Strong Increase of Correlations in Liquid Glycerol Observed by Nonlinear Dielectric Techniques

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Abstract: Non-linear dielectric measurements are an important tool to access material properties and dynamics concealed in their linear counterparts, but the available data is often intermittent and on occasion even contradictory. Employing and refining a recently developed technique for high ac field dielectric measurements in the static limit, we ascertain non-linear effects in glycerol over a wide temperature range from 230 K to 320 K. We find that the temperature dependence of the Piekara factor a, which quantifies the saturation effect, changes drastically around 290 K, from $\partial a/\partial T = +1.4$ to -130 in units of 10^{-18} V^2 m^{-2} K^{-1}. These high values of $|a|$ quantify not only elevated dielectric saturation effects, but also indicate a temperature driven increase in higher order orientational correlations and considerable correction terms with respect to the central limit theorem. No signature of this feature can be found in the corresponding low field data.

Keywords: non-linear dielectric experiments; higher-order correlations; non-Gaussian parameter; central limit theorem; glycerol

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I. INTRODUCTION

Dielectric high field measurements of nonlinear dielectric effects (NDEs) can reveal material properties hidden to common, low field dielectric experiments.[1,2,3,4] The most fundamental NDE, termed dielectric saturation,[5] is caused by the upper bound of dipolar orientation upon increasing the field strength E. This results in a nonlinear field dependence of the polarization $P(E)$, and thus in a reduction of the static dielectric constant ε_s at elevated electric fields. On the other hand, an increase in ε_s is associated with the so called chemical effect. Like other nonlinear effects, these deviations scale, to first order, with E^2. Both effects are often quantified by the Piekara factor,[6]

$$a = \frac{\varepsilon_E - \varepsilon}{E^2} = \frac{\Delta\varepsilon_E}{E^2}\,. \tag{1}$$

Here, ε_E denotes the static ($\omega \to 0$) permittivity at elevated fields, while $\varepsilon = \varepsilon_{E\to 0}$ is its low field, *i.e.*, linear regime, counterpart. Due to the experimental challenges when determining NDEs, literature values for a tend to vary between reports,[7] in some cases by orders of magnitude, and even discrepancies regarding the sign of a can be found.[8]

In this work, we revisit the canonical glass former glycerol, commonly regarded as a model glass forming system. Various non-linear dielectric studies on glycerol have been published.[9,10,11,12] However, only few focus on the static limit associated with the Piekara factor,[8,12] and none have systematically covered a range of temperatures. The existing data hint at an increase of the magnitude of the NDE with increasing temperature, but only two data points are available: $a = -1.4\times10^{-16}$ m^2 V^{-2} at 217 K,[12] and $a = -5.9\times10^{-16}$ m^2 V^{-2} at 298 K.[8] Such a temperature dependence contrasts expectations based on mean-field theories and thus deserves further scrutiny.

Here, we utilize a sinusoidal field at a fixed frequency and subject the sample to a sequence of different field amplitudes within a few milliseconds to determine the Piekara factor over a wide temperature range, 230 K $\leq T \leq$ 320 K. The advantages of this approach over more common techniques have been described in detail earlier.[13] Surprisingly, a significant change of the temperature dependence of a is detected: While saturation is the dominant effect observed in the entire temperature range, its magnitude is small at low T, but increases rapidly by a factor of ≈ 10 for temperatures exceeding 290 K. At the same time, no analogous changes in the linear ε are visible. From these features of $a(T)$, we conclude that bulk glycerol at $T > 290$ K is associated with substantial higher-order correlations and increasing deviations from Gaussian statistics of the macroscopic dipole.

II. EXPERIMENTAL SETUP

Glycerol (Mallinckrodt, 99.8 %) was used as received. The sample material was placed in a spring loaded titanium plate capacitor cell with electrode diameters 17 mm and 20 mm. For most experiments, monodisperse silica microspheres (diameter 9.2 μm, Cospheric) were used as spacer material. As a comparison, additional samples were prepared with polyimide spacer rings (thickness 8 μm and 13 μm, Goodfellow), instead. In order to control and measure the sample temperature, we used a Leybold RDK 6–320 Coolpak 6200 closed cycle He-refrigerator cryostat with a Lakeshore Model 340 temperature controller with Si-diode (DT-470-CU, ΔT = 0.3 K) sensors.

