

Nonlinear features in the dielectric behavior of propylene glycol

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(Received 1 November 2006; revised manuscript received 13 December 2006; published 5 February 2007)

We investigate the nonlinear dielectric effects in a glass-forming polar liquid, propylene glycol, by high-voltage frequency-domain impedance experiments. The peak amplitudes of the sinusoidal electric fields are varied between 14 and 283 kV/cm. Two competing nonlinear effects are observed: a decrease of the dielectric constant reminiscent of the Langevin effect and an increase of the dielectric loss that originates from the irreversible transfer of energy from the electric field to the slow degrees of freedom of the viscous liquid. By virtue of the frequency dependence of the two features, the positive and negative changes are easily separable. Both effects can be rationalized quantitatively without adjustable parameters.

DOI: [10.1103/PhysRevB.75.064302](https://doi.org/10.1103/PhysRevB.75.064302)

PACS number(s): 64.70.Pf, 65.20.+w, 77.22.-d

I. INTRODUCTION

The dynamics of supercooled liquids are characterized by substantial deviations from simple exponential decays regarding the correlation functions that reflect the structural relaxation behavior.^{1,2} The nature of the dispersion of relaxation time constants in these complex materials has been the focus of numerous studies.³ Empirically, relaxation processes often follow the Kohlrausch-Williams-Watts (KWW) (Ref. 4) law for some normalized correlation function $\varphi(t)$,

$$\varphi(t) = \exp[-(t/\tau_0)^\beta] = \int_0^\infty g(\tau)e^{-t/\tau}d\tau. \quad (1)$$

The observation and recognition of the heterogeneous nature of structural relaxation has provided the picture of somewhat independent and spatially separated modes, i.e., the dynamics are partitioned into dynamically distinct domains.^{5,6} These domains are being associated with lifetimes that are slightly longer than the average structural relaxation time,^{7,8} and spatial dimensions of several nanometers are expected.^{9,10} Much longer lifetimes of heterogeneity have been reported only for temperatures within a range of a few degrees around T_g .¹¹ While the existence of dynamical heterogeneity is well established, details regarding the nature of the exchange process that limits the lifetime of heterogeneity and of the topologies and length scales involved are not available.^{12,13}

For understanding the dynamics of supercooled liquids and the glass transition, it is crucial to improve our knowledge of the topologies and spatial scales of the distinct domains, and to what extent these depend on temperature.^{14,15} In a recent theoretical study, Bouchaud and Biroli provide a link between frequency-dependent nonlinear susceptibilities and the length scale of heterogeneities.¹⁶ In view of this strong motivation, it is highly desirable to investigate the frequency-resolved susceptibilities of supercooled liquids beyond their linear-response regime and beyond the limitation to the steady-state cases. In dielectric relaxation experiments, electric fields that drive the response outside the linear range are relatively easily achieved and a number of nonlinear dielectric features have been reported.¹⁷⁻²³ However, a detailed field dependence of the complete relaxation or loss spectrum of a simple liquid is not available. The aim of this work is to

provide the information and interpretation of electric-field-induced deviations from the linear (first-order) susceptibility. Two distinct effects are observed in propylene glycol: a field-induced decrease of the steady-state permittivity and an increase of the higher frequency loss amplitude at increased fields relative to the low-field limit. The lowered permittivity is the field dependence expected on the basis of the Langevin or orientational saturation effect. The loss increase is explained in terms of the energy a dielectric (with $\epsilon'' > 0$) absorbs from the external field and the concomitant increase in the fictive temperatures.²⁴

