

Nonlinear dielectric response of plastic crystals

P. Lunkenheimer, M. Michl, and A. Loidl

Abstract This article summarizes ongoing experimental efforts on non-linear dielectric spectroscopy on plastic crystals. In plastic crystals, the relevant dipolar orientational degrees of freedom are fixed on a crystalline lattice with perfect translational symmetry. However, while they can reorient freely in the high-temperature plastic phase, they often undergo glassy freezing at low temperatures. Hence, plastic crystals are often considered as model systems for structural glass formers. It is well known that plastic crystals reveal striking similarities with phenomena of conventional supercooled liquids. However, in most cases they can be characterized as rather strong glass formers. Non-linear dielectric spectroscopy is an ideal tool to study glass-transition phenomena, providing insight into cooperative phenomena or hidden phase transitions, undetectable by purely linear spectroscopy. In the present article, we discuss dielectric experiments using large electric ac fields probing the nonlinear 1ω and the third-order harmonic 3ω susceptibility. In the 1ω experiments, we find striking differences compared with observations on conventional structural glass formers: at low frequencies plastic crystals do not approach the trivial response, but reveal strong additional nonlinearity. These phenomena document the importance of entropic effects in this class of glassy materials. The harmonic third-order susceptibility reveals a hump-like shape, similar to observations in canonical glass formers, indicating the importance of cooperativity dominating the glass transition. In the frequency regime of the secondary relaxations only minor non-linear effects can be detected, supporting arguments in favor of the non-cooperative nature of these faster dynamics processes. Based on a model by Bouchaud and Biroli, from the hump observed in the 3ω susceptibility spectra, the temperature dependence of the number of correlated particles can be determined. We document that the results in plastic crystals perfectly well scale with the results derived from measurements on conventional glass formers, providing evidence that in plastic crystals the non-Arrhenius behavior of the relaxation times also arises from a temperature dependence of the energy barriers due to growing cooperative clusters.

P. Lunkenheimer (✉), M. Michl, A. Loidl
Experimental Physics V, Center for Electronic Correlations and Magnetism, University of
Augsburg, 86159 Augsburg, Germany
e-mail: peter.lunkenheimer@physik.uni-augsburg.de

Keywords Plastic crystals · Glassy crystals · Supercooled liquids · Nonlinear dielectric spectroscopy · Harmonic susceptibility · Relaxation dynamics · Glass transition · Non-Arrhenius behavior

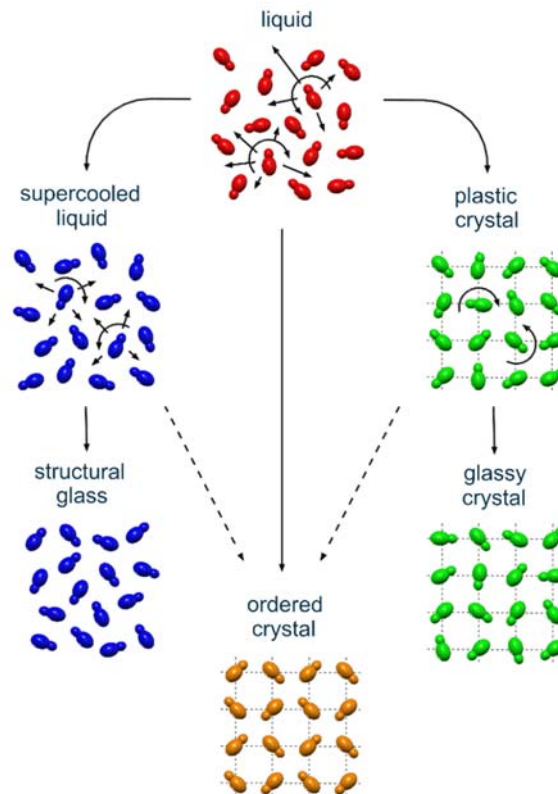
1. Introduction

Plastic crystals (PCs) are often considered as model systems for structural glass formers. While in PCs the centers of mass of the molecules are fixed on a crystalline lattice with translational symmetry, their orientational degrees of freedom more or less freely fluctuate at high temperatures and often show glassy freezing at low temperatures (Fig. 1) [1]. The molecules of most PCs have rather globular shape and relatively weak mutual interactions, providing little steric hindrance for reorientational processes. This often leads to high plasticity, thus explaining the term "plastic crystal" first introduced by Timmermans [2] many decades ago. The reorientational relaxation dynamics of PCs, as detected, e.g., by dielectric spectroscopy, in many respects resembles the dynamics of structural glass formers [1,3,4]. Especially, often complete orientational ordering at low temperatures can be avoided by supercooling the high-temperature dynamically disordered state. Just as for glass-forming liquids, this leads to a continuous slowing down of molecular dynamics over many orders of magnitude, which can be nicely followed by monitoring the reorientational relaxation dynamics by broadband dielectric spectroscopy [1]. For low temperatures, finally a static orientationally disordered state is reached which sometimes is called "glassy crystal" (Fig. 1) [5]. Correspondingly, an "orientational-glass temperature" T_g^o can be defined. It should be mentioned, however, that the term "orientational glass" for this glassy state may be ambiguous because it is often used to exclusively denote the orientationally disordered state of mixed crystals, believed to arise from frustrated interactions due to substitutional disorder [6,7]. In contrast, the glassy-crystal state in PCs is non-ergodic and represents a true analogue of the structurally disordered glassy state of conventional glass-formers.

The freezing of the molecular dynamics of PCs exhibits many of the puzzling characteristics of canonical (i.e. structural) glass formers. This especially includes the non-exponentiality of the time-dependence and the non-Arrhenius behavior of the temperature dependence of this dynamics, both hallmark features of the glassy state of matter [8,9,10,11,12]. Therefore, investigating and understanding the glassy freezing in PCs is an important step on the way to a better understanding of glass forming liquids and the glass transition in general. Indeed, in literature there are various examples for

such studies, many of them employing dielectric spectroscopy, which directly senses the reorientational motions [1,13,14,15,16,17]. Such investigations are usually performed by detecting the *linear* dielectric response of the sample material to an applied ac electrical field of moderate amplitude (typical voltages are of the order of 1 V). However, in recent years it has become clear that the *nonlinear* response of glass-forming matter, detected under high fields of up to several 100 kV/cm, can reveal a lot of valuable additional information about glassy freezing [18,19,20,21,22,23,24,25,26,27] (see also the other chapters of the present book). Thus, it seemed natural to apply such methods to PCs, too, which indeed was done in several recent works [28,29,30,31]. The present chapter will provide an overview of such nonlinear dielectric investigations of PCs.

