many materials, particularly polymers and glasses, have been analyzed using the Kohlrausch–Williams–Watts stretched exponential relaxation function in both the time and frequency domains. This function is currently of considerable experimental and theoretical interest. Unfortunately, no relatively simple and accurate approximation representing the small-signal frequency response of stretched exponential relaxation has been available. Thus it has been impractical to obtain accurate parameter estimates from fitting of frequency response data or to discriminate well between Williams–Watts response and that of other similar response models. Here we develop such an approximation for both dielectric systems and for intrinsically conducting ones (e.g., defect hopping materials). It is in complex form and allows fitting of both real and imaginary parts of all the data simultaneously (e.g., by complex nonlinear least squares) or of either part separately. For appropriate data, which need not be electrical, fitting with the new approximation can yield parameter estimates accurate to about 0.1%. Comparison of the results of the present fitting method to those of a more approximate one are presented.

I. INTRODUCTION

The empirical stretched exponential transient response function

$$q(t) = q_0 \exp[-(t/\tau_0)^{\beta}] \quad (1)$$

and its frequency response transform have been widely used for about the last 20 years to analyze the small-signal electrical (and mechanical and optical) response of a wide variety of materials, from polymers and proteins, to spin glasses and amorphous semiconductors. For example, for dielectric systems $q(t)$ might describe the decay of polarization of a charged sample when the electrodes are shorted. Because reasonable agreement between the above function and data has often been found, much theoretical work, either statistically based or involving a microscopic model, has appeared which leads to exact or approximate stretched exponential response. Here we shall not recite the voluminous literature involved; many of the appropriate references are given in Refs. 1–3. Since Kohlrausch[4] first suggested Eq. (1) for a mechanical response situation, and Williams and Watts[5] have popularized the utility of its frequency response transform, we will refer to Eq. (1) as the Kohlrausch stretched exponential (KSE) and to the corresponding response in the frequency domain as that of the Williams–Watts (WW) function (WWF).

Unfortunately, there currently exist no simple and accurate representations of WW frequency response which can be used in fitting response data (real and imaginary parts or imaginary part only) to the WW function. The problem arises because this function in its basic integral definition involves a very rapidly oscillating integrand over much of the response range of interest and is thus very difficult and inconvenient to calculate accurately. Although series and other approximate expressions have been presented (see Refs. 2, 3, 5, and 6, and references cited therein), they are too complex and/or too approximate to allow accurate estimates of such parameters as τ_0 and β to be obtained from fitting frequency response data.

But the situation has changed recently. First, accurate tables of functions directly related to the normalized WWF have been presented.[3] They cover the range 0.1(0.1)1 for β and span the region from 10^{-3} to 2.5×10^3 for $z \equiv \omega\tau_0$, the normalized frequency variable. Second, in an article with a title similar to the present one, the authors of Ref. 2 have used the tabular results mentioned above to develop a simplified method of fitting $\epsilon''(\nu)$ data, where ϵ'' is the imaginary part of the complex dielectric constant; $\epsilon = \epsilon' - i\epsilon''$; $\nu \equiv (\omega/2\pi)$ is the frequency of measurement; and $i \equiv \sqrt{-1}$.

The work of Ref. 2 represents a considerable advance and provides a useful approximate approach to the fitting problem. Nevertheless, there is still room for improvement when (a) one wants to know how well data actually fit the WWF, and (b) one wishes more accurate estimates of the unknown parameters of the model. The Ref. 2 approach finds parameter estimates independently of one another and uses only a few points of the $\epsilon''(\nu)$ data to determine them. Better estimates could be obtained if all appropriate $\epsilon''(\nu)$ data were used (omitting any data in the tails not belonging to the relaxation process of interest), and even better ones would be obtained if complex nonlinear least squares (CNLS) fitting of both $\epsilon'(\nu)$ and $\epsilon''(\nu)$ data were carried out.[7] Such fitting yields an estimate of the standard deviation of the overall fit, σ_f, parameter estimates, and estimates of their standard deviations as well. It may be applied to either $\epsilon''(\nu)$ or $\epsilon'(\nu)$ data or, most appropriately, to both together. Finally, the Ref. 2 method has only been applied to dielectric data. It would be useful to have available an approach allowing accurate fitting of dielectric or conductive system data and even nonelectric data. We describe and illustrate one below which uses all the data available and is appropriate for CNLS fitting. In the following, the background and development of the present method are described; a procedure to improve parameter estimates is discussed; and the new method is applied to the same data used in Ref. 2. For those who are only interested in using the fitting function, it is defined by Eqs. (2), (13)–(16), and (17). The results in Table I may be used to improve the accuracy of parameter estimates obtained with the method.

II. A FITTING PROCEDURE FOR GENERAL WILLIAM-WATTS TYPE DATA

Let us assume that one is dealing with complex frequency response data obtained from either a dielectric or conductive system, and it is desired to compare the data with the WWF. To do so one needs an accurate three-parameter approximation to the WWF. Such an approximation will be developed below.