For each sample, we performed a low field dielectric measurement, employing a Hewlett Packard 4284 precision LCR meter. Selected spectra of $\varepsilon^*(\omega) = \varepsilon' - i\varepsilon''$ for one sample are shown in Fig. (1), with the permittivity ε' plotted in panel (a) and the dielectric loss ε'' in panel (b), both versus frequency $\nu = \omega/2\pi$. These profiles are consistent with earlier reports on the dielectric properties of glycerol.[14] Such spectra served to verify the sample quality, determine the actual sample thickness, and to identify the optimal test frequency ω for the high field experiment. This test frequency at which high field measurements of ε_E are best performed should on the one hand be situated well within the static plateau of ε', *i.e.*, at time scales well below those of the structural relaxation. On the other hand, a low loss is preferred to avoid heating the sample with strong ac-fields and thus changing the static permittivity. The arrow in Fig. (1b) marks a good frequency of 4 kHz for high field measurements at T = 250 K: it is situated well within the plateau region of $\varepsilon'(\omega)$ and close to the minimum of ε''. Since the actual sample thickness may deviate from the nominal spacer dimensions, a correction factor was found for each sample as the ratio of the measured low field static permittivity and a reference value,[15] calculated by

$$\varepsilon(T) = -38.88 + 21416\ \mathrm{K}/T + 0.02727\ \mathrm{K}^{-1}\, T\,. \tag{2}$$

For the high field experiments, the dc-bias free voltage patterns,

$$E(t) = E_0 \sin(\omega t)\,, \tag{3}$$

were generated by a Stanford Research Systems DS-345 arbitrary waveform generator and increased in amplitude by a factor of 100 via a Trek PZD-350 amplifier. A Nicolet Sigma 100 digital oscilloscope then acquired the sample current and voltage data, where the low potential side of the sample capacitor is connected to the ground via a 100 Ω or 300 Ω shunt.

The measurements were performed using field patterns described earlier,[13] or analogous ones with 6 (*cf.* Fig. (2a)) or 12 zones with a sequence of field amplitudes at a fixed frequency. With a low repetition rate that corresponds to a duty cycle of < 10 %, the field pattern of only several milliseconds duration is applied 5000 times to improve the signal-to-noise ratio by averaging. Each zone spans multiple wave periods, and dielectric properties are calculated for each period separately. Therefore, potential time dependent changes of ε_E within a zone, *e.g.*, due to heating effects, can easily be detected.

III. RESULTS AND DISCUSSION

Figure (2a) shows a 6-zone field sequence as typically applied for the high field experiments. After a short transient time with low field strength, the ac amplitude E_0 is increased in five steps, until the highest amplitude E_{max} is reached. The final zone (VI) features the same amplitude as a previous one (III) and thus acts as a probe to detect potential field induced longer term changes in the sample. In panel (b), one exemplary set of measurement results for different T is presented in terms of the relative change of the static permittivity, $\Delta\varepsilon_E/\varepsilon = (\varepsilon_E - \varepsilon)/\varepsilon$. For all measurements leading to the curves in Fig. (2b), the maximum field amplitude $E_{\text{max}} = 58$ kV cm^{-1} and field frequency $\nu = \omega/2\pi = 20$ kHz are identical. For each temperature, $\Delta\varepsilon_E/\varepsilon$ decreases significantly at the higher field strengths, indicating saturation as the dominant NDE. This effect is more pronounced at higher temperatures, reaching a decrease of ε_E of 0.3 % for the highest field at 315 K.

It can be observed that no systematic change in ε_E occurs over time in any of the zones, indicative of the absence of significant heating effects. For the measurement with the highest power absorption (T=300 K, $\nu = 20$ kHz, $E_{\text{max}} = 88$ kV cm^{-1}), the influence of field induced heating on ε_E has been estimated as detailed previously.[13] With a power uptake of $p = 1.59$ W in zone (V) of that measurement and a thermal conductivity of $\kappa = 0.292$ W m^{-1} K^{-1}, we find the average increase of temperature to be $\Delta T = 18$ mK. Using $\partial\varepsilon / \partial T = 0.216$ K^{-1},[15] the heating induced change in the permittivity amounts to -4.0×10^{-3}, less than 5 % of the observed total change under these conditions, $\Delta\varepsilon_E = -81.5\times10^{-3}$.

From curves such as those presented in Fig. (2), the Piekara factor was determined via

$$a = \frac{\partial\varepsilon_E}{\partial E_0}, \tag{4}$$

which is equivalent to $a = \Delta\varepsilon_E/E^2$ whenever higher order susceptibilities are negligible. The process of this analysis is visualized in Fig. (3): The left side, panels (a) and (b), reproduces Fig. (2) for one exemplary measurement. As can be seen in panel (b), the average ε_E for each zone is determined and shown as horizontal lines. The resultant values can be plotted against the quadratic field, E_0^2, see the symbols in panel (c). Since the points show the expected E_0^2-field dependence, an equivalent of the Piekara factor can be gained from the slope of a linear fit, see triangle and solid line in Fig. (3c).