Fig. 1 Schematic representation of the possible transitions of a liquid of dipolar molecules (represented by asymmetric dumbbells) into a structural glass, an ordered crystal, or a glassy crystal [1]



Among the pioneering nonlinear experiments on *structural* glass formers were dielectric hole-burning experiments, which provided the first experimental verification that the non-exponentiality of the relaxation dynamics in these materials arises from its heterogeneity [32]. Later on, measurements of the field-induced variation of the dielectric permittivity revealed further valuable information on this phenomenon [20,33] and on the nonlinear behavior of secondary relaxation effects [25] like the Johari-Goldstein relaxation [34] or the excess wing [11,35]. Moreover, high-field measurements recently have also provided important hints at the origin of the characteristic non-Arrhenius temperature dependence of glassy dynamics. Particularly, based on a model by Bouchaud, Biroli, and coworkers [36,37], measurements of the higher-order harmonic susceptibilities χ_3 and χ_5 seem to indicate that this phenomenon arises from an increase of molecular cooperativity when approaching T_g at low temperatures [23,26,27] (see also the chapter by Albert *et al.* in the present book). In this way, important clues about the true nature of the glass transition were obtained, which seems to be due to an underlying thermodynamic phase transition [23,26,27,38]. Finally, Johari has recently demonstrated [39,40] that nonlinear dielectric effects can also arise from the reduction of configurational entropy induced by the external field, leading to an increase of the α relaxation time and, thus, a field-induced rise of the viscosity.

Nonlinear measurements on plastic crystals should be able to reveal analogous information on the role of heterogeneity, cooperativity, and entropy in this class of disordered materials. However, it is not self-evident that the results should be similar to those in structural glass formers: For example, in a material exhibiting translational symmetry, heterogeneity can be expected to be of different nature and, indeed, it was suggested that the dynamics of single molecules in PCs may be intrinsically non-exponential and heterogeneity alone cannot explain the experimental observations [41,42]. Moreover, the intermolecular interactions that lead to cooperativity also should be influenced by the fact that the molecules are located on fixed lattice positions. Indeed, the deviations of glassy dynamics from thermally-activated Arrhenius behavior, often ascribed to cooperativity [8,43,44], are generally weaker for PCs than for canonical glass formers [1,45]. Within Angell's strong-fragile classification scheme [46] this implies that PCs are rather strong glass formers (despite also exceptions are known [47,48,49]). This is demonstrated in Fig. 2, showing Angell plots of the α -relaxation times τ_α of a number of supercooled liquids [frame (a)] and PCs (b) measured in our group [1,11,47,48,50,51]. In this type of T_g -scaled Arrhenius plot [52], simple thermally activated behavior, $\tau \propto \exp(E/T)$ (with E the energy barrier in K) leads to a straight line

with a slope of about 16 (dashed line) characterized as "strong" dynamics. In contrast, "fragile" glass formers exhibit pronounced curvature in this plot and, consequently, a steep slope m close to T_g . The latter parameter is commonly used to parameterize the deviations from Arrhenius behavior of glass formers [53,54]; an example for very large fragility with $m = 170$ is shown as dotted line in Fig. 2. Comparing frames (a) and (b) in Fig. 2 nicely reveals that, in general, PCs indeed tend to be stronger in the strong/fragile classification scheme than most canonical supercooled liquids [1,45]. Note also the interesting case of ethanol, which can be prepared both in a supercooled-liquid and a PC state and is clearly stronger in the latter phase [1,55,56]. For three of the PC systems included in Fig. 2(c) (indicated by closed symbols), nonlinear dielectric spectroscopy results will be discussed in the present work.

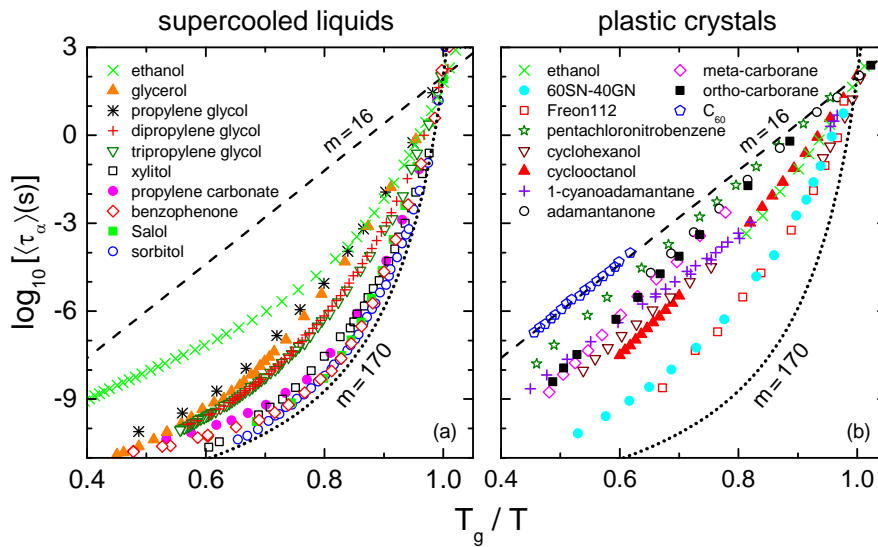


Fig. 2 Angell plot of the α -relaxation times of various supercooled liquids (a) [11,50,51] and PCs (b) [1,47,48]. The dashed lines demonstrate maximally strong behavior; the dotted lines indicate extremely high fragility. In (b), the data for the PCs treated in the present work are shown as closed symbols