First, it is useful to discuss a way of treating both dielectric and conductive system response in a unified fashion.[1,8] Let us therefore introduce the normalized dimensionless response function

$$I_i = \frac{U_i - U_{i\infty}}{U_{i0} - U_{i\infty}}, \quad (2)$$

where $i = \epsilon$ or Z; thus $U_\epsilon \equiv \epsilon \equiv \epsilon' + i\epsilon_n''$, and $U_Z \equiv Z = Z' + iZ''$, an impedance. Here $\epsilon_n'' \equiv -\epsilon''$. Then U_{i0} and $U_{i\infty}$ are the $\omega \to 0$ and $\omega \to \infty$ limits of U_i. This normalization is standard for dielectric systems but has been less used for conductive ones. Now it has been shown[8] that when a formal expression for $I_i(\omega)$ has been found for $i = \epsilon$ (or vice versa), the same expression can be applied with $i = Z$ to represent a conductive system, one which exhibits exactly the same frequency response and thus leads to the same shape when plotted in the complex plane at the Z level as does the I_ϵ at the ϵ level. This means that a normalized WWF approximation may be used for either a dielectric or a conductive system. We shall consider the $i = \epsilon$ situation first and show the $i = Z$ extension later.

The tabular results of Dishon *et al.*,[3] involving the normalized frequency variable $z \equiv \omega\tau_0$, may readily be transformed to the I_i form. Let this WW I_i be designated $I_{\rm WW}$ for both $i = \epsilon$ and $i = Z$. We shall develop an accurate approximation to $I_{\rm WW}$ which can be used in fitting.

But experimental data involve U_i, not I_i, since U_{i0} and $U_{i\infty}$ are initially unknown. Since data are usually obtained at either the admittance Y or impedance level, one should also consider fitting at the actual measurement level. For $i = \epsilon$, Eq. (2) leads to

$$\epsilon = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) I_\epsilon. \quad (3)$$

Let C_C be the capacitance of the empty measurement cell. Then $C_\infty \equiv C_C\epsilon_\infty$, the geometrical capacitance, and $C_0 \equiv C_C\epsilon_0$. The admittance corresponding to ϵ (actually ϵ_ϵ here) is $Y_\epsilon = Z_\epsilon^{-1} = i\omega C_C \epsilon$, or

$$Y_\epsilon = i\omega[C_\infty + (C_0 - C_\infty) I_\epsilon]. \quad (4)$$

The equivalent circuit for Eq. (4) is shown in Fig. 1(a), where

$$Z_x = Z_{x\epsilon} = [i\omega(C_0 - C_\infty) I_\epsilon]^{-1}. \quad (5)$$

If the dielectric system were somewhat conducting, one would need to add a parallel resistor to $Z_{x\epsilon}$, but we shall ignore this possibility.

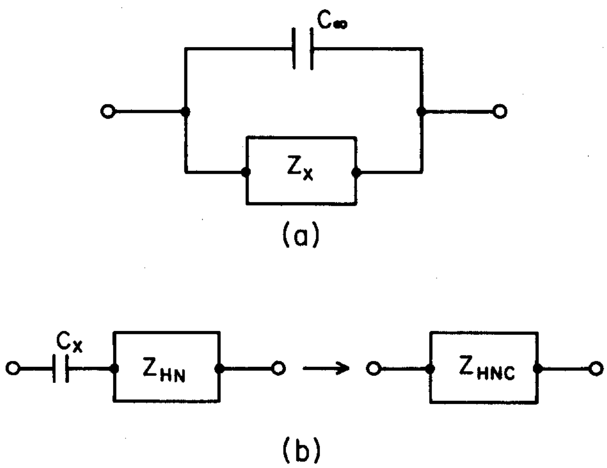

FIG. 1. (a) A simple general circuit for fitting data from dielectric or conductive systems. Here C_∞ is the geometrical capacitance. (b) Stages in the development of a useful Williams–Watts fitting approximation, the HNC function.

The above results show that if I_ϵ were a two parameter function approximating the WWF $I_{\rm WW}$, say $I_{\epsilon \rm WA}$, and involving $\psi_{\rm WW} \equiv \beta$ and $\tau_{\rm WW} \equiv \tau_0$, one would fit appropriate complex data to the Fig. 1(a) circuit and obtain estimates of C_∞, $(C_0 - C_\infty)$, $\tau_{\rm WW}$, and $\psi_{\rm WW}$. Estimates of these four parameters, estimates of the standard deviations of the parameters, and σ_f could all be obtained most accurately and appropriately using CNLS fitting.

We now consider how the $I_{\rm WW}$ "data" may be used to find a good approximating function $I_{\epsilon \rm WA}$. Since the $I_{\rm WW}$ results do not contain ϵ_∞, they may be taken for present convenience as representing actual errorless dielectric data,

$$\epsilon_{\rm WW} = \epsilon_0 I_{\rm WW}, \quad (6)$$

for which $\epsilon_0 = 1$ and $\epsilon_\infty = 0$. We may thus ignore ϵ_∞ and C_∞ in the determination of $I_{\epsilon \rm WA}$ from $I_{\rm WW}$. Let us further write, for the present $\epsilon_\infty = 0$ case,

$$\epsilon_A = \epsilon_{0A} I_{\epsilon \rm WA}. \quad (7)$$

When an ϵ model is fitted to $\epsilon_{\rm WW}$ data, it is clear that the estimate of the ϵ_{0A} parameter obtained will be an estimate of ϵ_{0A}, here unity. Incidentally, the quantity ϵ_{0A}/ϵ_0 was implicitly taken fixed at unity by Lindsey and Patterson in their detailed comparison[6] of Williams–Watts and Davidson–Cole[9] functions. For actual data, ϵ_0 [or, more generally, $(C_0 - C_\infty)$] is never known *ab initio*; it should therefore be taken as a free parameter in the fitting of real data to an approximate fitting function.