II. EXPERIMENTS

The liquid of this study, propylene glycol (PG), is purchased from Aldrich (1,2 propanediol, purity $\geq 99.5\%$) and used as received. In order to determine the impedance at high electric ac fields, higher voltages and thinner samples relative to typical conditions are required. Samples are prepared between two lapped and polished brass electrodes (16 and 20 mm diameter), separated by a Teflon ring of 10 μm thickness with 14 mm inner and 20 mm outer diameter (see capacitor in Fig. 1). The ring covers the circumference of the smaller electrode and is meant to prevent sample failures due to the higher electric fields at the edges. The electrodes are spring-loaded to assure a temperature invariant stress on the Teflon ring. The sample cell is held in a Novocontrol Quatro cryostat at the desired temperature. The impedance is determined by a Solartron SI-1260 gain/phase analyzer, with the generator voltage amplified by a factor of 100 using a Trek PZD-700 high-voltage amplifier. The voltage at the sample is recorded via input V1 of the SI-1260 using the voltage monitor output of the amplifier (internally attenuated by a factor of 200) and the current is recorded via input V2 as the voltage drop across a 50 Ω resistor. A 500 Ω resistor is used in series with the sample capacitor to protect the equipment against the high voltages resulting from a possible dielectric breakdown. The 500 Ω resistor is calibrated and its value is subtracted from the measured impedance. The high-voltage part of the setup is outlined in Fig. 1.

Sinusoidal electric fields, $E(t) = E_0 \sin(\omega t)$, without dc offset are applied to the sample. The range of peak fields used here extends from 14 to 283 kV/cm. At each frequency, the

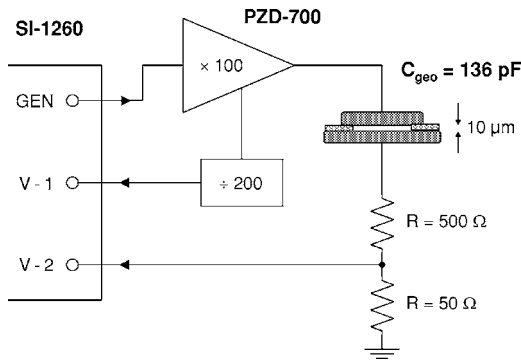


FIG. 1. Experimental setup for impedance measurements at voltages up to 300 V based upon the Solartron SI-1260 gain/phase analyzer. High voltages are provided by a Trek PZD-700 amplifier with a built-in voltage monitor signal for a direct return to the V-1 input. The current is measured at the V-2 input as voltage drop across a 50 Ω resistor. The 500 Ω resistor protects the input in the case of a shorted sample. The electrode distance is defined by a 10 μm Teflon spacer ring that covers the entire edge of the smaller disk.

high voltage is typically applied for five cycles, followed by a 20-cycle zero-field cooling period and by the lower voltage measurement using $E_0=14$ kV/cm, i.e., $10V_{\text{rms}}$ across 10 μm . It has been checked that in all cases the number of high-field cycles used is sufficient to ensure the absence of significant transient effects. At the same time, the number is kept small enough to avoid phonon heating, which is easily discriminated from the present effects because a change in phonon temperature shifts the entire loss curve to higher frequencies. Also, varying the number of cycles a factor of 2 up or down has virtually no effect on the results. Much longer application of the high field is avoided because this would increase the phonon temperature of the sample. All field-induced changes shown here are completely reversible.

III. RESULTS AND DISCUSSION

The “low”-field dielectric spectra of PG measured at a field of 14 kV/cm are displayed in Fig. 2. Within the present experimental resolution, these conditions are equivalent to the low-field limit. Consistent with previous dielectric results on PG, this supercooled liquid exhibits the typical features of a single-component polar viscous liquid: broadened and asymmetric loss profiles, pronounced non-Arrhenius temperature dependence of the characteristic relaxation time, and a high dielectric constant that decreases with increasing temperature. The curves are well approximated by Havriliak-Negami (HN)²⁵-type dielectric functions,

$$\hat{\epsilon}(\omega) = \epsilon_\infty + \Delta\epsilon[1 + (i\omega\tau)^\alpha]^{-\gamma}, \quad (2)$$

where ϵ_∞ is the dielectric constant in the high-frequency limit and $\Delta\epsilon = \epsilon_s - \epsilon_\infty$ is the relaxation strength, with ϵ_s being the static dielectric constant. The exponents α and γ ($0 < \alpha, \alpha\gamma \leq 1$) quantify the symmetric and asymmetric broadening, respectively. After correcting for the Teflon area, the approximate fit parameter values for $T=180$ K are $\epsilon_\infty=4$, $\epsilon_s=88$, $\alpha=0.85$, and $\gamma=0.76$. In this narrow temperature range, the