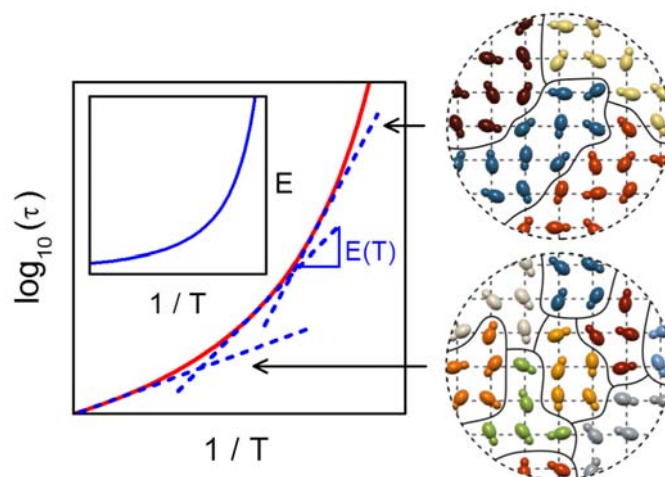


Fig. 3 A possible explanation of the non-Arrhenius behaviour of PCs. Left: Schematic Arrhenius representation of the temperature-dependent relaxation time of PCs for Vogel-Fulcher-Tammann behavior (solid line). A temperature-dependent apparent activation energy E (inset) can be estimated from the slope in this plot (indicated for three temperatures by the dashed lines). This increase of E may be ascribed to an increase of the size of CRRs (schematically indicated by molecules of same color at the right)

In Ref. [1] we suggested that the strong behavior of PCs can be understood when considering the proposed relation of fragility and of the energy landscape in configuration space [57,58]. Based on the inverse proportionality of effective energy barrier and configurational entropy assumed within the Adam-Gibbs theory [59], the material-dependent variation of fragility of glass-formers can be rationalized assuming that higher fragility arises from a higher density of minima in the potential-energy landscape [57,58]. Within this framework, the overall lower fragility of PCs compared to supercooled liquids may be explained by their additional order due to the existence of a crystalline lattice, which leads to a reduced density of energy minima [1]. As discussed in Refs. [47,48], the only exceptions are Freon112 and mixtures of succinonitrile and glutaronitrile, where additional conformational and/or substitutional disorder leads to a more complex energy landscape and, thus, more fragile behavior. It is an interesting question how this energy-landscape picture is related to the explanation of non-Arrhenius behavior by increasing molecular cooperativity (causing an increasing

effective energy barrier experienced by the molecules; Fig. 3), when a supercooled liquid or PC is cooled towards its T_g . The more complex energy landscape of fragile glass formers as depicted, e.g., in Ref. [57] implies that at high temperatures many different configurational states can be exploited by the system while at lower temperatures only few, low-energy states are accessible. Within the cooperativity framework mentioned above, this may well correspond to the many, relatively small cooperatively rearranging regions (CRRs) [59] assumed to exist on a rather short time scale at high temperatures while close to T_g there are much less, much larger, and more stable CRRs as schematically indicated in Fig. 3. In contrast, in strong glass formers the variation of accessible states within the less complex energy landscape should be less pronounced, corresponding to a weaker variation of the size and number of the CRRs when approaching T_g . Dielectric measurements of higher-harmonic susceptibilities, being able to test possible temperature-dependent variations of the number of dynamically correlated molecules, can give a clue if these variations indeed are rather weak in the strong PCs, which would corroborate the discussed analogy of energy-landscape and cooperativity scenario.

There are various ways to perform nonlinear dielectric measurements of glassforming materials [18,19] (see also the other chapters in the present book). In the following, we mainly discuss two different types of experiments applied to PCs: i) The detection of the complex dielectric permittivity ϵ^* under high ac fields and its comparison to ϵ^* measured in the linear regime [28,29,31]. ii) The measurement of higher harmonics of the dielectric susceptibility, especially of the 3ω component χ_3 , performed under high ac fields, too [28,31]. In addition, PCs were also investigated by simultaneously applying a small ac and a high dc bias field [30]. Details on the experimental techniques applied to detect the nonlinear dielectric response can be found, e.g., in [18,19].

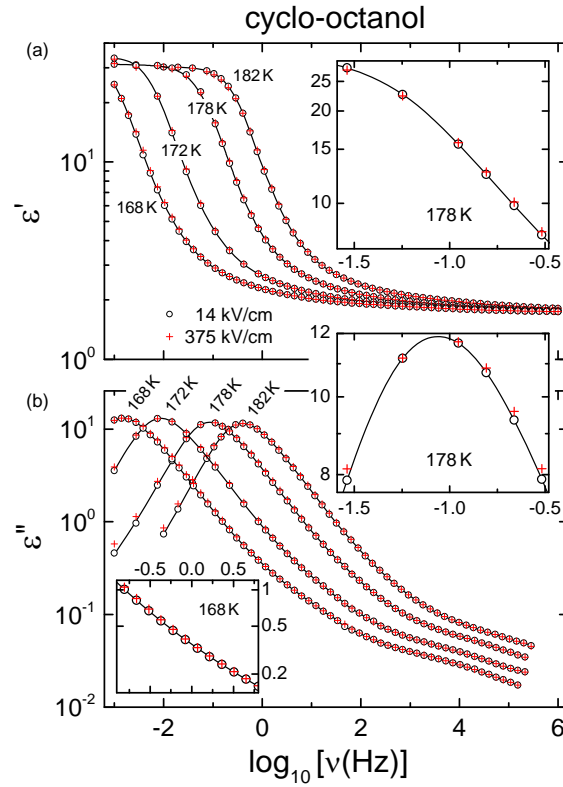
2. Nonlinear Measurements of the Dielectric Permittivity

2.1 Main Relaxation Process

To our knowledge, the first nonlinear dielectric measurements of a plastic crystalline material reported in literature were performed on cyclo-octanol [28]. It is a typical PC, well characterized by linear dielectric spectroscopy [60,61]. Its plastic state is most easily investigated by first supercooling the transitions into two different orientationally ordered states, known to occur at 265 and 220 K [62,63,64], and then performing

