Comparison of methods for estimating continuous distributions of relaxation times

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The nonparametric estimation of the distribution of relaxation times approach is not as frequently used in the analysis of dispersed response of dielectric or conductive materials as are other imittance data analysis methods based on parametric curve fitting techniques. Nevertheless, such distributions can yield important information about the physical processes present in measured material. In this letter, we apply two quite different numerical inversion methods to estimate the distribution of relaxation times for glassy Li$_{0.5}$La$_{0.5}$TiO$_3$ dielectric frequency-response data at 225 K. Both methods yield unique distributions that agree very closely with the actual exact one accurately calculated from the corrected bulk-dispersion Kohlrausch model established independently by means of parametric data fit using the corrected modulus formalism method. The obtained distributions are also greatly superior to those estimated using approximate functions equations given in the literature.

PACS numbers: 77.22.Gm 02.70.Rt 02.30.Za 02.50.Ng 02.60.-x 02.30.Sa 02.60.-i 66.30Dn 61.47.Fs 72.20.i 66.10.Ed
Keywords: Distribution of relaxation times; dielectric relaxation; least squares approximations; Monte Carlo methods; inverse problems

Broadband dielectric (also known as immittance or impedance) spectroscopy is widely used to characterize materials and to help understand the mechanisms involved in such challenging areas of condensed-matter physics as conductivity, molecular relaxation, liquid-glass transition etc.

In this experimental technique an electrical property of the material is recorded as a function of frequency $\omega$; and power of different DRT estimation procedures for a well-defined data situation.

Experimental data, with $M = 52$ points, for the Li$_{0.5}$La$_{0.5}$TiO$_3$ (LLT) glass at 225 K 12, expressed as...
the complex resistivity and dielectric levels, were found to involve an appreciable component associated with electrode polarization effects. LLT conducts by ionic hopping and involves a finite dc resistivity, $\sigma_0 \equiv \sigma(0)$. Further analysis of data for this material over a range of temperatures established that both $\sigma_0$ and the characteristic relaxation time of the dispersion of the bulk material, $\tau_\sigma$, were thermally activated with $T\sigma_0$ and $\tau_\sigma$ having the same activation energies $\Delta\epsilon$.

Such behavior indicates that it is most appropriate to identify the bulk dispersive response of this material with a conductive-system dispersion of resistivity relaxation times, rather than with a dielectric-system distribution of permittivity relaxation times, one where $\sigma_0$ would be naturally interpreted as a leakage conductivity unrelated to the bulk dielectric dispersion process. Since conductive-system response has already been analyzed for this data set, and since it has been shown by data fitting that it may often be difficult to discriminate between fits of conductive-system and dielectric-system models when only a single data set is available, we have elected to compare the two different DRT estimation procedures by determining their dielectric-system DRTs from the present data expressed at the complex permittivity level.

The two analysis methods considered here will be designated I and II. Method I involves a weighted nonlinear least squares approach for estimating dielectric distribution strength points, $g_i$, at corresponding relaxation-time values $\tau_i$, with $1 < i < N$. It allows either discrete or continuous DRTs to be estimated in terms of the $\{g_i, \tau_i\}$ values and their uncertainties, with the set of $\tau_i$'s either taken fixed or free to vary. Better results are nearly always obtained with $\tau_i$'s taken free, as in the present work. In addition, the data may be in temporal response form or in the frequency domain involving complex response or either its real or imaginary part. An extensive fitting and inversion program named LEVM that includes Method I is available for free downloads. Method II is based on a constrained least-squares with the Monte Carlo procedure. It leads to delta sequence distributions when applied to discrete DRTs. Recently, a method rather similar to that of II has been independently proposed, one that uses nonparametric Bayesian statistics for solving similar inversion problems.

Since we are interested in the dielectric DRT for the dispersive bulk relaxation process, it is important to eliminate the contributions to the data arising from partly blocking electrode effects before estimating the DRT. To do so, a KWW response model, the KD, involving a stretched-exponential shape parameter $\beta_D$, a characteristic relaxation time $\tau_\epsilon$, and a $\Delta\epsilon$ strength parameter, was used for fitting the original full data with inclusion of free parameters to model the electrode effects, the high-frequency-limiting bulk dielectric permittivity, $\epsilon_\infty$, and $\sigma_0$. The fit was excellent and yielded the follow-
in terms of a general DRT formalism, the complex dielectric permittivity may be expressed as

\[ \varepsilon(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \int_{-\infty}^{\infty} \frac{g(\ln \tau) d \ln \tau}{1 + i \omega \tau} \]  

(1)

where, \( \varepsilon_\infty \equiv \varepsilon'(\infty) \) and \( \varepsilon_s \equiv \varepsilon'(0) \) (the quantity \( \Delta \varepsilon \equiv \varepsilon_s - \varepsilon_\infty \) is defined as the dielectric strength), and \( g(\ln \tau) \) is the distribution function. For a delta sequence distribution \[ \delta \] Eq. (1) leads to simple Debye response \[ \varepsilon(\omega) \equiv \varepsilon_{\Delta \varepsilon}(\omega) \]. Both applied methods I and II are based on Eq. (1) and are further described in Ref. Macdonald \[ \delta \] and Ref. Tuncer \[ \delta \], respectively.