Let us start our search for a useful $I_{\epsilon \rm WA}$ function with that of Havriliak and Negami (HN),[10] which can be written at the present ϵ level as

$$\epsilon_{\rm HN} = \epsilon_{0A} I_{\rm HN} = \epsilon_{0A} / [1 + (i\omega\tau_{\rm HN})^{\psi_1}]^{\psi_2}, \quad (8)$$

where ψ_1 and ψ_2 fall in the range [0,1]. Since $z = \omega\tau_{\rm WW}$, this result may be rewritten as

$$\epsilon_{\rm HN} = \epsilon_{0A} / [1 + (izt_{\rm HN})^{\psi_1}]^{\psi_2}, \quad (9)$$

where $t_{\rm HN} \equiv \tau_{\rm HN}/\tau_{\rm WW}$. The HN function has been used to fit considerable dielectric data. Note that when $\psi_1 \equiv 1$ it reduces to the Davidson–Cole (DC) function, when $\psi_2 \equiv 1$

to the Cole–Cole[11] (CC) function, and when $\psi_1 \equiv \psi_2 \equiv 1$ to simple one-time-constant Debye response.

By CNLS fitting, with unity weighting, of the $\epsilon_A = \epsilon_{HN}$ function of Eq. (9) to the ϵ_{WW} data, we find that neither the DC nor the more general HN function yields a satisfactory approximation. Results for $\psi_{WW} = 0.5$ are shown in Fig. 2. Notice particularly the deviations of the ϵ_{0A}/ϵ_0 estimates from unity. Although even the HN function is unsatisfactory, Kenkel[12] has found that a reasonably good approximation to ϵ_{WW} is obtained when one uses, at the dielectric level, a capacitor $(C_0 - C_\infty)$ in series with a CC function defined at the impedance level. We have found that this composite function is also a better approximation than that provided by a capacitor in series with a DC function. But these results nevertheless suggested that the WWF might be even better approximated by a capacitor in series with a HN function at the Z level, as in Fig. 1(b).

Let us begin by writing the independent series combination

$$Z_\epsilon = (i\omega C_x)^{-1} + \frac{R_y}{[1+(i\omega\tau_{HN})^{\psi_1}]^{\psi_2}}, \quad (10)$$

where it is necessary that $C_x \equiv (C_0 - C_\infty)$ for proper ϵ behavior as $\omega \to 0$. But we need a unified distributed element with minimum number of free parameters. Let us therefore take R_y as the following function of τ_{WW}, C_x, and ψ_{WW}:

$$R_y \equiv (\tau_{WW}/C_x) r_{HNC}(\psi_{WW}), \quad (11)$$

with $r_{HNC}(0) = 1$. Note that in order to yield a good approximation to the WWF, the ψ_1 and ψ_2 parameters of Eq. (10) must also be functions of ψ_{WW}. For $\psi_{WW} \to 1$, $\psi_1 \to 1$, and $\psi_2 \to 0$. Then one obtains just the capacitor C_x and the resistor R_y in series, yielding Debye response, as required in this limit. Further, $R_y C_x$ is the Debye τ_{WW} value for $\psi_{WW} = 1$.

Finally, let us write $\tau_{HN} \to \tau_{HNC}$ and define $t_{HNC}(\psi_{WW}) \equiv \tau_{HNC}/\tau_{WW}$, with $t_{HNC}(0) = 1$. Now the resulting impedance, a Z_ϵ, is

$$Z_{HNC} = C_x^{-1}\left[(i\omega)^{-1} + \frac{\tau_{WW} r_{HNC}}{[+(i\omega\tau_{WW} t_{HNC})^{\psi_1}]^{\psi_2}}\right]$$

$$= (\tau_{WW}/C_x)\left[(iz)^{-1} + \frac{r_{HNC}}{[1+(izt_{HNC})^{\psi_1}]^{\psi_2}}\right]. \quad (12)$$

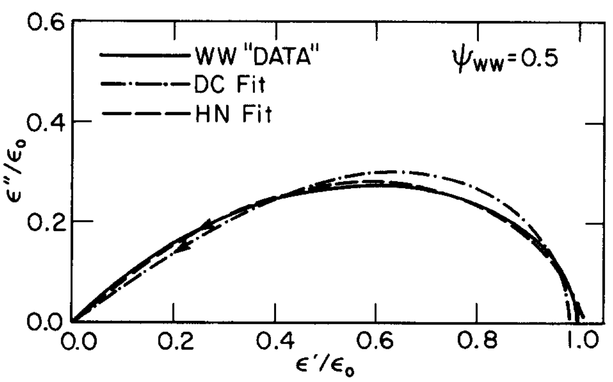

FIG. 2. Comparison in the normalized complex dielectric constant plane of accurate $\psi_{WW} = 0.5$ WW data with Davidson–Cole and Havriliak–Negami results obtained with complex nonlinear least squares (CNLS) fitting.