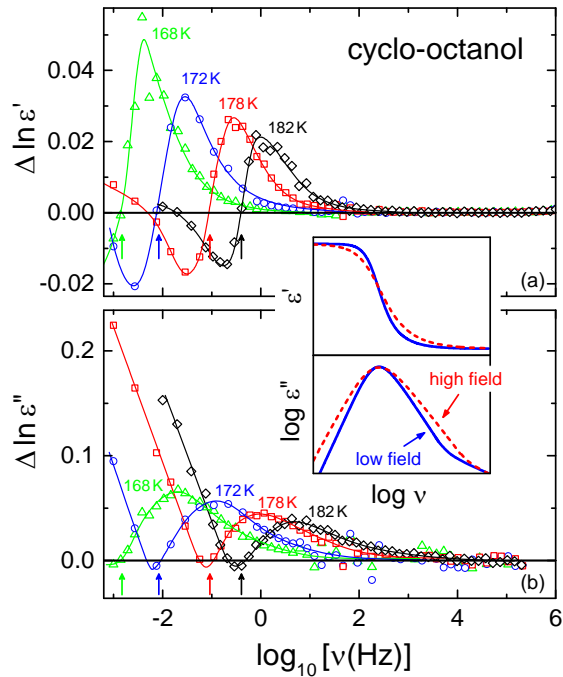
measurements under heating. T_g^o of cyclo-octanol is about 168 K [61]. Its linear dielectric response in the PC phase is shown by the open symbols in Fig. 4 for four temperatures [28]. The steplike decrease in the dielectric constant $\varepsilon'(\nu)$ and the peak in the loss $\varepsilon''(\nu)$, both shifting to higher frequencies with increasing temperature, reveal the typical signatures of a relaxational process. The latter was identified with the main reorientational motion of the molecules, assigned as α relaxation [60,61], which exhibits glassy freezing, non-exponentiality, and rather mild non-Arrhenius behavior. In fact, with a fragility parameter $m \approx 33$ [60,61], cyclo-octanol can be classified as a rather strong glass former (cf. Fig. 2).

Fig. 4 Dielectric constant (a) and loss spectra (b) of plastic-crystalline cyclo-octanol measured at various temperatures and at low and high ac fields as indicated in the figure [28]. The insets provide magnified views demonstrating the field-dependence in the α -peak region (right insets) and the lack of significant field-induced variation at higher frequencies (lower left inset). The lines are guides to the eyes



The plusses in Fig. 4 represent the spectra obtained for a high electric field of 375 kV/cm. In the region of the α relaxation, a small but significant difference of the high-field and low-field spectra is revealed (see also right insets of Fig. 4). In Fig. 5, the difference of the high- and low-field spectra is plotted. A common way to represent such data is plotting the quantity $\Delta \ln \varepsilon = \ln \varepsilon_{hi} - \ln \varepsilon_{lo}$ for $\varepsilon = \varepsilon'$ or $\varepsilon = \varepsilon''$ [20,25] where ε_{hi} and ε_{lo} denote the results for high and low fields, respectively. The arrows indicate the α -peak positions ν_α at low fields [cf. Fig. 4(b)]. Obviously, $\Delta \ln \varepsilon''$ exhibits a "V-shaped" behavior with the tip of the "V" in the region of the α -peak frequency. Correspondingly, $\Delta \ln \varepsilon'$ shows a zero-crossing close to ν_α with negative and positive peaks at $\nu < \nu_\alpha$ and $\nu > \nu_\alpha$, respectively. Especially at low frequencies, these difference spectra qualitatively differ from those observed in canonical glass formers, which usually only exhibit a weak nonlinear effect at $\nu < \nu_\alpha$ [20,25].

Fig. 5 Difference of the logarithmic high- and low-field dielectric spectra of plastic-crystalline cyclo-octanol as measured for high fields of 375 kV/cm and for various temperatures (cf. Fig. 4) [28]. The arrows indicate the α -peak frequencies. The lines are drawn to guide the eyes. The inset schematically indicates a field-induced broadening, which would lead to qualitatively similar difference spectra as in the main frames



This overall behavior seems to be a common motif in nonlinear difference spectra of PCs [28,29,31]. An example from Richert and coworkers is provided in Fig. 6. It shows the relative difference of high- and low-field loss spectra of a plastic-crystalline mixture of neopentylglycol and cyclo-hexanol [29] ($T_g^o \approx 155$ K [65]). Here the quantity $(\epsilon''_{hi} - \epsilon''_{lo})/\epsilon''_{lo}$ is shown, which is comparable to $\Delta \ln \epsilon''$ if the factor $(\epsilon''_{hi}/\epsilon''_{lo} - 1)$ is small. Again the V-shape shows up rather close to ν_{α} , indicated by an arrow in Fig. 6. This is the case for spectra collected at different applied high fields, which can be scaled onto each other as demonstrated in Fig. 6. In Ref. [29], qualitatively similar difference spectra were also reported for plastic-crystalline cyanocyclohexane. Thus it seems that, especially concerning the pronounced field-induced increase of ϵ'' at low frequencies and the corresponding decrease of ϵ' , PCs seem to exhibit qualitatively different nonlinear behavior than canonical glass formers [20,25,33].

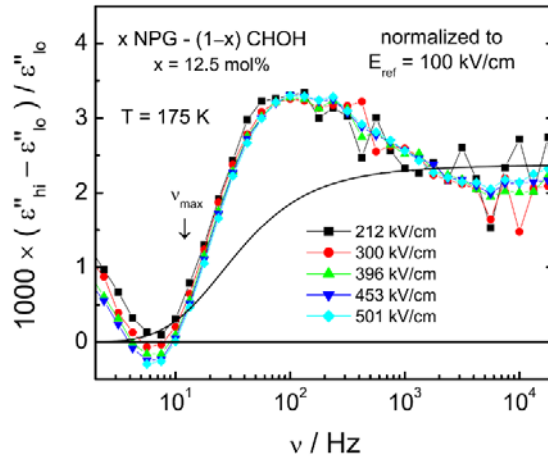


Fig. 6 Relative difference of high- and low-field loss spectra as measured in a mixture of neopentylglycol and cyclo-hexanol [29]. Curves for different high fields are shown which were scaled onto each other. The smooth solid line was calculated according to the box model (see [29] for details). Reprinted from [29] with the permission of AIP Publishing.

As further examples of this quite general nonlinear behavior of PCs, Fig. 7 shows $\Delta \ln \epsilon''$ for a mixture of 60% succinonitrile and 40% glutaronitrile (60SN-40GN) [31]

and for *ortho*-carborane [28,31], both well-established PCs with orientational-glass temperatures $T_g^o \approx 144$ K and 120 K, respectively [48,66,67]. While *ortho*-carborane exhibits very strong glass-forming characteristics ($m \approx 20$ [66]), 60SN-40GN was shown [48] to be exceptionally fragile ($m \approx 62$) when compared with most other PCs [1] [cf. Fig. 2(b)]. Irrespective of this difference, just as for the other PCs (Figs. 5 and 6) for both materials a V-shaped behavior of $\Delta \ln \varepsilon''$ is observed, too. In contrast to the other compounds, for 60SN-40GN $\Delta \ln \varepsilon''$ does not approach zero at the minimum. In Ref. [31], this was ascribed to additional contributions from field-induced transitions between different molecular conformations in this material.