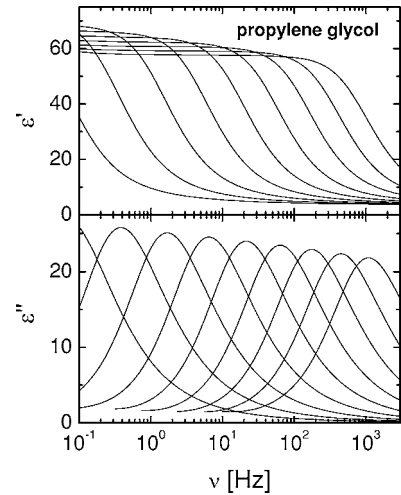


FIG. 2. Experimental results for the dielectric permittivity $\epsilon'(\nu)$ and loss $\epsilon''(\nu)$ of propylene glycol at temperatures $T=174$ – 198 K in steps of 3 K. The curves are recorded at a common (low) field of $E_0=14$ kV/cm.

dielectric strength $\Delta\epsilon$ changes with temperature as $d \ln \epsilon/dT = -0.96\% \text{ K}^{-1}$ in terms of the relative change.

The most obvious effect of a high electric field is a change of the dielectric loss amplitude that amounts to an increase of almost 10% in the present range of parameters. These field-induced changes are shown as the spectrum of relative increases, $\Delta \ln \epsilon''(\nu)$, for various field strengths in Fig. 3. These $\Delta \ln \epsilon''(\nu)$ curves feature a very characteristic frequency dependence: practically no effect for frequencies below the loss peak at ν_p , but a substantial increase of the loss that extends across the entire high frequency wing. Within the current experimental ranges and resolution, the frequency dependence of these $\Delta \ln \epsilon''(\nu)$ profiles is temperature-invariant. In such a narrow range of absolute temperature, changes in the behavior are expected only if the shape of the loss spectrum itself depends on temperature, which is not the case for the present results. The explanation of this field

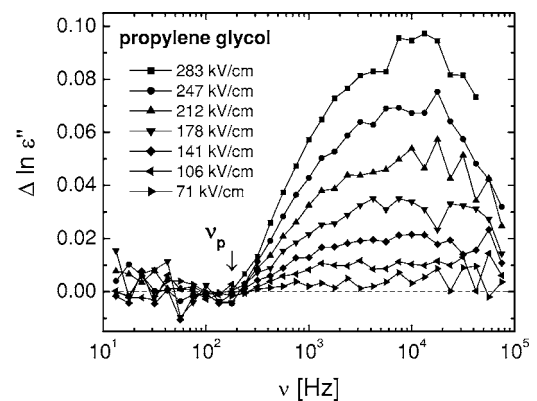


FIG. 3. Experimental results for the field-induced relative change of the dielectric loss, $\Delta \ln \epsilon''(\nu)$, in propylene glycol for fields between $E_0=283$ and 71 kV/cm in the order from top to bottom curve, as indicated. All results are obtained at a temperature of $T=192$ K, where the loss peak is positioned at $\nu_p=180$ Hz as indicated by the arrow.

effect is analogous to a recent treatment that focused on glycerol,²⁴ where frequency-resolved heat capacity data are available.²⁶ As detailed in the following, the irreversible transfer of energy from the electric field to the slow degrees of freedom within the liquid is made responsible for the departures from linearity, with the basic ideas originating from studies of dielectric hole burning (DHB).^{27–29}

