Novel Approach to the Analysis of Broadband Dielectric Spectra

H. Schäfer and E. Sternin
Department of Physics, Brock University, St. Catherines, Ontario, Canada L2S 3A1

R. Stannarius, M. Arndt, and F. Kremer
Fakultät für Physik, Universität Leipzig, 04103 Leipzig, Germany

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Broadband dielectric spectra are usually fitted to a superposition of contributions from one or several parametrized processes (Debye, Havriliak-Negami, etc.). This work proposes instead to extract continuous distributions of relaxation times from complex dielectric spectra by solving a Fredholm integral equation using the Tikhonov regularization technique with a self-consistent choice of the regularization parameter. This method is stable with respect to the noise and resolves multiple dynamical processes. An experimental example of salol adsorbed on microporous glass is analyzed.

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Broadband dielectric spectroscopy (10^{-2}–10^{9} Hz) is widely used to study molecular dynamics in complex systems such as glass-forming liquids and liquid crystalline materials (e.g., [1–4]). Sample polarization in an external electric field depends both on geometrical factors and on the mobility of molecular segments, molecules, or clusters of molecules. From the dielectric response one can obtain dipolar strengths, dielectric losses, and correlation times of the relaxation processes present in the system.

A single Debye process has the following well-known frequency dependence of the complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$:

$$\varepsilon^*(\omega) - \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau} = \frac{\Delta\varepsilon}{1 + i\omega\tau}, \qquad (1)$$

where τ is the relaxation time, ε_0 is the static (dc) permittivity, and $\varepsilon_\infty = \varepsilon(\omega \to \infty)$. In practice, one often observes a superposition of several relaxation processes with different τ values, or even a continuous distribution of relaxation times. The spectra may also contain features due to cooperative relaxation phenomena, e.g., in glass-forming liquids. In these cases Eq. (1) is no longer adequate, and the complex spectra of $\varepsilon^*(\omega)$ are usually described using phenomenological functions (as reviewed in [5]).

Typically, a superposition of several such functions provides a satisfactory multiparameter fit to the experimental data. However, relating the parameters so obtained to the intrinsic physical properties of the material is not always straightforward. A further drawback of such an approach is the inherent difficulty of separating processes with comparable relaxation times. A proper choice of the number of processes used to fit the data is not always obvious, and additional *a priori* assumptions have to be made.

An alternative way to describe a dielectric relaxation spectrum is in terms of an ensemble of Debye processes with a continuous relaxation time distribution, $g(\tau)$. For Eq. (1), $g(\tau)$ reduces to a δ function, while the superposition methods [5] correspond to line shapes with several symmetrically or asymmetrically broadened peaks of $g(\tau)$. Unfortunately, direct extraction of $g(\tau)$ from $\varepsilon^*(\omega)$ is a mathematically ill-posed problem [6–8]. This difficulty may be one of the reasons why the spectra are usually treated as superpositions of a few parametrized functions. If a direct calculation of $g(\tau)$ from $\varepsilon^*(\omega)$ could be performed reliably, in a manner similar to the Fourier transformation between time and frequency domains, then several problems arising from the use of empirical functions could be avoided. Having obtained $g(\tau)$, one could then seek a physical interpretation in the τ domain rather than in the frequency domain.

Attempts to develop a suitable numerical algorithm have been made previously, e.g., Tschoegl's second approximation method [9] and the histogram method of Imanishi, Adachi, and Kotaka [10]. However, the ambiguity of the extracted $g(\tau)$, which arises from the ill-posed nature of the problem, has not yet been satisfactorily resolved. In this work, we present an algorithm which can extract $g(\tau)$ directly from dielectric spectra reliably, unambiguously, and without biasing the results.