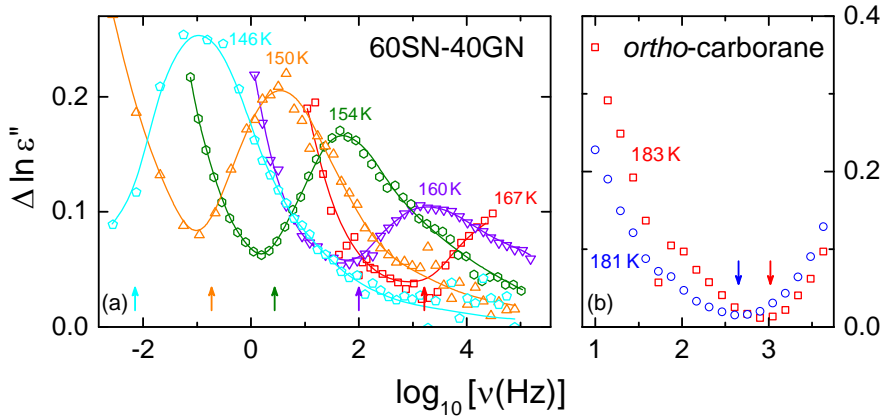


Fig. 7 Difference of the logarithmic dielectric-loss spectra of plastic-crystalline 60SN-40GN and *ortho*-carborane as measured for high fields of 357 kV/cm and 90 kV/cm, respectively, and for various temperatures [28,31]. The arrows indicate the α -peak positions. The lines in (a) are drawn to guide the eyes

The case of *ortho*-carborane illustrates an experimental problem that one may encounter when performing nonlinear measurements of PCs: As the nonlinear dielectric response commonly is much smaller than the linear one, usually very high electrical fields E are necessary to enable its detection. Therefore, accounting for the relation $E \sim 1/d$, the sample thickness d should be as thin as possible. This can be much more easily achieved when the investigated material is liquid during preparation, enabling the use of capacitors with thin spacers (e.g., glass fibers,

Teflon foils, or silica microspheres [20,25,26,29,30,31]). However, in contrast to supercooled liquids, many materials exhibiting a PC phase are not liquid at room temperature. Fortunately, often they can be easily melted at only moderately enhanced temperatures, enabling their filling into capacitors. This is, however, not the case for *ortho*-carborane, which tends to sublime at elevated temperatures [66]. This material instead has to be prepared from powder, pressing a thin platelet between polished stainless-steel plates that serve as electrodes [28]. The minimum thickness achieved in this way was of the order of 100 μm , much larger than the few μm thickness that can be reached for liquid samples. Consequently, higher fields had to be applied to compensate for this effect, which only was possible in a limited frequency range [Fig. 7(b)].

It should be noted that the common nonlinear behavior of PCs around the α -peak frequency as documented in Fig. 5 - 7 is consistent with a field-induced broadening of the observed relaxation features. This becomes clear by a comparison with the inset of Fig. 5, which schematically indicates such a scenario with somewhat exaggerated field-induced effects for clarity reasons [28]. The behavior shown there is well consistent with the experimental data. Remarkably, this broadening also occurs at the low-frequency flank of the α peak, causing the mentioned increase of $\Delta \ln \varepsilon''(\nu)$ at low frequencies [Figs. 5(b), 6, and 7]. Thus, the high-field spectra can no longer be described by the Cole-Davidson (CD) function [68], for which $\varepsilon''(\nu)$ increases linearly (i.e. with a slope one in the log-log plot) at the left flank of the loss peak. The CD function is found to reasonably fit the α relaxation of many glass formers [11] and plastic crystals [1], including cyclo-octanol [61]. Usually, peak broadening observed in the relaxation dynamics of glassy matter is ascribed to heterogeneity arising from the disorder in the material, which induces a distribution of relaxation times [9,10]. However, as discussed in Ref. [28], it is not clear why a high field should increase heterogeneity and such an explanation of this field-induced broadening seems unlikely.

In contrast to the low-frequency behavior, the field-induced increase of ε'' and ε' at frequencies, $\nu > \nu_\alpha$, found in PCs (Figs. 5 - 7) [28,29,31] resembles the behavior in structural glass formers [20,25,33]. Within the framework of the box model, considering the dynamic heterogeneity of glassy matter [69,70], this nonlinear effect was ascribed to a selective transfer of field energy into the heterogeneous regions, accelerating their dynamics and leading to an effective broadening at the right flank of the α relaxation peak (and a corresponding effect in ε') [18,20,29,33]. However, the continuous increase of $\Delta \ln \varepsilon''(\nu)$ found at $\nu < \nu_\alpha$ in PCs, cannot be accounted for in this way. This

discrepancy is also revealed by the solid line shown in Fig. 6, which was calculated according to the box model [29]. Obviously, within this model the field effects in ε'' are expected to approach zero for low frequencies, in agreement with the behavior in most supercooled liquids but in marked contrast with the findings in the PCs. In contrast, at $\nu > \nu_\alpha$, a positive field effect with the correct order of magnitude is predicted. In Ref. [29], the deviations in this region were ascribed to the suggested intrinsic non-exponentiality of PCs [41,42]. This notion implies that, in contrast to canonical glass formers, in PCs only part of their non-exponential relaxation behavior arises from heterogeneity.

It should also be noted that the negative values of $\Delta \ln \varepsilon'$ detected at $\nu < \nu_\alpha$ [Fig. 5(a)] again are at variance with the box model as developed for supercooled liquids. In principle, negative values of $\Delta \ln \varepsilon'$, corresponding to a reduction of the low-frequency dielectric constant, may be explained by saturation effects of the polarization [71,72,73]. However, instead of the minimum revealed by Fig. 5(a), in this case a low-frequency plateau in $\Delta \ln \varepsilon'(\nu)$ is expected as found, e.g., in glass-forming 1-propanol [74].

An explanation for the puzzling low-frequency nonlinear properties of PCs discussed above was provided in Ref. [29], based on recent theoretical considerations by Johari [39,40]. Within this framework, the high external field is assumed to result in a reduction of configurational entropy. Via the relation of entropy and relaxation time that is assumed within the Adam-Gibbs theory of the glass transition [59], this should induce an increase of the relaxation time, resulting in a slight increase of the glass temperature. This entropy effect should, however, only lead to significant nonlinear contributions at low frequencies, $\nu < \nu_\alpha$, because the molecular rearrangements associated with the entropy reduction are too slow to follow the ac field at high frequencies [29]. This is in good accordance with the experimental findings at low frequencies documented in Figs. 5 - 7, which cannot easily be explained by other contributions as discussed above.