The model assumes heterogeneous dynamics, i.e., dynamically distinct domains within which the dielectric and the thermal relaxation proceeds exponentially with identical values for τ , i.e., with locally correlated time constants for $\hat{\epsilon}(\omega)$ and $\hat{c}_p(\omega)$. The overall susceptibility is thus given by a superposition of independent Debye peaks with the probability density $g(\tau)$ governing the number of relaxing units associated with the relaxation time τ . In support of this view, it has been shown for glycerol that $g(\tau)$ is virtually identical for dielectric relaxation $\hat{\epsilon}(\omega)$ and for the dynamic heat capacity $\hat{c}_p(\omega)$.³⁰ The application of an external sinusoidal electric field, $E(t)=E_0\sin(\omega_0 t)$, will lead to the absorption of energy, and for a sample of volume V this amounts to $Q = \pi\epsilon_0 E_0^2 \epsilon''(\omega_0) V$.^{31,32} For each domain, the energy gain term averaged over one period is given by the power $p = Q\omega_0/2\pi$, while the energy loss term is a matter of the thermal relaxation time with which the excess fictive temperature $T_e = T_f - T_{\text{bath}}$ approaches the phonon temperature T_{bath} . At steady-state conditions, the time derivative of T_e is zero and the heat balance equation becomes $T_e = \tau p / C_p$. For the dynamically distinct domains associated with a certain time constant τ , both the heat capacity and the dielectric loss are assumed proportional to the number of molecules, $g(\tau)d\tau$. As a result, the terms $Vg(\tau)d\tau$ originating from ϵ'' and C_p cancel and the fictive temperature change reads

$$T_e(\tau) = \frac{\epsilon_0 E_0^2 \Delta\epsilon}{2\Delta c_p} \frac{\omega_0^2 \tau^2}{1 + \omega_0^2 \tau^2} = T_e^0 \frac{\omega_0^2 \tau^2}{1 + \omega_0^2 \tau^2}, \quad (3)$$

where ϵ_0 is the permittivity of vacuum and Δc_p is the (volumetric) heat capacity step associated with the slow modes. For a given frequency ω_0 , the τ -dependent term in Eq. (3) implies that domains associated with slower relaxation modes, $\tau \gg 1/\omega_0$, will experience an increase of their fictive temperature by T_e^0 , while faster modes with $\tau \ll 1/\omega_0$ will remain unchanged. The predicted plateau for $\tau \gg 1/\omega_0$ is a consequence of two competing effects: domains with a more distant τ absorb less energy because their loss at ω_0 is small, but their rate of energy transfer to the bath is reduced accordingly. For frequencies ω_0 below the loss peak of the sample, domains with $\tau > 1/\omega_0$ will not be found and the field effect thus disappears for sufficiently low frequencies, as predicted quantitatively by the current model.

To determine the magnitude of the effect expected for PG, we need the values of the dielectric relaxation strength of $\Delta\epsilon=88$, the heat capacity contribution $\Delta c_p = 1.5 \text{ J K}^{-1} \text{ cm}^{-3}$,³³ and the field of $E_0=283 \text{ kV/cm}$, which results in an excess temperature limit of $T_e^0=0.21 \text{ K}$. Based on the activation energy $E_A^{\text{eff}} = d(\ln \tau)/d(1/k_B T)$ for viscous PG, this value of T_e^0 translates into a relative relaxation time change of $\Delta\tau/\tau = \Delta \ln \tau = -0.1$. For the high-frequency wing of the dielectric loss, the slope for PG is $d \ln \epsilon''/d \ln \omega$