Our algorithm is based on solving an integral equation. We make an explicit assumption that individual relaxation processes in the sample are Debye-like and independent of each other, and that the superposition principle holds for $\varepsilon^*(\omega)$. We introduce the normalization condition ([11], pp. 317,318)

$$\int_D g(\tau)\, d(\ln\tau) = 1\,. \qquad (2)$$

The real and imaginary parts of the dielectric spectrum $\varepsilon^*(\omega)$ are then represented by

$$\varepsilon'(\omega) = \varepsilon_\infty + \Delta\varepsilon \int_D \frac{g(\tau)}{1 + \omega^2\tau^2}\, d(\ln\tau), \qquad (3)$$

$$\varepsilon''(\omega) = \frac{\sigma_0}{\varepsilon_0}\omega^{-s} + \Delta\varepsilon \int_D \frac{g(\tau)\,\omega\tau}{1 + \omega^2\tau^2}\, d(\ln\tau), \qquad (4)$$

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where the first term in $\varepsilon''(\omega)$ accounts for the conductivity and electrode polarization effects. σ_0 is the dc conductivity and $\Delta\varepsilon\, g(\tau)\, d(\ln\tau)$ is the combined relaxation strength of all processes in the range between $\ln\tau$ and $\ln\tau + d(\ln\tau)$. The integration is performed over the entire domain D of $\ln\tau$.

A discrete set of experimental data, $\varepsilon_j^{(\delta)}, j = 1, \ldots, m$, is always incomplete, i.e., known at a limited number of frequency sampling points ω_j, and affected by the noise δ_j,

$$\varepsilon_j^{(\delta)} = \varepsilon_j + \delta_j\,, \tag{5}$$

where the "exact data" $\varepsilon_j = \varepsilon_j(g(\tau), \varepsilon_\infty, \Delta\varepsilon, \sigma_0, s)$ are completely determined by $g(\tau)$, ε_∞, $\Delta\varepsilon$, σ_0, and s through Eqs. (3) and (4),

$$\varepsilon_j = \begin{cases} \varepsilon'(\omega_j), & j = 1, \ldots, m\,, \\ \varepsilon''(\omega_{j-m}), & j = (m+1), \ldots, 2m\,. \end{cases} \tag{6}$$

A numerical analysis of such data should provide $g(\tau)$ and the parameters ε_∞, $\Delta\varepsilon$, σ_0, and s. However, for noisy data one can only expect to obtain approximations $\tilde{g}(\tau)$, $\tilde{\varepsilon}_\infty$, $\Delta\tilde{\varepsilon}$, $\tilde{\sigma}_0$, and $\tilde{s}$. In general, obtaining reasonable approximations from noisy relaxation data is a rather ambitious undertaking. Equations (3) and (4) are essentially Fredholm integral equations of the first kind and thus belong to the class of so-called "ill-posed" problems. That is, for any set of noisy data $\{\varepsilon_j^{(\delta)}\}$, an infinite number of approximations to $g(\tau)$ result in equally good fits $\varepsilon_j(\tilde{g}(\tau), \tilde{\varepsilon}_\infty, \Delta\tilde{\varepsilon}, \tilde{\sigma}_0, \tilde{s})$ to the input data in the least-squares or maximum error sense. Almost all of those approximations are, in fact, wrong which can be demonstrated using the Riemann-Lebesque theorem [6]. For this reason, simple least-squares or linear programming algorithms are not appropriate for dealing with such integral equations.

Tikhonov regularization algorithm (TRA) [7,8] is known to provide reliable solutions of such integral equations. For a given fixed value of the exponent s, TRA minimizes the following expanded least-squares expression with respect to $g(\tau)$, ε_∞, $\Delta\varepsilon$, and σ_0:

$$\Phi(g(\tau), \varepsilon_\infty, \Delta\varepsilon, \sigma_0) = \sum_{j=1}^{2m} [\varepsilon_j^{(\delta)} - \varepsilon_j]^2 + \lambda \|g''\| \tag{7}$$

subject to $g(\tau) \geq 0$. Here λ is the regularization parameter (RP) and g'' denotes the second derivative of $g(\tau)$ with respect to $\ln\tau$. The first term in Eq. (7) is the usual least-squares term which guarantees compatibility of the fit with the data. TRA introduces the second term which constrains the smoothness of $g(\tau)$.