In Fig. 3, the complex dielectric permittivity raw data for LLT are presented without transformation. As evident in the inset of Fig. 3, the data include two different processes, with the right spur part representing low-frequency electrode polarization effects. The dashed vertical line \((- - -)\) in the inset indicates the approximate crossover position (shown at 40 krad\(^{-1}\)) from bulk dielectric system dispersion to conductivity and double-layer effects \[ \delta \]. Since all the open-circle fit points in the figure enclose their corresponding solid data points symmetrically, one may conclude that the fit is excellent.

After we remove the contributions of the ohmic conductivity and electrode effects to the raw data, as described above, the pure dielectric-system dispersion is obtained and is presented in Fig. 4 and denoted by \( \varepsilon_{\Delta \varepsilon} \). This data set, implicitly involving the KD-model DRT, was next used to estimate the DRT by the inversion methods I and II. Some of these results are shown in Fig. 3 and 4. The thick solid line is that of the KD DRT calculated directly from the data of Fig. 2 using Eq. (2) \((- - -)\) and Eq. (3) \((- \cdot -)\). The inset shows the method II estimates using the raw data of Fig. 2 compared with the scaled exact DRT (all divided by a factor of 100).
member that increasing the number of randomly selected \(\tau\) values used in method II improves the DRT estimates; \(\sim 25000\) \(\tau\) values were used in the present work.

Method II selects random \(\tau\) values over a wider range than those defined by the range of the original frequency window. The range of the original data \((\varepsilon_R)\) is about \(2 \text{ k rads}^{-1} < \omega < 200 \text{ M rads}^{-1}\) corresponding to \(5 \text{ n s} < \tau < 500 \mu \text{s}\), somewhat smaller than the \(\tau\) range following from the exact data of Fig. 4, as defined above.

In order to illustrate the utility of method II, its DRT determined for the raw \(\varepsilon_R\) data is shown in the inset of Fig. 4 with solid vertical lines and is compared to the actual distribution. Note that the presence of electrode effects results in an added distribution with a peak at \(\tau = 100 \mu \text{s}\). In addition, the distributions obtained from the \(\varepsilon_R\) and \(\varepsilon_{\text{mce}}\) data sets are nearly the same for \(\tau < 10 \mu \text{s}\) except for the presence of a small peak of the \(\varepsilon_R\) distribution estimate near \(\tau \sim 32 \text{ n s}\). This could possibly be due to the raw data where no \textit{a priori} assumption is made of the presence of KD-model response \((\varepsilon_{\text{mce}})\). Also note the effects of the relaxation-time cutoff for fast processes at \(\tau < 1 \text{ ps}\).

To further emphasize the utility of the numerical in-
version methods for estimating a DRT, we compare our results with those of Böttcher and Bordewijk in Fig. 1. They derived approximate DRT expressions from the real and imaginary parts of the dielectric permittivity and their derivatives with respect to natural logarithm of angular frequency \((\ln \omega)\). Two such approximation distribution functions \(g\) are listed below.

\[
\begin{align*}
g_1(\ln \omega^{-1}) &= 2 \varepsilon''(\omega)(\pi \Delta \varepsilon)^{-1}, \\
g_2(\ln \omega^{-1}) &= -\Delta \varepsilon^{-1} d\varepsilon'/d\ln \omega,
\end{align*}
\]

where the Fig. 1 data fit result for \(\Delta \varepsilon\), 136.93, is used along with \(\varepsilon_{\text{mce}}\) data set values. Clearly these expressions lead to broader distributions and to far less accurate DRT estimates than our inversion ones. In the inset of Fig. 4 method II DRT estimates obtained from the raw data are again illustrated, together with those following from the application of Eqs. 2 and 3.

In conclusion, two approaches for estimating DRT in conductive and dielectric systems are applied to experimental LLT dielectric permittivity data at 225 K. Both methods are capable of yielding well defined unique distributions for a given data set.

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