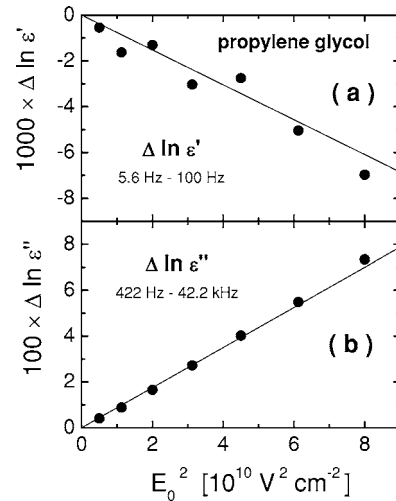


FIG. 4. Averaged field-induced relative change, $\Delta\epsilon/\epsilon = \Delta \ln \epsilon$, of the dielectric properties of PG at $T=192 \text{ K}$ vs the squared electric field, E_0^2 , where the linear behavior shows that the effects depend quadratically on the electric field. The data refer to averages over the specified frequency ranges. (a) Average field-induced relative change of the dielectric constant, $\Delta \ln \epsilon'(\nu)$, for frequencies between 5.6 and 100 Hz. (b) Average field-induced relative change of the dielectric loss, $\Delta \ln \epsilon''(\nu)$, for frequencies between 422 Hz and 42.2 kHz. Note the difference in ordinate scales. The lines represent the proportionalities, $\Delta \ln \epsilon' = -7.6 \times 10^{-14} (E_0 \text{ V}^{-1} \text{ cm})^2$ and $\Delta \ln \epsilon'' = +8.7 \times 10^{-13} (E_0 \text{ V}^{-1} \text{ cm})^2$, respectively.

≈ -0.65 , which will predict an increase of the loss reaching $\approx 7\%$. Consistent with this result, the magnitude of the average $\Delta \ln \epsilon''$ increase amounts to 7.5% at our highest electric field of 283 kV/cm. The field dependence of the effect is shown as $\Delta \ln \epsilon''$ (taken as average in the range $422 \text{ Hz} \leq \nu \leq 42.2 \text{ kHz}$) versus E_0^2 in Fig. 4(b), which reveals the expected linearity. The line in Fig. 4(b) reflects the above prediction, $\Delta \ln \epsilon'' = +8.7 \times 10^{-13} (E_0 \text{ V}^{-1} \text{ cm})^2$ or +7% at $E_0 = 283 \text{ kV/cm}$. The complete permittivity and loss spectrum at high fields can be obtained by evaluating $\tau^* = \tau + \Delta\tau$ via $T_e(\tau)$ for each frequency ω_0 and then determining the distribution average using

$$\hat{\epsilon}(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) = \epsilon_\infty + \Delta\epsilon \int_0^\infty g(\tau) \frac{1}{1 + i\omega\tau^*} d\tau, \quad (4)$$

as done previously for glycerol.²⁴

One might wonder why rationalizing the above electric field heating effects requires the assumption of heterogeneity, while the dispersion observed in dynamic heat capacity studies can be explained without such a picture. In a calorimetric or similar experiment, heat to the sample is provided through the phonon bath and therefore never selective regarding fast or slow relaxation components. However, the energy of a strong low-frequency external electric field is selectively absorbed by a certain spectral range of the slow degrees of freedom and only this subensemble is modified. This spectral selectivity is the hallmark of heterogeneous dynamics.

Given these pronounced “heating” related changes of the dielectric spectra, it may seem hopeless to find evidence of