But for the ϵ_{WW} "data," we may take z as the frequency variable itself; then $\tau_{WW} = 1$. In order to make the HNC element a good approximation to ϵ_{WW}, we must determine the functions $r_{HNC}(\psi_{WW})$, $t_{HNC}(\psi_{WW})$, $\psi_1(\psi_{WW})$, and $\psi_2(\psi_{WW})$. To do so we used CNLS fitting of the I_{WW} data to the above HNC element, transformed to a normalized complex dielectric constant. Excellent fits were found for ψ_{WW} in the range 0.1(0.1)1 covered by the tabular data when the above four parameters were taken as free and disposable. See the discussion in the next section.

We have not tried to fit the numerical results for the above four functions exactly over the 0.1(0.1)1 ψ_{WW} range, but have sacrificed some accuracy for simplicity. Ordinary nonlinear least squares fitting yielded the following approximations:

$$\psi_1(\psi_{WW}) = \sin(\theta)[0.898\,79 + 0.088\,7811\psi_{WW}], \quad (13)$$

$$\psi_2(\psi_{WW}) = \mathrm{ctn}(\theta)[0.627\,503 + 0.614\,423\exp(-3.77327\psi_{WW})], \quad (14)$$

$$r_{HNC}(\psi_{WW}) = 1 + \mathrm{ctn}(\theta)[0.359\,585 + 34.1304\exp(-7.377\,36\psi_{WW}) + 1.862\,83\times 10^5\exp(-36.8585\psi_{WW})], \quad (15)$$

and

$$t_{HNC}(\psi_{WW}) = 1 + \{\mathrm{ctn}(\theta)[1.3672 + 136.604\exp(-8.040\psi_{WW}) + 1.6615\times 10^6\exp(-39.3333\psi_{WW})]\}, \quad (16)$$

where $\theta \equiv (\pi/2)\psi_{WW}$. Note that since $\psi_2 \to 0$ as $\psi_{WW} \to 1$, ψ_1 and t_{HNC} become unimportant when ψ_{WW} is very close to unity.

When the above relations are substituted into the first form of Eq. (12), one has available a new approximation to the WWF, which we shall call the HWW function. It may be used at any immittance level (and for nonelectrical situations as well), and its I_ϵ expression is just

$$I_{\epsilon HWW} = \left[1 + \frac{i\omega\tau_{WW} r_{HNC}}{[1+(i\omega\tau_{WW} t_{HNC})^{\psi_1}]^{\psi_2}}\right]^{-1}, \quad (17)$$

where the four functions involved are given by Eqs. (13)–(16). Note that it is necessary that $\psi_1\psi_2$ be less than unity in order to obtain the proper high frequency limiting behavior, that where $I \propto (i\omega)^{-(1-\psi_1\psi_2)}$. Because Eqs. (12) and (17) are only approximations to the WWF, we cannot expect them to yield perfect estimates of $(\epsilon_0 - \epsilon_\infty) \equiv \epsilon_x$, τ_{WW}, and ψ_{WW} even when fitted by CNLS to perfect WW data. They will instead yield estimates of these quantities which we shall denote $\hat{C}_x$ (or $\hat{\epsilon}_x$), $\hat{\tau}_{WW}$, and $\hat{\psi}_{WW}$. We shall consider actual fitting and adequacy of fit shortly.

Note that the distinction between the general HNC model, or distributed element, and the specific HWW model is as follows. The first involves the five free, disposable parameters C_x, $(R_y C_x) = \tau_{WW} r_{HNC}$, τ_{HNC}, ψ_1, and ψ_2, as in the first form of Eq. (12). When these parameters, many of which have no obvious physical interpretation, are free, the HNC can fit WW frequency response very well, and probably many other responses as well. On the other hand, the HWW function, the combination of Eqs. (17) and (13) to (16), being specifically tailored to the WWF, involves just the direct WW parameters, C_x, τ_{WW}, and ψ_{WW}, all physically meaningful.

We may now invoke the duality relation mentioned earlier to obtain an approximation function for conductive systems. To do so, we need merely rename $I_{\epsilon HWW}$ as I_{ZHWW} and consider it a normalized impedance. Then the shape of an $I_{\epsilon HWW}$ plot in the complex dielectric constant plane will be exactly the same as that of I_{ZHWW} in the 2D impedance plane. In order to show the inclusion of the C_∞ geometrical capacitance of Fig. 1(a) in the simplest way, we shall write the result for the response of the Fig. 1(a) circuit, with $Z_x \equiv Z_{ZHWW}$, at the admittance level. The result is

$$Y_Z = Y_{ZHWW} = i\omega C_\infty + \Bigg[R_0 + (R_0 - R_\infty) \times \left\{1 + \frac{i\omega\tau_{WW} r_{HNC}}{[1 + (i\omega\tau_{WW} t_{HNC})^{\psi_1}]^{\psi_2}}\right\}^{-1}\Bigg]^{-1}. \tag{18}$$

Note that five initially unknown parameters are involved, C_∞, R_0, R_∞, τ_{WW}, and ψ_{WW}. Similarly, for the Y_ϵ expression following from Eq. (17) for a dielectric system, there are four unknowns, C_∞, C_0, τ_{WW}, and ψ_{WW}.