A good estimate for λ is essential for the quality of the solution [12]. Too small values for λ result in artificial, physically meaningless structures in $\tilde{g}(\tau)$, while too large a λ tends to oversmooth the shape of $\tilde{g}(\tau)$ and to suppress information. The first attempt to apply regularization techniques to the analysis of the dielectric data [13] based on the CONTIN procedure of Provencher [14] used the so-called n-dimensional statistical F test to determine the value of RP. A significantly more reliable method for estimating an optimal RP value is the self-consistency (SC) method of Honerkamp and Weese [12,15]. It has proved successful in many numerical algorithms related to Fredholm integral equations [12,15–17]. The SC method guarantees that the approximation $\tilde{g}(\tau)$ is in the vicinity of the true $g(\tau)$ if s is either known in advance or correctly estimated.

Once the optimum value of RP is determined from the SC method, minimizing $\Phi(g(\tau), \varepsilon_\infty, \Delta\varepsilon, \sigma_0)$ yields $\tilde{g}(\tau)$, $\tilde{\varepsilon}_\infty$, etc. Finally, since these approximations are obtained for a given fixed value of s, the entire procedure must now be repeated sweeping an appropriate range of s values until a minimum in

$$\Psi(s) = \sum_{j=1}^{2m} [\varepsilon_j^{(\delta)} - \varepsilon_j(\tilde{g}, \tilde{\varepsilon}_\infty, \Delta\tilde{\varepsilon}, \tilde{\sigma}_0, s)]^2 \tag{8}$$

is found, which yields a reasonable approximation $\tilde{s}$.

Numerical implementation of this algorithm involves approximating the integral equation by an adequate matrix equation, i.e., selecting a set of logarithmically spaced points $\{\tau_i\}$ and then calculating $\tilde{g}_i = \tilde{g}(\tau_i)$ and the approximations $\tilde{\varepsilon}_\infty$, $\Delta\tilde{\varepsilon}$, $\tilde{\sigma}_0$, and $\tilde{s}$, using the set of noisy spectral data $\{\varepsilon_j^{(\delta)}\}$ and the guessed range of s as inputs.

Extensive simulation studies revealed that the algorithm is stable with respect to the noise, provides excellent resolution of multiple relaxation processes, and extracts line shapes closely approximating the true $g(\tau)$. For example, as shown in Fig 1, two slightly broadened Debye processes different in their relaxation times by much less than one decade are nearly impossible to distinguish directly from the dielectric spectra, yet are clearly separated in the τ domain. As expected, the resolution and the ability to extract the true line shape improve as the noise is reduced or the number of sampled frequencies is increased. The choice of the frequency window does not critically influence the resolution as long as all processes are largely in the sampled region.

In addition to resolving closely spaced discrete relaxation processes, the method is capable of extracting true continuous line shapes. This is essential when the underlying relaxation mechanisms are not known *a priori*. An asymmetric multimodal distribution with four Gaussian-broadened peaks is shown in Fig. 2(b) and the corresponding complex spectrum in Fig. 2(a). The discrete points in Fig. 2(b) show how well the calculated distributions reproduce the original "true" $g(\tau)$, and a physical interpretation is now possible in the τ domain.

Salol (phenyl salicylate) adsorbed on a (dielectrically inactive) porous glass with a pore size of 7.5 nm was chosen as an experimental test system. Such restrictive environments allow one to study distortion of cooperative behavior of glass-forming systems, effects of bulk-to-surface interactions, or reptation of polymers in