Entropy contributions to nonlinear dielectric properties have also been found for various structural glass formers, mostly by performing measurements under a strong bias field [30,75,76,77]. However, it seems that entropy-driven nonlinearity effects in PCs are generally stronger than those detected in such supercooled liquids [30,31]. In Johari's model [39], the impact of a high electrical field on the *reorientational* degrees of freedom of the molecules is considered. It indeed seems reasonable that the field may diminish the reorientational disorder of dipolar molecules and thus influence the entropy of the system. However, while in PCs there is only reorientational disorder, in structural

glass formers also *translational* disorder exists, which should be less influenced by the field. In contrast to structural glass formers, for the overall entropy of PCs molecular reorientations are the main source of entropy. Therefore one may speculate that for PCs the field-induced variation of reorientational disorder is of more importance than for canonical glass formers and that this is the reason for the different low-frequency nonlinear behavior of these two classes of glassy matter [31]. However, in a recent work [40], Johari pointed out that for cyclo-octanol intra-molecular degrees of freedom also strongly contribute to its overall entropy.

As noted, e.g., in Ref. [19], from the field-induced variation of the complex dielectric permittivity, the cubic susceptibility $\chi_3^{(1)}$ can be calculated. It is defined via the following relation for the time-dependent polarization $P(t)$, resulting from an applied time-dependent electrical field $E(t) = E_{ac} \cos(\omega t)$ [27,38]:

$$\begin{aligned} \frac{P(t)}{\varepsilon_0} = & \left| \chi_1^{(1)} \right| E_{ac} \cos(\omega t - \delta_1) + \frac{3}{4} \left| \chi_3^{(1)} \right| E_{ac}^3 \cos(\omega t - \delta_3^{(1)}) \\ & + \frac{10}{16} \left| \chi_5^{(1)} \right| E_{ac}^5 \cos(\omega t - \delta_5^{(1)}) \\ & + \frac{1}{4} \left| \chi_3^{(3)} \right| E_{ac}^3 \cos(3\omega t - \delta_3^{(3)}) + \frac{5}{16} \left| \chi_3^{(5)} \right| E_{ac}^5 \cos(3\omega t - \delta_5^{(3)}) \\ & + \frac{1}{16} \left| \chi_5^{(5)} \right| E_{ac}^5 \cos(5\omega t - \delta_5^{(5)}) + \dots \end{aligned} \quad (1)$$

Here the lower indices of χ correspond to the exponent of the electrical-field dependence (which defines $\chi_3^{(1)}$ as cubic susceptibility) while the upper ones signal the ω factor. The higher-order harmonic susceptibilities $\chi_3^{(3)}$ and $\chi_5^{(5)}$ are often simply denoted as χ_3 and χ_5 , respectively. It should be noted that $\chi_3^{(1)}$ contains essentially the same information as $\Delta \ln \varepsilon'(\nu)$ and $\Delta \ln \varepsilon''(\nu)$ plotted in Figs. 5-7 and can be directly calculated from the measured low- and high-field permittivities via

$$\left| \chi_3^{(1)} \right| = \frac{4}{3} \frac{1}{E_{ac}^2} \sqrt{(\Delta \varepsilon')^2 + (\Delta \varepsilon'')^2}$$

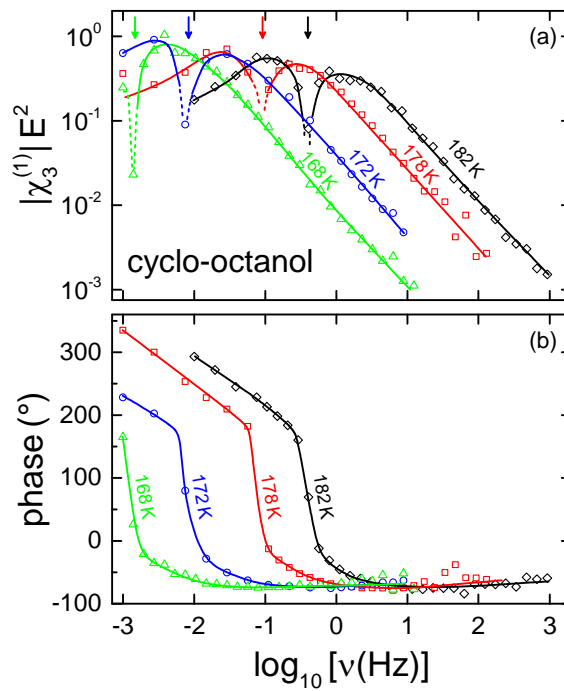
and

$$\arg[\chi_3^{(1)}] = \arctan\left(\frac{\Delta \varepsilon''}{\Delta \varepsilon'}\right)$$

with $\Delta \varepsilon' = \varepsilon'_{hi} - \varepsilon'_{lo}$ and $\Delta \varepsilon'' = \varepsilon''_{hi} - \varepsilon''_{lo}$ [19].

Figure 8 shows spectra of the modulus and phase of $\chi_3^{(1)}$ for plastic-crystalline cyclo-octanol. This should be compared to the corresponding results for two supercooled liquids (glycerol and propylene carbonate), recently published in Ref. [78]. The findings in this work were interpreted along similar lines as the higher-harmonic susceptibilities reported, e.g., in [23,26,27], namely within the theoretical framework by Bouchaud and Biroli [36] assuming molecular cooperativity leading to "amorphous order" that grows when the glass temperature is approached. The humped shape observed in the modulus spectra of various cubic susceptibilities in the region of ν_α can be well understood within this framework. As pointed out in Ref. [78], several common features (e.g., the hump and the similar phase behavior) found in the spectra of different nonlinear susceptibilities point to a common physical origin, dominated by cooperativity effects. Nonlinear entropy contributions as discussed in Johari's model [39] were shown to be consistent with this view.