The HWW Z_ϵ (or ϵ_ϵ) and Z_Z approximation functions are incorporated as separate unified distributed circuit elements in a very flexible CNLS fitting program available from one of the present authors (JRM). This routine allows many different circuit configurations to be used for fitting, with many different types of distributed elements incorporated as parts of the circuit employed. Thus, one can have additional resistors, capacitors, and distributed elements like the HN and HWW, all interconnected in different ways. Further, weighted real, imaginary, or complex data fitting can be carried out.

III. ACCURACY OF THE APPROXIMATION AND SOME FITTING RESULTS

Figure 3 shows comparisons in the complex dielectric constant plane of WW data and the results of fitting the HWW function to these data. For each ψ_{WW} value, the full data set of Dishon *et al.*[3] was used, 99 data points covering about 6.5 decades of frequency. In spite of the large number of points, their distribution was such that a few of the $\psi_{WW} \lesssim 1$ curves show an odd straight-line region at the left of their peaks. These regions arise because the plotting routine connects adjacent points with straight lines, indicating here the absence of data points sufficiently close together to yield the illusion of a smooth curve.

It is clear from Fig. 3 that the fits were excellent, except at the very lowest frequencies of the $\psi_{WW} = 0.1$ and $\psi_{WW} = 0.2$ curves. As can be seen, the range of variation of ϵ''/ϵ_0 was small for these curves, especially for that with $\psi_{WW} = 0.1$. The lack of sufficient data at the extremes of frequency resulted in much less accuracy for the $\psi_{WW} = 0.1$ HNC parameters than that for the higher ψ_{WW} values.

Table I shows a number of important results obtained from unity-weight fitting of the ϵ_{WW} data. First one sees the standard deviation estimates for the overall fit σ_f using the HNC and the HWW models. They differ for each specific ψ_{WW} value for two reasons. First the HNC fitting involved one more degree of freedom than did that for the HWW. Second, the HWW parameter expressions, Eqs. (13)–(16), are not exact but are only good approximations to the actual numerical estimates of these parameters obtained in the HNC fitting. It is nevertheless gratifying that σ_{fHNC} and σ_{fHWW} are as comparable as they are.

The small numerical values of the σ's indicate that the fits obtained were very good, in agreement with the comparisons shown in Fig. 3. When using the present HWW model for either dielectric or conductive fitting of data believed to be of WW character, one should not expect to obtain σ_f/U_{ix} values much smaller than those shown here even when the data are of perfect WW character, as are the ϵ_{WW} results we have used. Here $U_{ix} \equiv U_{i0} - U_{i\infty}$ is the important data scaling factor; $U_{\epsilon x} = U_x = \epsilon_0 = 1$ (or $C_x = 1$) in the present fitting. Some statistical variation is to be expected, but it will generally lead to larger σ_f/U_{ix} values than those shown here. When σ_f/U_{ix}, obtained from a CNLS fit with the HWW model, is found to be an order of magnitude or larger than the values shown here, one can certainly conclude that the data are not well represented by the WWF.

The three remaining columns of Table I are the heart of our present results. They show how estimated parameter values differ from true values for HWW fits to exact WW data. Because the estimates were generally so close to the true values, we have shown their estimated relative deviances rather than their actual values. For each value we

TABLE I. Standard errors of fit for the HNC and HWW, and HWW fit correction functions.

$\hat{\psi}_{WW}$ or ψ_{WW}	$10^4\sigma_{fHNC}$	$10^4\sigma_{fHWW}$	$u(\hat{\psi}_{WW})$ $[1-(\hat{\psi}_{WW}/\psi_{WW})]$	$v(\psi_{WW})$ $[1-(\hat{\tau}_{WW}/\tau_{WW})]$	$w(\psi_{WW})$ $(1-\hat{U}_x/U_x)$
0.1	8.8	7.6	-1.8	-21.14	6.52×10^{-2}
0.2	4.3	6.6	$(-6.62\pm0.04)\times10^{-2}$	$(-4.91\pm0.47)\times10^{-2}$	$(2.87\pm0.37)\times10^{-3}$
0.3	8.6	6.4	$(1.92\pm0.03)\times10^{-2}$	$(2.34\pm0.15)\times10^{-2}$	$(-3.35\pm0.22)\times10^{-3}$
0.4	11	8.3	$(2.19\pm0.04)\times10^{-2}$	$(0.87\pm1.31)\times10^{-3}$	$(-3.05\pm0.22)\times10^{-3}$
0.5	9.8	8.3	$(7.52\pm0.44)\times10^{-3}$	$(-0.76\pm9.38)\times10^{-4}$	$(-2.11\pm0.18)\times10^{-3}$
0.6	7.3	6.7	$(8.66\pm3.51)\times10^{-4}$	$(-9.57\pm0.62)\times10^{-3}$	$(-8.60\pm1.35)\times10^{-4}$
0.7	4.4	5.0	$(-2.36\pm0.26)\times10^{-3}$	$(-3.64\pm0.39)\times10^{-3}$	$(-1.78\pm0.96)\times10^{-4}$
0.8	2.0	2.5	$(-3.06\pm0.13)\times10^{-3}$	$(6.28\pm0.17)\times10^{-3}$	$(-0.71\pm4.63)\times10^{-5}$
0.9	0.52	0.56	$(-1.23\pm0.03)\times10^{-3}$	$(9.18\pm0.03)\times10^{-3}$	$(-2.55\pm1.02)\times10^{-5}$
1.0	···	10^{-10}	0	0	0