Using this procedure, values of a have been derived for a multitude of measurements for different temperatures, spacer materials, plate distances, and field parameters. These results are presented in Fig. (4) as a function of T. As can be seen from the measurements done with silica spheres as spacers (solid symbols), the temperature dependence of the Piekara factor undergoes a significant change within the portrayed T-range. While clearly negative for all measurements, the absolute value of a remains relatively small up to approximately $T = 280$ K. The temperature dependence is almost linear from -1.4×10^{-16} V^2 m^{-2} at 230 K to -0.8×10^{-16} V^2 m^{-2} at 270 K, and an extrapolation of this trend would lead to $a = 0$ at around 320 K. Instead, for temperatures higher than 285 K, the value of a drops considerably, from -2.3×10^{-16} V^2 m^{-2} to -35×10^{-16} V^2 m^{-2} at 320 K, *i.e.*, a factor of more than 10.

The values for $|a|$ produced by measurements using polyimide spacers (open symbols) tend to be smaller than with silica microspheres, which is likely a matter of enhanced electrostriction due to the lack of a spacer as solid as SiO_2. This deviation is similar for both the 8 μm and 13 μm films, ruling out a sample thickness dependent cause. Nevertheless, the steep drop of the Piekara factor above room temperature can qualitatively be confirmed across all experiments. It should also be noted that values of a for glycerol reported earlier[12] at 217 K and around room temperature[8] do agree with our results within the uncertainty of either source, see respectively the grey pentagon and box in Fig. (4).

This rapid change in behavior is especially interesting because it is not reflected at all in the linear regime measurements. The inset of Fig. (4) shows literature values of the static permittivity for the same T-range as in the main plot.[15] These results show that ε decreases continuously from 60.5 at 230 K to 36.4 at 322 K, with no perceivable irregularities or changes in the T-dependence near 290 K. Instead, the data is well described by the function of Eq. (2) (solid line) over the entire temperature range. The lack of any unusual behavior of $\varepsilon(T)$ where $a(T)$ changes slope and magnitude also implies that no signature of this $a(T)$ feature will be found in the Kirkwood correlation factor g_K, which gauges two-particle orientational correlations.[16]

What does this dramatic increase of $|a|$ with temperature tell us about the liquid and about our understanding of nonlinear dielectric effects? To answer this, we turn to the theoretical aspects of permittivity at high electric fields. The polarization density of permanent dipoles induced by the external field is a series in odd powers of E:

$$P(E) = \varepsilon_0(\chi_1 E + \chi_3 E^3)\,, \tag{5}$$

where ε_0 is the permittivity of vacuum, and the expansion is truncated after the third-order term.

For the present type of high ac-field experiments, the material specific nonlinear dielectric susceptibility χ_3 is related to $\Delta\varepsilon_E$ as:[17]

$$\Delta\varepsilon_E = \frac{3}{4}\chi_3 E_0^2\,. \tag{6}$$

The induced polarization can alternatively be calculated[1] by the perturbation expansion in powers of the vacuum field E_{vac} and moments of the dipole moment M of the sample (see Supplementary Material for details of the derivation),

$$P(E) = \beta E_{vac}\frac{\langle M^2\rangle}{\varepsilon_\infty \Omega} - (\beta E_{vac})^3 \frac{\langle M^2\rangle^2}{2\varepsilon_\infty^3 \Omega^2 \rho} B_V\,. \tag{7}$$

Here, $\rho = N/\Omega$ is the liquid's number density and $\beta = (k_B T)^{-1}$. The angular bracket $\langle \ldots \rangle$ denotes an ensemble average in the absence of the field, *i.e.*, when $\langle M\rangle = 0$. The parameter B_V, defined at constant-volume conditions, is the first non-vanishing correction to the Gaussian statistics of the dipole moment for a finite sample with N particles,

$$B_V = N\left[1 - \frac{\langle M^4\rangle}{3\langle M^2\rangle^2}\right]. \tag{8}$$

The term in the brackets is the non-Gaussian Binder parameter,[18] which decays to zero as N^{-1} far from the point of structural instability. Given that $\chi_3 \propto B_V$, the Piekara coefficient quantifies the first non-vanishing, $\propto 1/N$, correction to the Gaussian statistics of the dipole moment of a macroscopic sample stipulated by the central limit theorem. From Eqs. (6) and (7), the Piekara coefficient becomes

$$a = -\frac{3\varepsilon_0\beta}{8\rho}\left(\frac{\varepsilon^2 - \varepsilon\varepsilon_\infty}{\varepsilon_\infty}\right)^2 B_V \,. \tag{9}$$

