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Inversion of dielectric spectra into 2D distributions of activation energy and relaxation time

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Abstract

The superposition of Debye-like relaxation processes with different relaxation times, $\tau = \tau_0 \cdot \exp(W/k_BT)$, has a 2Ddistribution, $G(W, \ln \tau_0)$ of activation energy, W, and pre-exponential factor, τ_0 . With a novel method we evaluate Gvia inversion of temperature dependent broadband dielectric data. Simulations as well as experimental data demonstrate the validity of the analysis. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The permittivity, $\varepsilon = \varepsilon_1 - i\varepsilon_2$, of independently superposed Debye-like relaxations is often written as [1]

$$\varepsilon(\omega) = \Delta \varepsilon \cdot \int \frac{g_T(\ln \tau)}{1 + i\omega\tau} d\ln \tau + \varepsilon_{\infty}, \qquad (1)$$

where $\Delta \varepsilon$ denotes the relaxation strength and ε_{∞} is the high frequency permittivity. The normalized distribution function, g_T , describes the contribution of the respective relaxation times, τ , to an isothermal frequency spectrum at temperature T (see Fig. 1). If τ is given by the Arrhenius function then $\tau = \tau_0 \exp(W/k_BT)$. Depending on the physical mechanism either the activation energy, W, or the pre-exponential factor, τ_0 , or both may vary. Thus, g_T is only a projection of an underlying 2D distribution, $G(W, \ln \tau_0)$ and sums up the contributions of all $(W, \ln \tau_0)$ -pairs yielding the same τ s. Although different algorithms allow the inversion of broadband data into g_T (see Refs. [2–4]), the above description has two fundamental shortcomings: (i) there is no information on the contributing Ws and τ_0 s, (ii) a mathematical inversion may also be possible for hierarchical processes [5], where g_T has no physical meaning.

2. Procedure

 $G(W, \ln \tau_0)$ determines the change of shape of $\varepsilon(\omega)$ with varying temperature, i.e.

$$\epsilon(\omega, T) = \Delta \epsilon(T) \int \int \frac{G(W, \ln \tau_0)}{1 + i\omega\tau(T, W, \ln \tau_0)} d(\ln \tau_0) dW + \epsilon_{\infty}(T) - i \frac{\sigma_{dc}(T)}{\epsilon_0 \omega}$$
(2)

(σ_{dc} denotes a possible dc-conductivity). For a hierarchical process a 2D inversion into a temperature-independent *G*-function is impossible, since

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Fig. 1. Dielectric function vs. frequency for a PETG-blend containing 3.9% of polyaniline [7]. Solid lines: experiment; filled circles: Eqs. (4) and (5) with parameters from a fit of ε_1 (dashed line: eye-guide). The deviation between measured data and fit is within the experimental error $\Delta \varepsilon_1 \simeq \Delta \varepsilon_2 \simeq 0.02$. Since $\varepsilon_2 \ll \varepsilon_1$, it becomes noticeable only in the imaginary part: $0.25\% \simeq \Delta \varepsilon_1/\varepsilon_1 \ll \Delta \varepsilon_2/\varepsilon_2 \simeq 10\%$.

Eq. (2) is an unambiguous definition of a distributed process (provided precise experimental data in a sufficiently large frequency and temperature range is available). We use a single sweep technique allowing the determination of ε over nearly nine decades of frequency [6]. The precision is set by an analytic calibration as a function of temperature. For a numerical analysis we choose a sufficiently fine discretion of energy and ln τ_0 -space, which allows us to approximate a distribution of arbitrary shape:

$$G(W, \ln \tau_0) = \sum_{i,j} c_{ij} \varphi_{ij}$$
(3)

with real coefficients $c_{ij} \ge 0$ and based on step functions: $\varphi_{ij} = 1$ for $W_i \le W < W_{i+1}$ and $(\ln \tau_0)_j \le \ln \tau_0 < (\ln \tau_0)_{j+1}$, and $\varphi_{ij} = 0$ otherwise. We substitute *G* in Eq. (2) and perform the $(\ln \tau_0)$ -integration:

$$\varepsilon_1(\omega, T) = \Delta \varepsilon(T) \sum_{i,j} c_{ij} r_{ij}(\omega, T) + \varepsilon_{\infty}(T), \qquad (4)$$

$$\varepsilon_2(\omega, T) = \Delta \varepsilon(T) \sum_{i,j} c_{ij} k_{ij}(\omega, T) + \frac{\sigma_{\rm dc}(T)}{\varepsilon_0 \omega}, \qquad (5)$$

where r_{ij} and k_{ij} are known:

$$r_{ij} = \Delta_{ij}^2 - \frac{1}{2} \int_{W_i}^{W_{i+1}} \ln\left(\frac{1 + (\omega\tau_{j+1})^2}{1 + (\omega\tau_j)^2}\right) dW,$$
(6)

$$k_{ij} = \int_{W_i}^{W_{i+1}} \{\arctan(\omega\tau_{j+1}) - \arctan(\omega\tau_j)\} \, \mathrm{d}W, \qquad (7)$$