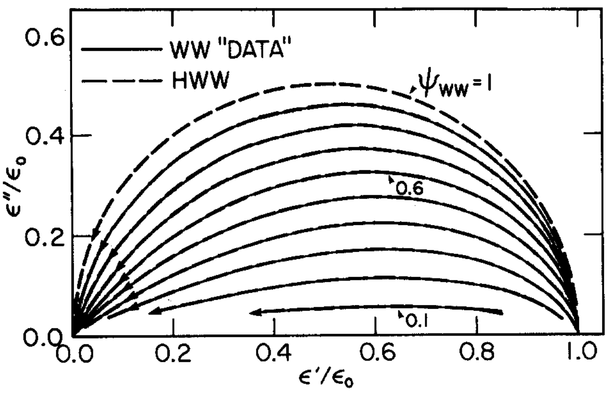

FIG. 3. Comparison in the normalized complex dielectric constant plane of accurate WW data with CNLS fitting results of the HWW model to these data.

also show the standard deviation of the quantity, except for the lower accuracy $\hat{\psi}_{WW}$ and $\psi_{WW} = 0.1$ results. It is particularly useful to show the standard deviation estimates because when a standard deviation is comparable to or larger than the quantity with which it is associated, no credence can be attached to this quantity and it may as well be set to zero. An extreme example is the $\psi_{WW} = 0.5$ value of v in Table I.

It should be noted that the HNC parameter approximation formulas of Eqs. (13)–(16) were developed without using the $\psi_{WW} = 0.1$ fitting results since the I_{WW} data were insufficient to yield good numerical parameter estimates for this value of ψ_{WW}. Further, the $\psi_{WW} = 1$ pure Debye data were also not directly used in the least squares fitting which led to Eqs. (13)–(16) since the necessary values of the parameters were known in this limit. When the HWW model was used for pure Debye data (see last row of the table), we obtained a perfect fit (within the double-precision accuracy of the calculations) and exact (to about 14 decimal places) parameter estimates.

Because the $\psi_{WW} = 0.1$ data was not used in the development of the HWW approximate model, the large results for $\psi_{WW} = 0.1$ shown in Table I represent quite chancy extrapolations. Nevertheless, they are included here since they are likely to be of more use than nothing for estimation of WW parameters when $\psi_{WW} < 0.2$.

The purposes of fitting a model to data are to see how well the model fits and, if the fit is sufficiently good, to obtain estimates of the values of the parameters of the model so their physical significance can be assessed and interpreted. When the HWW is used to fit appropriate data and the resulting σ_{fHWW}/U_{ix} is less than about 10^{-2}, one will obtain meaningful estimates of the WW parameters ψ_{WW}, τ_{WW}, and U_{ix}. Although we have defined $w \equiv [1 - (\hat{U}_x/U_x)]$ in Table I, the factor $\hat{U}_x/U_x$ is equal to $\hat{\epsilon}_x/\epsilon_x$ (or $\hat{C}_x/C_x$) in the $i = \epsilon$ case and to $\hat{R}_x/R_x$ in the $i = Z$ case, where $R_x \equiv R_0 - R_\infty$. Thus, in general we may write $w = [1 - \hat{U}_{ix}/U_{ix}]$.

The results of Table I show that when the HWW yields a good fit to a set of data, the raw estimates $\hat{\psi}_{WW}$, $\hat{\tau}_{WW}$, and $\hat{U}_{ix}$ obtained from CNLS fitting will be no more than about 1% from the true WW values for most of the ψ_{WW} range. Such accuracy may be sufficient for many purposes. But the Table I results allow one to obtain parameter estimates which are about ten times more accurate if WW data is in fact involved. First notice that the u function depends on $\hat{\psi}_{WW}$, while the v and w ones are functions of ψ_{WW}, the true value of the WW exponent. Now the table may be used in the following way to obtain much improved estimates of ψ_{WW}, τ_{WW}, and U_x. We shall designate the new estimates with two superscript carets.

To illustrate the method, suppose $\hat{\psi}_{WW} = 0.45$. One may now use linear, graphical, or curvilinear interpolation between the $\hat{\psi}_{WW} = 0.4$ and the $\hat{\psi}_{WW} = 0.5$ u values in the table to find an estimate of $u(0.45)$. Curvilinear interpolation yields $u(0.45) \simeq 0.0142$. Then the improved estimate of ψ_{WW} follows from

$$\hat{\hat{\psi}}_{WW} = \hat{\psi}_{WW}/[1 - u(\hat{\psi}_{WW})]. \tag{19}$$

In the present case, this yields $\hat{\hat{\psi}}_{WW} = 0.4565$. This result may now be taken as the best available estimate of ψ_{WW}. Thus, we next take $\hat{\hat{\psi}}_{WW} = \psi_{WW}$ and interpolate using the $v(\psi_{WW})$ and $w(\psi_{WW})$ functions in Table I. We obtain $v(0.4565) \simeq 3.4 \times 10^{-4}$ and $w(0.465) \simeq -2.52 \times 10^{-3}$. These results yield $\hat{\hat{\tau}}_{WW} = 1.000\,34 \hat{\tau}_{WW}$ and $\hat{\hat{U}}_x = 0.9975\,\hat{U}_x$.