Fig. 8 Modulus (a) and phase (b) of the cubic susceptibility $\chi_3^{(1)}$ of plastic-crystalline cyclo-octanol, measured at various temperatures for a field of 375 kV/cm. The lines are guides to the eyes



An inspection of the $\chi_3^{(1)}$ spectra of cyclo-octanol in Fig. 8 reveal some similarities to those in the supercooled liquids [78]: Just as for the latter, a hump shows up in the modulus spectra about half a decade above the α -peak frequency ν_α [Fig. 8(a)]. Moreover, $|\chi_3^{(1)}(\nu)|$ exhibits a spikelike minimum where it seems to approach zero. Just as for the canonical glass-formers, this minimum is accompanied by a strong jump in the phase [Fig. 8(b)]. (In Fig. 2 of Ref. [78], the phase becomes negative at low frequencies but it is a matter of definition if angles above 180° are represented as positive or negative values.) However, Fig. 8 also reveals some differences to the behavior in the supercooled liquids: In plastic-crystalline cyclo-octanol, the minimum in the modulus and the jump in the phase occur at higher frequency, namely just at ν_α , while in Ref. [78] it was found at least a factor of three below ν_α . This effect seems to impede the full formation of the hump in the modulus of the PC. Moreover, the phase at frequencies below the jump is still strongly frequency dependent, while it is nearly constant in the supercooled liquids. In Ref. [78] the anomalies in the $\chi_3^{(1)}$ spectra were ascribed to a transition from the "trivial" saturation response dominating at low frequencies [71,72,73] to the correlation-dominated regime at higher frequencies. Especially, the saturation effect leads to a reduction of ε' , while correlations seem to enhance it. At the frequency of the anomalies, both effects seem to compensate. In the present case of plastic-crystalline cyclo-octanol, similar arguments can be used when assuming a transition from correlation-dominated behavior at $\nu > \nu_\alpha$ to entropy-dominated nonlinearity at $\nu < \nu_\alpha$. Nonlinear saturation and entropy effects are both expected to be most pronounced at low frequencies. In the $\chi_3^{(1)}$ spectra (and thus probably also in the other cubic susceptibilities [78]), their main difference seems to be the essentially frequency-independent behavior of the first compared to the frequency-dependent nonlinear response of the latter. The comparison of the $\chi_3^{(1)}$ results on a PC (Fig. 8) and those on supercooled liquids in Ref. [78] seem to corroborate the notion that entropy effects mainly dominate the low-frequency nonlinear response in PCs, in contrast to saturation effects in supercooled liquids.

2.2 Secondary Relaxations

Just as found for many supercooled liquids, plastic crystals are known to exhibit secondary relaxation processes, termed β relaxations, which are faster than the main reorientational process, usually denoted as α relaxation [1]. As shown by Johari and Goldstein [34], β relaxations seem to be an inherent property of the glassy state of matter. To distinguish such processes from relaxations arising from more trivial effects as, e.g., intramolecular motions, they are nowadays commonly denoted as Johari-Goldstein (JG) relaxations. The microscopic origin of JG relaxations is still controversially discussed. For example, they were ascribed to motions of molecules within "islands of mobility" [34], small-scale motions within a fine structure of the energy landscape experienced by the molecules [79,80,81], or various other mechanisms (e.g., [82,83,84,85]).

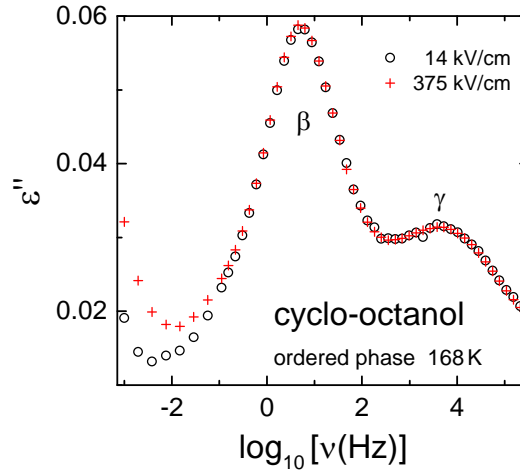
The shoulders observed at the high-frequency flanks of the peaks in the loss spectra of cyclo-octanol, shown in Fig. 4(b), indicate the presence of two faster secondary processes. Examining data covering a broader temperature and frequency range indeed reveals clear evidence for these processes, which were termed β and γ relaxation [61]. By applying a universal criterion, valid for different classes of glass formers, strong hints were obtained that the β relaxation of cyclo-octanol is a genuine JG relaxation process [85,86]. As seen in the left inset of Fig. 4, there is no significant difference of the high- and low-field results for the loss in the region of the β relaxation. Obviously, the field-induced variation of ϵ'' is small in this region and, consequently, the difference spectra shown in Fig. 5 strongly decrease at high frequencies. This is also the case for 60SN-40GN [Fig. 7(a)] where the nonlinearity also becomes weaker in the regime of its secondary relaxations [31]. For the neopentylglycol/cyclo-hexanol mixture shown in Fig. 6 and for cyanocyclohexane, a decrease of the difference spectra at high frequencies was also observed, which, however, seems to be more gradual than for the other PCs [29].

The weaker nonlinearity of PCs in the regime of their secondary relaxations resembles the corresponding effect found for the excess-wing region of supercooled liquids like glycerol [25,74]. The excess wing shows up as a second, more shallow power law at the high-frequency flank of the α peak of some glass formers [11,35,87]. In various works it was suggested to be caused by a JG relaxation-peak that is partly submerged under the dominating α peak (e.g., [88,89,90]). Therefore, the reduction or even absence of a nonlinear effect at high frequencies in the PCs may well have the same origin as the negligible nonlinearity in the excess-wing region

of the supercooled liquids [25,74]. As discussed, e.g., in Ref. [25], this finding is consistent with the relation of nonlinearity and molecular cooperativity suggested in Ref. [36] if having in mind that secondary relaxations are often assumed to be of non-cooperative nature [83,91,92]. However, it should be noted that in the region of the very strong secondary relaxation of glassforming sorbitol, well-pronounced nonlinear effects were found [19,93], a fact that could be explained within the framework of the coupling model [94].

As discussed in Ref. 95, based on time-resolved measurements, the number of high-field cycles applied to the sample may play a crucial role in the detection of equilibrium values for the nonlinearity. For example, the degree of nonlinearity in the high-frequency region of supercooled liquids seems to clearly depend on the number of applied cycles [95] and similar behavior was also reported for PCs [29]. However, experiments with different cycle numbers performed for 60SN-40GN did not reveal any differences [31]. While the details of this behavior are not finally clarified, in any case, the nonlinearity in the regime of high-frequency processes seems to be smaller than for the main relaxation in most glasslike materials investigated until now.