other sources of nonlinear dielectric behavior that are not related to the absorption of energy. On the other hand, both the observations and the model predictions agree that these effects remain absent at sufficiently low frequencies. In the regime where $\nu \ll \nu_p$, the dielectric loss becomes small and the absorption of energy from the external electric field is negligible even at high fields. In terms of the loss, this is seen as $\Delta \ln \varepsilon''(\nu < \nu_p) \approx 0$ in Fig. 3, and the above model equally predicts $\Delta \ln \varepsilon'(\nu < \nu_p) \approx \Delta \ln \varepsilon_s \approx 0$ for the low-frequency permittivity and steady-state dielectric constant ε_s . Dielectric nonlinearities such as the Langevin or polarization saturation effect are not frequency or loss magnitude specific and are thus best observed in terms of how the field affects the value of ε_s . The result of analyzing the present data along these lines is depicted in Fig. 4(a), which shows a decrease of the low-frequency permittivity in terms of $\Delta \ln \varepsilon'$ (taken as average in the range $5.6 \leq \nu \leq 100$ Hz) with increasing field. According to Fig. 4, the field dependence of ε_s is well approximated by the relation $\Delta \ln \varepsilon_s = -7.6 \times 10^{-14} (E_0 \text{ V}^{-1} \text{ cm})^2$, and thus reversed in direction and around ten times smaller than that of the higher-frequency loss which follows $\Delta \ln \varepsilon'' = +8.8 \times 10^{-13} (E_0 \text{ V}^{-1} \text{ cm})^2$.

Based upon the dipole moment of PG of $\mu = 2.25 \text{ D}$,³⁴ a temperature of $T = 192 \text{ K}$, and a field of $E_0 = 283 \text{ kV/cm}$, the Langevin function argument is determined as $a = \mu E / kT = 0.08$ for the present highest field. The nonlinearity originating from dielectric saturation of the dipole orientation can be estimated by comparing the Langevin expression, $\langle \cos \theta \rangle = L(a) = \coth(a) - 1/a$, with its low-field limit $a/3$ for $a = 0.08$. This calculation results in an expected relative change of -0.034% for the average $\cos \theta$, but the validity of this approach is limited to noninteracting dipoles. For the polarization or permittivity of a pure polar liquid, the expected changes are larger, as detailed below.

It is common practice to express the field dependence of the steady-state permittivity as $\varepsilon_s(E^2) = \varepsilon_s(0) \times [1 - \lambda E^2]$, where $\varepsilon_s(0)$ refers to the zero-field limit.³⁵ The meaning of λ is the relative reduction of ε with the squared electric field, i.e., $\lambda = -\Delta \ln(\varepsilon_s) / E^2$, whereas the Piekara factor refers to the absolute increase $\Delta \varepsilon_s / E^2 = -\lambda \varepsilon_s$. For water at 293 K, for instance, a Piekara factor of $\Delta \varepsilon_s / E^2 = -8 \times 10^{-16} \text{ m}^2 \text{ V}^{-2}$ has been reported and explained in terms of the Langevin effect.^{36,37} In the present case of PG, we find an effect of similar magnitude, $\Delta \varepsilon_s / E_0^2 = -7 \times 10^{-16} \text{ m}^2 \text{ V}^{-2}$. Therefore, the decrease of the steady-state permittivity observed for PG may be due to dielectric saturation.

In order to assess this nonlinear feature of ε_s , we use van Vleck's calculation of the dielectric saturation for pure polar liquids in terms of the Piekara factor,^{38,39}

$$\frac{\Delta \varepsilon_s}{E^2} = \frac{\varepsilon_s(E^2) - \varepsilon_s(0)}{E^2} = -\frac{N\mu^4}{45\varepsilon_0 V(kT)^3} \frac{\varepsilon_s^4(\varepsilon_\infty + 2)^4}{(2\varepsilon_s + \varepsilon_\infty)^2(2\varepsilon_s^2 + \varepsilon_\infty^2)}, \quad (5)$$

where N is the number of particles, V is the volume, and $\varepsilon_s = \varepsilon_s(0)$ is the steady-state dielectric constant in the low-field limit. The value of the molecular volume $\nu = V/N$ for PG is estimated from the molar weight $M_w = 76.09 \text{ g/mol}$