 $\Delta_{ij}^2 = (W_{i+1} - W_i) \cdot \ln(\tau_{j+1}/\tau_j), \text{ and } \tau_j = \exp [(\ln \tau_0)_j + W/(k_{\rm B}T)]. \text{ A comparison of Eq. (4) or}$ Eq. (5) with experimental data via a simple least squares algorithm does not allow us to evaluate the normalized distribution (the coefficients c_{ii}). The problem is ill-conditioned, i.e. small errors in the experimental data as well as the error introduced by the discretization may result in nonphysical contributions to the solution. Therefore, we use a 2D extension of the structure interference method, which was developed originally to obtain 1d size-distributions from X-ray data [7]. Solutions belonging to different random discretizations $\{\ldots W_i \ldots\} \times \{\ldots (\ln \tau_0)_i \ldots\}$ are averaged so that non-physical structures disappear. The fit also evaluates $\varepsilon_{\infty}(T)$, $\sigma_{dc}(T)$, and $\Delta \varepsilon(T)$ [the product $\Delta \varepsilon(T) c_{ij}$ in Eqs. (4) and (5) is factorized via the normalization condition $\sum_{i,j} c_{ij} \Delta_{ij}^2 = 1$]. Extrapolation of Cole–Cole plots $(\varepsilon_2 \text{ vs. } \varepsilon_1)$ can serve to get initial values for ε_{∞} while those for c_{ij} may be set to zero.

3. Results

For numerical tests we choose 2D distributions, G, and calculate the corresponding permittivities. After adding random noise we apply the inversion algorithm and average 100 solutions. The result is compared to the original distribution (see Fig. 2). The method is stable with respect to noise up to 10%.

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Fig. 2. Numerical test: (a) original distribution; (b) distribution obtained from the permittivity data (see text).

For a more difficult and realistic test we use the real part of the experimental data shown in Fig. 1. The β -relaxation of PETG (a modification of polyethyleneterephtalate) is observed [8]. Polar carboxyl groups (COO) of the main chains relax independent of each other so that these processes are expected to be parallel and not hierarchical. The distribution function displayed in Fig. 3 is an average of 40 solutions of Eq. (4) on different 50×60 (*W*, ln τ_0)-grids. The complex permittivity calculated on its basis (Eqs. (4) and (5) with $\sigma_{dc} = 0$) fits the experimental data (see Fig. 1). The main contribution (85%) of *G* to ε lies between 0.25 and 0.75 eV.

4. Discussion

To get independent experimental evidence for the existence of the distribution shown in Fig. 3, we use thermally stimulated depolarization currents (TSDC). A sample is polarized on cooling and the depolarization current is measured on heating. Applying the polarizing field only in small temperature windows (thermal sampling) allows us to decompose a relaxation into smaller peaks (see Fig. 4) and to determine a set of $(W, \ln \tau_0)$ -pairs



Fig. 3. Distribution obtained from the ac-data shown in Fig. 1 and from TSDC experiments (filled circles; scaled).



Fig. 4. Depolarization current normalized to the heating rate for the system shown in Fig. 1. Dashed line: complete relaxation. Solid lines: decomposed spectrum (thermal sampling).

[9]. Under certain conditions the contribution to *G* can be evaluated, which is proportional to the respective peak area. The result is displayed in Fig. 3 (filled circles) and confirms the 2D analysis. However, the TSDC-distribution is broadened since the sampled peaks are not single relaxations but subsets of *G* resulting in larger peak areas. The linear relationship for the *W*'s and $\ln \tau_0$'s on the ridge of *G* corresponds to the well-known compensation law: $\tau_0 = \tau_1 \exp(-W/(k_B T_0))$, where T_0 denotes the compensation temperature [10].

5. Conclusions

A novel dielectric analysis allows to determine 2D distributions of activation energy and relaxation time. Thus the concept of distribution functions can be tested and the physical origin of the broadening of dielectric relaxations can be elaborated.

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