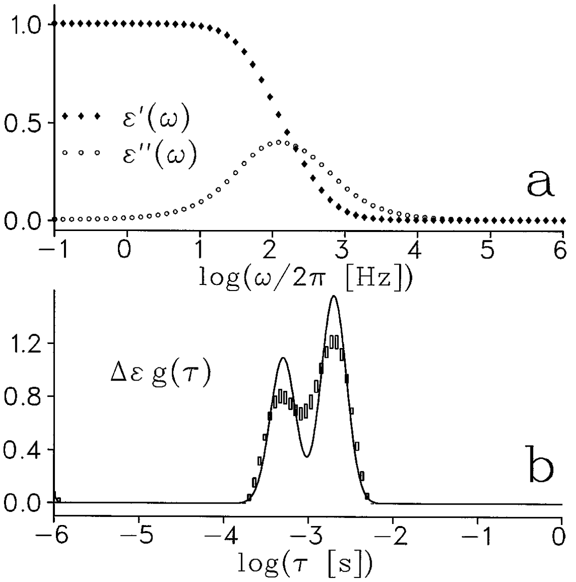

FIG. 1. (a) A complex dielectric spectrum, simulated using Eqs. (3) and (4) for $m = 60$ logarithmically spaced frequencies. Gaussian random numbers of the amplitude of 0.3% of $\max[\varepsilon'(\omega)]$ are added to simulate the noise, and $\Delta\varepsilon = 1$. (b) $\tilde{g}_i$ numerically extracted from the spectra for 100 values of $\ln\tau_i$ are plotted as discrete points. The true line shape is shown with a solid line for comparison. The vertical size of the plotting symbols in (b) represents the range of confidence provided by the algorithm.

nanolabyrinths. Previous dielectric studies have established that the dielectric behavior of the system is basically governed by three processes: relaxation of molecules in a liquid bulklike environment, relaxation of molecules influenced by the interface, and a contribution due to Maxwell-Wagner (MW) polarization effects [18,19]. A conventional data analysis yielded reasonably good fits of the data to superpositions of three Havriliak-Negami functions [18].

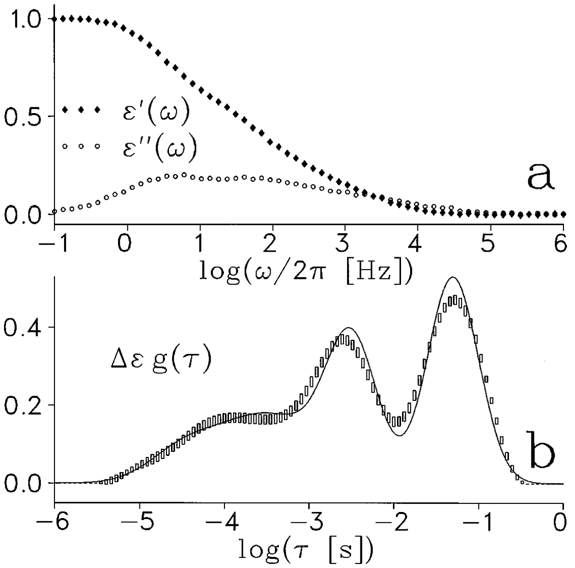

FIG. 2. (a) A complex dielectric spectrum, simulated as in Fig. 1(a), but from a multimodal distribution $g(\tau)$ with four Gaussian-broadened peaks. (b) $\tilde{g}_i$ numerically extracted from the spectra (discrete symbols, vertical size is the range of confidence) closely reproduce the true line shape (a solid line).

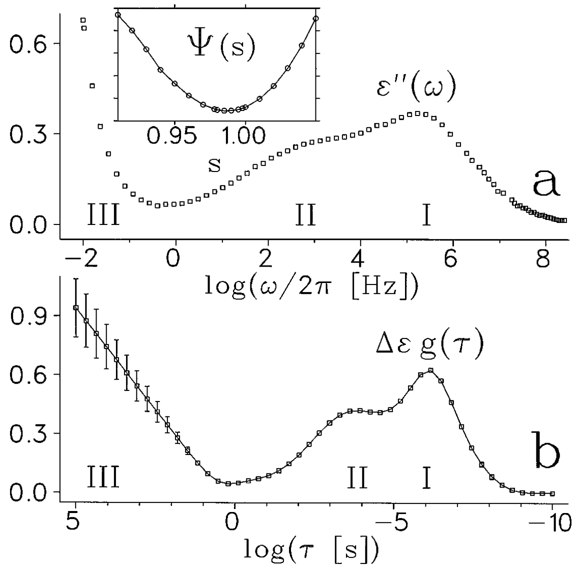

FIG. 3. (a) Dielectric loss data ε'' of the salol on a microporous glass of 7.5 μm pore size at $T = 251$ K. (b) $\tilde{g}(\tau)$ calculated by TRA. The inset in (a) illustrates the process of estimating $\tilde{s}$ by finding a minimum of $\Psi(s)$ (see text). Three processes are clearly separated: I, relaxation in a liquid bulklike environment; II, relaxation influenced by the interface; and III, Maxwell-Wagner polarization. The values found are $\tilde{s} \approx 0.99$, $\tilde{\sigma}_0/\tilde{\varepsilon}_0 \approx 0.036$, and $\Delta\tilde{\varepsilon} \approx 4.3$ (in agreement with [20]).