As a final fitting example, we apply the present methods to the data of Sasabe and Moynihan[13] used by Weiss *et al.*[2] to illustrate their approximate analyses method for WW data.[13] Only seven $\varepsilon''/\varepsilon''_m$ vs ν data values were used and they were less accurate than the original data since they were digitized from a small published figure. Although they thus do not allow a very significant test of the present approach, some instructive results are found. Here ε''_m is the maximum (peak) value of $\varepsilon''(\nu)$. Its actual value does not appear in the original paper.[13] Unfortunately, Weiss *et al.* did not recognize that the actual data were given in normalized form as $\varepsilon''/\varepsilon''_m$ vs ν rather than as ε'' vs ν. Thus they determined ε''_m independently from the data (implicitly assuming $\varepsilon''/\varepsilon''_m = \varepsilon''$) and obtained the estimate $\varepsilon''_m = 0.981$ rather than the correct (for the above assumption) value of unity. All their quoted original data ε'' values are actually $\varepsilon''/\varepsilon''_m$ values.

Our nonlinear least squares fit of the above data using the HWW model yielded the following estimates:

$$\hat{\psi}_{WW} = 0.5991(1 \pm 7.9 \times 10^{-3}),$$
$$\hat{\tau}_{WW} = 1.821 \times 10^{-4}(1 \pm 1.2 \times 10^{-2})\text{s},$$
$$\hat{U}_{\epsilon x} = 3.0352(1 \pm 7.1 \times 10^{-3}),$$

and

$$\sigma_f/\hat{U}_{\epsilon x} = 1.05 \times 10^{-3}.$$

Here we have taken $U_{\epsilon x} = (\varepsilon_0 - \varepsilon_\infty)/\varepsilon''_m$, and the $\pm$ terms are estimated relative standard errors. We tried to determine a separate $\varepsilon_\infty/\varepsilon''_m$ parameter from the fitting but the data were too few and did not extend to sufficiently high frequencies to allow a meaningful estimate to be obtained.

The relatively small value of $\sigma_f/\hat{U}_{\epsilon x}$ suggests that the data are indeed well fitted by the WWF, but data covering a wider frequency range (as in the original paper) would be needed to confirm this hypothesis. Since $\hat{\psi}_{WW}$ is likely to be between 0.593 and 0.604 according to the above result, it is scarcely worthwhile to apply the improvement technique described earlier. Thus, although it yields $\hat{\hat{U}}_{WW} \simeq 0.5996$, we shall take $\hat{\psi}_{WW} \simeq \psi_W = 0.60$. Then the v and w results in Table I lead to

$$\hat{\hat{\tau}}_{WW} \simeq 1.804 \times 10^{-4} \text{ s}$$

and

$$\hat{\hat{U}}_{\epsilon x} \simeq 3.033.$$

For the present ratio-type data there is another test of the appropriateness of the WWF available. For $\psi_W = 0.6$ we find from the original exact I_{WW} data that the correct value of $U_{\epsilon x}(0.6)$ is 3.096, about two percent larger than the estimates above and about three standard deviations larger as well. This large a difference is quite improbable for true WW data but may arise here from the paucity and inaccuracy of the data.

There is a misprint in the Weiss *et al.* paper which needs mentioning before we can directly compare their WW parameter estimates with ours. In order to agree with earlier definitions and with the tabular exact ε_{WW} data,[3] the parameter A appearing in their Eq. (4) and elsewhere should be replaced by πA_0, so that $A_0 = A/\pi$. Their original A is not equal to $(\varepsilon_0 - \varepsilon_\infty)$ as stated but to $\pi(\varepsilon_0 - \varepsilon_\infty)$ for ordinary ε data. Thus the redefined A, A_0, equals $(\varepsilon_0 - \varepsilon_\infty)$. Another correction to A, pertinent here only because of the interpretation of the $(\varepsilon''/\varepsilon''_m)$ data as ε'' data, arises from the use by Weiss *et al.* of their inappropriate $\varepsilon''_m = 0.981$ estimate. To obtain $\hat{U}_{\epsilon x}$ values comparable to those determined directly from the present fit, the Ref. 2 values of $\hat{A}$ must be divided by (0.981π). This has been done to obtain the $\hat{U}_{\epsilon x}$ values quoted below.