An alternative view of nonlinear polarization is delivered by mean-field theories when the induced polarization is given by the Langevin function $L(x)$:

$$P(E) = \rho m\, L(\chi_c \beta m E_{vac}) \,. \tag{10}$$

The effective electric field acting on a molecular dipole m is given by the product of the vacuum field and the cavity-field susceptibility χ_c. The series expansion of the Langevin function leads to the mean-field prescription $B_V = (2/5)\varepsilon_0\chi_c$ in Eq. (9). Two estimates for χ_c are commonly used in theories of dielectrics: the Onsager cavity field $\chi_c^O = 3/(2\varepsilon_s + \varepsilon_\infty)$ and the Lorentz virtual cavity field $\chi_c^L = (\varepsilon_s + 2\varepsilon_\infty)/(3\varepsilon_s\varepsilon_\infty)$. These two prescriptions yield $a(T)$ curves that contrast the experimental findings in a qualitative fashion, see Fig. (4), implying that dielectric saturation alone can not account for the present results. This signals the failure of mean-field theories to describe the nonlinear dielectric response, as all orientational correlations are disregarded in this approach.

IV. SUMMARY AND CONCLUSIONS

In summary, this study of the nonlinear dielectric behavior of glycerol has employed a recently introduced technique for non-linear dielectric measurements in the static limit.[13] Applying a series of ac fields with increasing strength to the sample during each measurement, we can immediately monitor the expected E^2 dependence of non-linear effects, as well as ascertain the absence of heating due to the sample irreversibly absorbing energy from the field. This allows us to determine the strength of the nonlinear dielectric effect, quantified by the Piekara factor a, across a wide temperature window from 230 K to 320 K for glycerol. Within this range, we identify a significant change in the T dependence of the strength of the nonlinear effect. At low temperatures, the absolute value of a is small and decreases further upon increasing T. Above the melting temperature of glycerol at $T_m = 290$ K, however, $|a|$ increases steeply, rising by more than a factor of ten between 290 K and 320 K. These results indicate the onset of increased higher-order (three- and four-particle) orientational dipole correlations which result in more significant deviations from Gaussian statistics in a macroscopic fluid, counter to the expectations based on the central limit theorem. The surprising feature of this observation is that the high-temperature liquid shows multi-body orientational correlations which are stronger than those in the supercooled regime.

SUPPLEMENTARY MATERIALS

See supplementary material for derivations and details regarding the theoretical aspects.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts of interest to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

FIGURE CAPTIONS

FIG. 1. Selected low field dielectric spectra for glycerol, with the respective temperatures indicated in the legend. Panel (a) shows the permittivity, $\varepsilon'(\omega)$, panel (b) the dielectric loss, $\varepsilon''(\omega)$. The arrow indicates an ideal frequency for the high field measurements, where $\varepsilon' \approx \varepsilon$ and ε'' is small (see text).

FIG. 2. (a) Schematic representation of the field amplitude sequence of the ac field with six zones. The percentage values indicate E_0/E_{max} for each zone. (b) Field induced relative change of $\Delta\varepsilon_{\mathrm{E}}$ for a single sample, exposed to this sequence with constant frequency, $\nu = 20$ kHz, and the same maximum field strength, E_{max}, for each of the different temperatures.

FIG. 3. (a) Schematic field protocol for the ac field sequence with six zones. (b) ε_{E} values measured over the course of one field sequence, with the symbols representing the results for each period and horizontal bars indicating the mean value for each zone. (c) Symbols reflect the mean ε_{E} values as a function of the squared field strength. The slope of a linear fit (triangle and solid line) corresponds to the Piekara factor.

FIG. 4. Temperature dependence of the Piekara factor of glycerol. The solid diamonds indicate results for the use of silica spheres as spacer material (with the line serving as a guide to the eye), open symbols are for data obtained with polyimide film spacers of 13 (green triangles up) or 8 μm (blue triangles down) thickness. The gray pentagon labeled 'Samanta' indicates a value from ref. 12 and the gray square labeled 'Marcus' gives the range of values taken from ref. 8. Mean-field predictions according to Onsager cavity field and Lorentz virtual cavity field (see text) are indicated by the dash-dotted and dotted lines, respectively. The inset depicts literature data for $\varepsilon(T)$ from ref. 15, using the same T range as the main plot. The solid line curve of the inset is a fit to $\varepsilon(T)$ according to Eq. (2).

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