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Nonlinear dielectric response of Debye, α, and β relaxation in 1-propanol

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ABSTRACT

We present nonlinear dielectric measurements of glass-forming 1-propanol, a prototypical example for the monohydroxy alcohols that are known to exhibit unusual relaxation dynamics, namely an additional Debye relaxation, slower than the structural α relaxation. Applying high ac fields of 468 kV/cm allows for a detailed investigation of the nonlinear properties of all three relaxation processes occurring in 1-propanol, namely the Debye, α, and β relaxation. Both the field-induced variations of dielectric constant and loss are reported. Polarization saturation and the absorption of field energy govern the findings in the Debye-relaxation regime, well consistent with the suggested cluster-like nature of the relaxing entities. The behavior of the α relaxation is in good accord with the expectations for a heterogeneous relaxation scenario. Finally, the Johari–Goldstein β-relaxation in 1-propanol seems to exhibit no or only weak field dependence, in agreement with recent findings for the excess wing of canonical glass formers.

1. Introduction

In recent years, the investigation of the nonlinear dielectric properties of glass-forming materials has gained increasing interest (see, e.g., [1–13]). In conventional dielectric spectroscopy, the linear response of a material to moderate electrical fields is detected [14–16]. In contrast, the application of high fields up to several 100 kV/cm drives the investigated glass former into the nonlinear regime and can reveal important additional information about the glass transition and the glassy state of matter. For example, dielectric hole-burning experiments have first proven the heterogeneous nature of glassy dynamics [17]. Further valuable information on the dynamic heterogeneity of glass formers was gathered by detecting the alteration of the permittivity under high ac fields [1,3]. Moreover, based on a model by Bouchaud, Biroli, and coworkers [18,19], the increase of molecular cooperativity when approaching the glass transition was investigated by measurements of the higher-order susceptibility χ_3 [7–9,13].

Compared to most of the dipolar glass-forming liquids that are typically investigated by dielectric spectroscopy, many monohydroxy-alcohols were found to show unusual relaxation dynamics: The slowest and, in most cases, dominating relaxation process revealed in their low-field dielectric spectra does not correspond to the structural relaxation process, i.e. the molecular motion governing, e.g., viscous flow [20–23]. Instead, this so-called Debye process is usually ascribed to the much slower motions of clusters (chain or ring-like structures) formed by several hydrogen-bonded alcohol molecules [10,23,24]. However, the details of these relaxational motions still need to be clarified. In spectra of the dielectric loss, this process shows up as a peak whose spectral shape can be well described by the Debye function, $\varepsilon''(\nu) = \Delta\varepsilon\,\omega\tau_D / [1 + (\omega\tau_D)^2]$, where $\omega = 2\pi\nu$ is the angular frequency, $\Delta\varepsilon$ is the relaxation strength, and τ_D is the relaxation time. In contrast, the loss peak arising from the structural α relaxation, which is the dominating spectral feature in most other glass-forming liquids and which also contributes to $\varepsilon''(\nu)$ at $\omega > 1/\tau_D$ in monohydroxy alcohols, usually does not follow this function. Instead it is significantly broadened and often asymmetrically shaped. This can be ascribed to the heterogeneous nature of glassy dynamics [25], leading to a distribution of relaxation times, i.e. each single molecule relaxes in accord with the Debye theory, but the relaxation times are different for different molecules. However, the molecular dynamics in the environment of the mentioned supramolecular clusters in the monohydroxy alcohols, which is dominated by the α-relaxation time $\tau_\alpha \ll \tau_D$, is much faster than the cluster motion itself. Thus, any heterogeneity in the material is blurred by these faster molecular fluctuations and a monodispersive Debye-shaped loss peak is observed.

In the present work, we investigate the nonlinear dielectric response of 1-propanol, a prototypical material that was among the first examples, where the non-canonical behavior of monohydroxy alcohols was unequivocally demonstrated [20]. In earlier works by R. Richert and coworkers, strong variations in the nonlinear properties of different monohydroxy alcohols were found [6,10,11]. In [11], this finding was ascribed to differences in the ability of high electrical fields to affect the equilibrium of cluster shapes fluctuating between polar open-chain and nonpolar ring-like structures. However, 1-propanol seems to be unaffected by this mechanism [11] and, thus, is an ideal candidate to investigate in detail the nonlinear behavior for the single-dispersive case, lacking any heterogeneity. Nonlinear dielectric experiments on

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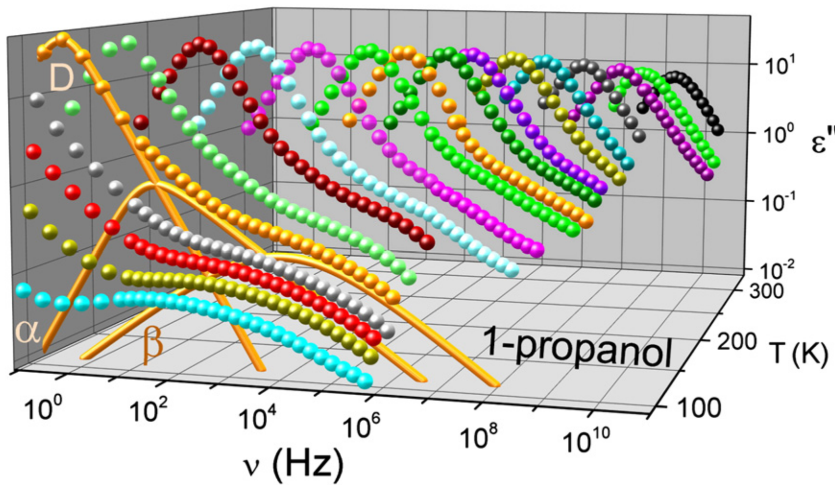