Weiss *et al.*[2] derived four different sets of $\hat{\psi}_{WW}$, $\hat{\tau}_{WW}$, and $\hat{U}_{\epsilon x}$ estimates from these same data using their three-point approximate method. Their values fell in the following ranges:

$$0.59 \leqslant \hat{\psi}_{WW} \leqslant 0.61; \quad 1.80 \times 10^{-4} \leqslant \hat{\tau}_{WW} \leqslant 1.82 \times 10^{-4};$$

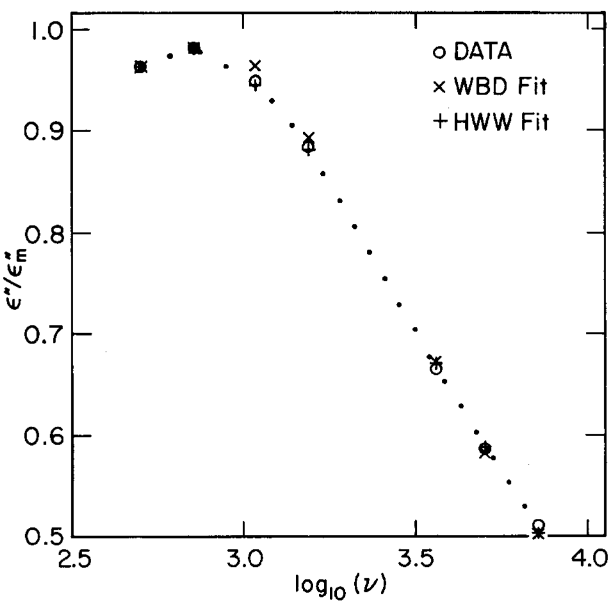

FIG. 4. Complex dielectric plane plot of dielectric data (Ref. 2); fitting results using the HWW model, and fitting results of Weiss, Bendler, and Dishon (Ref. 2). The dots are included here to help guide the eye.

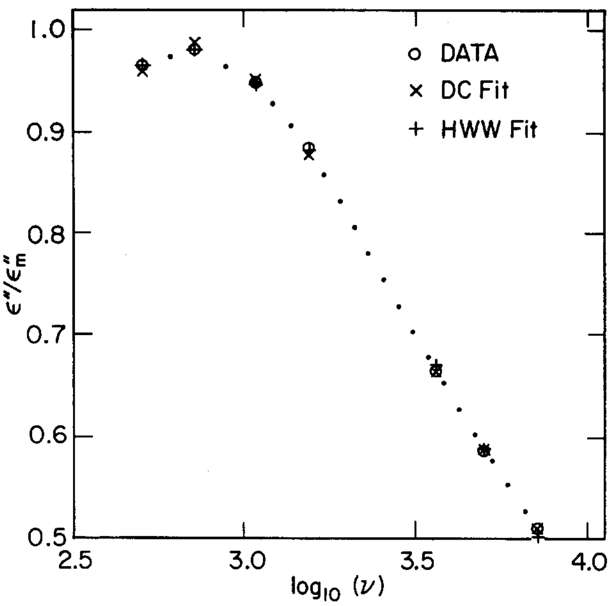

FIG. 5. Complex dielectric plane plot of dielectric data (Ref. 2); fitting results using the HWW model; and fitting results using the Davidson–Cole (DC) model.

and

$$3.05 \leqslant \hat{U}_{\epsilon x} \leqslant 3.14.$$

Using the set $\hat{\psi}_{WW} = 0.60$, $\hat{\tau}_{WW} = 1.81 \times 10^{-4}$s, and $A = 9.54$ ($U_{\epsilon x} = 3.095$), they calculated estimated values of ε'' for each frequency. When we take these values, consider them as new data ε'', and fit using the HWW, we find the new estimates

$$\hat{\psi}_{WW} = 0.6223(1 \pm 7.8 \times 10^{-3}),$$
$$\hat{\tau}_{WW} = 1.743 \times 10^{-4}(1 \pm 1.1 \times 10^{-2})\text{s},$$
$$\varepsilon''_m \hat{U}_{\epsilon x} = 2.954(1 \pm 6.7 \cdot 10^{-3}),$$

and

$$\sigma_f/\varepsilon''_m \hat{U}_{\epsilon x} = 1.16 \times 10^{-3}.$$

In turn, these values lead to

$$\hat{\psi}_{WW} = 0.6223,$$
$$\hat{\hat{\tau}}_{WW} = 1.737 \times 10^{-4}\text{s},$$

and

$$\varepsilon''_m \hat{U}_{\epsilon x} = 2.944.$$

The resulting values of $\hat{U}_{\epsilon x}$ and $\hat{\hat{U}}_{\epsilon x}$ are 3.011 and 3.001, respectively. Since these values, obtained by using all the data together, differ somewhat from those used to produce the data, we thus get some idea of the uncertainties inherent in the Weiss *et al.* approach. It would certainly be useful in providing initial estimates of WW parameters to be used in a HWW CNLS fitting.

Figures 4 and 5 show some of the fitting results graphically. The WBD points in Fig. 4 are those of Weiss, Bendler, and Dishon.[2] Figure 5 includes the results of a DC fit of the original data. It yielded an estimate of $U_{\epsilon x}$ of $\hat{U}_{\epsilon x} = 3.0553(1 \pm 6.1 \times 10^{-3})$ and a value of $\sigma_f/\hat{U}_{\epsilon x}$ of about 1.08×10^{-3}. It does not yield estimates of ψ_{WW} and τ_{WW}, of course,[6] but led to $\hat{\psi}_{DC} = 0.428(1 \pm 1.1 \times 10^{-2})$ and $\hat{\tau}_{DC}$

$=4.479\times10^{-4}(1\pm1.9\times10^{-2})$. Since this fit is nearly as good as that with the HWW, it is clear that the present data are insufficient to allow a firm choice to be made between the DC and the WW models.

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