We analyzed dielectric spectra of the salol system measured at 44 temperatures between 227 and 313 K. A typical spectrum and the corresponding calculated $\tilde{g}(\tau)$ are shown in Fig. 3. Here, too, three separate processes are clearly recognizable. It must be pointed

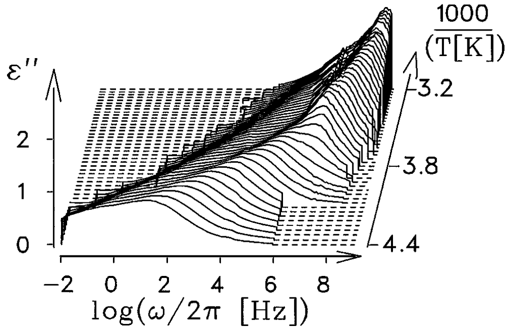

FIG. 4. Dielectric loss data of salol on a microporous glass of 7.5 μm pore size as a function of temperature. The solid lines indicate spectral regions where the relaxation processes I and II from Fig. 3 dominate. The data from the regions indicated by the dashed lines are either not available or not used to exclude the influence of the Maxwell-Wagner process.

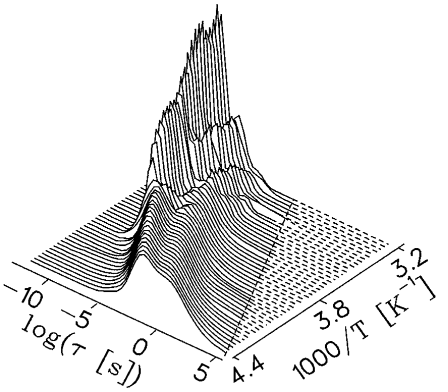

FIG. 5. Relaxation time distributions as a function of temperature, as extracted from the dielectric loss data of Fig. 4. The region shown with dashed lines does not reflect the influence of the Maxwell-Wagner process which is excluded for this calculation.

out, however, that our algorithm did not require an *a priori* assumption of three processes. A complete set of temperature-dependent spectra of salol is shown in Fig. 4 (for clarity, only the dielectric loss data ε'' are used). The main physical interest in these spectra is restricted to the resolution and evaluation of the two higher frequency processes (I and II in Fig. 3), thus the data analysis is limited to the frequency range above the low-frequency MW process (III in Fig. 3).

The power of transforming the frequency-domain spectrum into a τ-domain distribution function is evident in Fig. 5, where $\tilde{g}(\tau)$ calculated from the data of Fig. 4 is shown. A dramatic temperature dependence of the two relaxation processes is observed. At lower temperatures, an almost constant bimodal line shape of $\tilde{g}(\tau)$ shifts to smaller $\ln(\tau)$ values linearly with decreasing $1/T$. At a temperature of about $260-270$ K the line shape of $\tilde{g}(\tau)$, its first and second moments, and its temperature dependence undergo a dramatic change. None of these crucial features is clearly discernible from the dielectric loss spectra of Fig. 4.

To summarize, the purpose of this Letter is to introduce a novel and reliable method for extracting continuous relaxation time distributions of Debye fundamental processes directly from the broadband dielectric spectra. The rigorous numerical approach introduced here is well suited for analyzing both complex dielectric spectra and dielectric loss data only. Analysis of the salol spectra shows that a mapping from the frequency domain into the τ domain can greatly aid in the interpretation of the experimental data. In principle, this approach can be easily adapted to other types of fundamental relaxation processes, by changing the integral kernels in Eqs. (3) and (4); the algorithm is applicable to a wide range of kernel functions.

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