and the density of $\rho = 1.036 \text{ g/cm}^3$ as $\nu = 1.2 \times 10^{-28} \text{ m}^3$. The result is $\Delta \varepsilon_s / E^2 = -6.7 \times 10^{-16} \text{ m}^2 \text{ V}^{-2}$, equivalent to $\Delta \ln \varepsilon_s = -7.6 \times 10^{-14} (E_0 \text{ V}^{-1} \text{ cm})^2$. This field dependence is shown as a line in Fig. 4(a), and agrees favorably with the data. Note that this comparison does not involve an adjustable parameter and no temperature dependence of this slope is found within the present experimental range. Because the field-induced decrease observed as $\Delta \ln \varepsilon_s$ is assumed a frequency-invariant effect, the entire curves related to orientational polarization, $\varepsilon'(\omega) - \varepsilon_\infty$ and $\varepsilon''(\omega)$, should be affected. As a result, the above "heating" related nonlinearities are actually slightly more pronounced than they appear.

As a final point, we convince ourselves that Coulombic compression does not alter the above considerations. The attractive force F compressing the electrodes that results from the application of a field $E(t) = V(t)/d = E_0 \sin(\omega t)$ to a capacitor with area A and distance d is given by combining the equations $Fd = \frac{1}{2}QV$, $Q = CV$, and $C = \varepsilon \varepsilon_0 A / d$. The resulting stress F/a acts on the Teflon (PTFE) ring with supporting area $a = 4.7 \times 10^{-5} \text{ m}^2$ and an approximate Young's modulus of $Y = 1 \text{ GPa}$. Adding the mechanical effects of the sample would further decrease the net changes. The equations needed to quantify the effects are

$$F(t) = \frac{\varepsilon_s \varepsilon_0 A}{2} E^2(t) = \frac{\varepsilon_s \varepsilon_0 A}{4} E_0^2 [1 - \cos(2\omega t)],$$

$$\Delta \ln \varepsilon = -\frac{\Delta d}{d} = +\frac{F_0}{aY} = \frac{\varepsilon_s \varepsilon_0 A}{4aY} E_0^2, \quad (6)$$

where only the constant force component F_0 is considered, because the effects at 2ω will not influence the impedance measured at ω . For the present situation at the highest field of 283 kV/cm , the force is $F_0 = 31 \text{ N}$, the stress $F_0/a = 0.67 \text{ MPa}$, and the relative change of the distance d or capacitance C is below 6.7×10^{-4} . This upper estimate of the effect is a factor of 10 smaller than the changes resulting from dielectric saturation, see Fig. 4(a), and opposite in direction because the apparent ε_s would increase as a result of compressing the capacitor. The result confirms that electrode attraction can be disregarded as a significant source of nonlinearity in the current experiments.

IV. CONCLUSIONS

The dielectric permittivity and loss of viscous propylene glycol is investigated by impedance techniques at harmonic fields as high as 283 kV/cm . Two distinct nonlinear features have been identified in the supercooled liquid near its glass transition temperature T_g . For frequencies above the loss peak position, the dielectric loss experiences a pronounced increase that reaches a level of $+7.5\%$ at high fields. The origin of this effect is the absorption of energy from an external field by the slow modes, which increases the fictive temperatures of the slower domains. Within the framework of the present model, the resulting changes can be rationalized quantitatively only if it is assumed that dielectric and thermal relaxation times are heterogeneous and locally correlated regarding their time constants. Additionally, dielectric

saturation is identified at sufficiently low frequencies, where the “heating” effect remains absent. This field-induced decrease of the permittivity agrees with the behavior expected on the basis of van Vleck’s calculations of dielectric saturation on the level of Onsager’s treatment of pure polar liquids. The saturation effects remain small compared with the changes originating from the absorption of energy and thus have little impact on the loss increase observed for the high-frequency wing. In conclusion, the expected results from dielectric saturation and energy absorption are sufficient to explain the observed deviations from linear response at high

fields across the entire dielectric spectra. Consequently, no changes in the behavior of PG itself are detected at fields up to 283 kV/cm.

ACKNOWLEDGMENTS

The authors thank J.-P. Bouchaud and D. L’Hôte for interesting discussions. This material is based upon work supported by the National Science Foundation under Grant No. DMR 0304640 (NIRT).

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