Fig. 1. Broadband dielectric loss spectra of glass forming 1-propanol at selected temperatures. The lines demonstrate the composition of the curve at 112 K by three separate relaxations peak arising from Debye (D), α, and β relaxation as obtained by fits of the data [26].

canonical glass formers as glycerol, checking for the field-induced variation of the permittivity, can be well understood considering dynamical heterogeneity [1,3]. Moreover, nonlinear glassy dynamics can also be interpreted in terms of cooperativity effects [7,8,13,18], another important aspect often invoked to explain the peculiarities of the supercooled and glassy state of matter. 1-Propanol represents a much simpler system where the first mentioned hallmark feature of glassy dynamics (heterogeneity) seems to be absent and the second (cooperativity) should play a smaller role only, as cluster–cluster interactions can be expected to be rarer than the intermolecular interactions in canonical glass formers. Moreover, extending the investigated frequency range to the region of the α and β relaxations will also provide information on the nonlinear behavior of these processes.

In the present work, we report the modification of the dielectric permittivity (real and imaginary part) by the application of high ac fields. The use of microspheres as capacitor-spacer material (see Section 2) allows for the application of very high fields of 468 kV/cm. Thus, the obtained permittivity results are of unprecedented precision and cover a broader frequency range than most earlier nonlinear investigations of glass forming materials.

2. Experimental procedures

The measurements were performed using a frequency-response analyzer in combination with a high-voltage booster "HVB 300", both from Novocontrol Technologies, enabling measurements with peak voltages up to 150 V at frequencies up to about 100 kHz. The sample material (1-propanol of 99.7% purity, anhydrous) was purchased from Aldrich and mixed with 0.05% silica microspheres (2.87 μm average diameter, monodisperse, plain) from Corpuscular Inc. When putting the sample between two lapped and highly polished stainless steel plates, these dielectrically neutral microspheres act as spacing material, leading to an extremely small plate distance enabling the application of very high fields of up to 468 kV/cm. A sample thickness of 3.2 μm was deduced from a comparison of the absolute values of ε'' with the published low-field results from [20,21]. For a verification of the obtained results, additional measurements with glass-fiber spacers of 30 μm diameter were carried out, using a high-voltage booster "HVB 4000", reaching voltages up to 2000 V and frequencies up to about 1 kHz. Similar to the procedure reported in Refs. [1,3], at each frequency we performed successive high- and low-field measurements, separated by a waiting time. To minimize the effects from phonon heating, few high-field oscillations (150 V, 468 kV/cm) were applied, followed by a cooling period achieved by applying a series of "waiting-oscillations" with 0.7 V only. Subsequently, a low-field measurement with 4.5 V (14 kV/cm) was carried out. At low frequencies typically 8 high-voltage cycles were applied while at higher frequencies the cycle number was larger (and determined by the processing speed of the experimental setup). For example, at 100 Hz, 30–50 cycles were applied, corresponding to a measurement time of 0.3–0.5 s and for $\nu \geq 1$ kHz, the field was always applied for one second. The number of applied "waiting-oscillations" was 27 times higher than the cycle number of the high-field measurement to ensure that the low-field data are not affected by the preceding high-field measurement. For cooling, a closed-cycle refrigeration system (CTI-Cryogenics) was used.

3. Results and discussion

3.1. Debye relaxation

Fig. 1 shows broadband loss spectra of 1-propanol obtained by conventional low-field dielectric spectroscopy, measured at various temperatures. As demonstrated in [26], where part of these data were already shown, these spectra can be reasonably fitted by the sum of

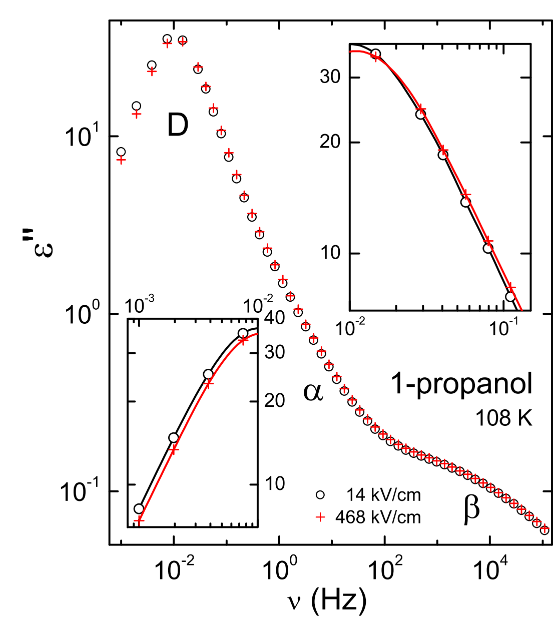

Fig. 2. Dielectric loss spectra of 1-propanol measured at 108 K and two different ac fields as indicated in the figure. The insets provide magnified views of the left and right flank of the Debye peak (the lines are guides to the eye).