Fig. 9 Dielectric loss spectra of cyclo-octanol in the orientationally ordered state at 168 K, measured at low and high field



Further information on the secondary relaxations in cyclo-octanol can be obtained by transferring the sample into an (at least partly) orientationally ordered state [61,62,63,64], which was achieved by heating the sample to 227 K after supercooling and keeping it there for 10 min. As shown in Ref. [61], the secondary relaxations persist in this more ordered state and can be investigated without interference from the dominating α relaxation. Figure 9 shows the results for the loss at 168 K, measured at low and high fields. Above about 1 Hz, in the region of the β and γ relaxations, within experimental resolution no field-induced variation is observed. This finding is in good agreement with those obtained for the plastic-crystalline phase in the secondary-relaxation region, discussed above (Figs. 4 and 5). The field dependence observed at the lowest frequencies may be ascribed to the α relaxation arising from residual amounts of the plastic-crystalline phase or to contributions from ionic conductivity, due to small amounts of impurities within the sample. Nonlinearities of ionic conductivity are well-known effects and are discussed in detail by Roling and coworkers (see, e.g., Ref. [96] and the chapter by B. Roling in the present book).

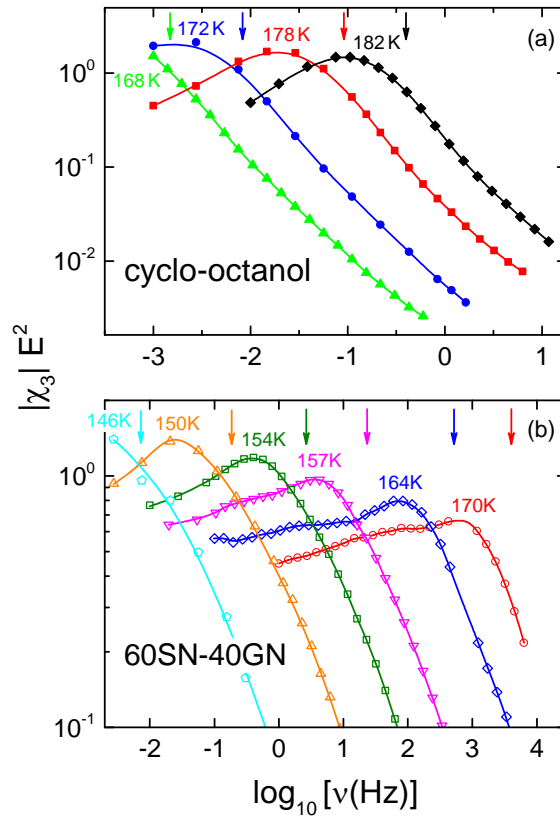
3. Third-order harmonic susceptibility

Another prominent way to detect the nonlinear dielectric response of a material is the measurement of higher harmonics of the dielectric susceptibility: At low fields, the polarization P and field E should be proportional to each other. Therefore, the application of a sinus ac field $E(t)$ results in a sinus polarization $P(t)$ with the same frequency. However, at high fields, P no longer is proportional to E and, thus, an applied sinus field with frequency ω can result in higher harmonics with frequency 3ω , 5ω , etc., which are quantified by the higher-order harmonic susceptibilities χ_3 , χ_5 , etc. as defined in Eq. (1). The even harmonics 2ω , 4ω , etc. should be zero because $P(E)$ should be equal to $-P(-E)$.

Figure 10 shows the modulus of $\chi_3 E^2$ for the PCs cyclo-octanol [28] and 60SN-40GN [31]. In both cases, a hump is observed at a frequency somewhat below ν_α , indicated by the arrows in Fig. 10. As mentioned in the introduction, such a humped shape of the χ_3 spectra is predicted within the model by Biroli and co-workers [36,37], to arise from molecular cooperativity, which is often assumed to be typical for glass forming systems [8,43,44,59]. Qualitatively similar spectral shapes of $\chi_3(\nu)$ were also found for various structural glass formers [19,23,26,75]. Within the theoretical

framework of Bouchaud and Biroli [36,37], the detection of a hump in PCs as documented in Fig. 10 indicates that the glassy freezing in PCs is also governed by molecular cooperativity [28]. A possible mechanism for generating molecular correlations in PCs could be lattice strains that reduce the hindering barriers for reorientational motions of neighboring molecules [28]. However, it should be noted that a hump in $|\chi_3|(\nu)$ can also be explained within the framework of other models [75,97,98,99,100,101].

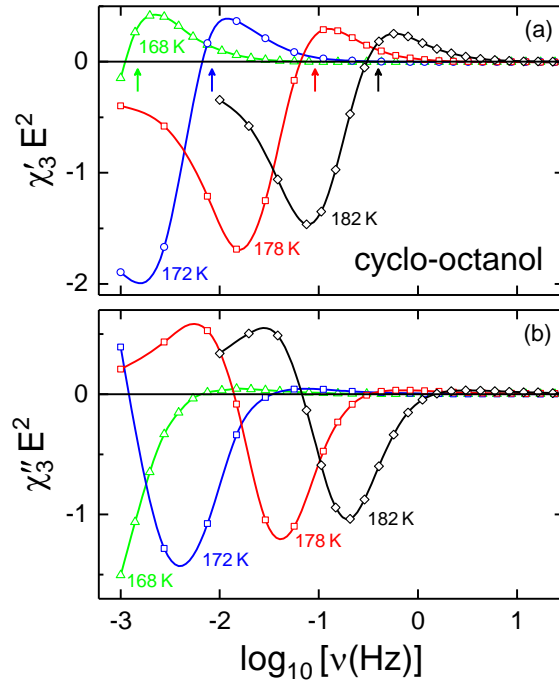
Fig. 10 Modulus of the third-order harmonic component of the dielectric susceptibility (times E^2) of cyclo-octanol (a) [28] and 60SN-40GN (b) [31], measured at various temperatures. The applied fields were 375 kV/cm and 357 kV/cm, respectively. The arrows indicate the corresponding α -peak frequencies. The lines are guides for the eyes.



About one decade below the hump frequencies, the $|\chi_3|E^2$ spectra of 60SN-40GN [Fig. 10(b)] reveal weak shoulders. In Ref. [31] it was speculated that these spectral

features arise from an additional slow relaxation process, for which indications were found in the linear dielectric spectra [48]. The microscopic origin of this process is unknown until now.

Fig. 11 Real and imaginary part of $\chi_3 E^2$ of cyclo-octanol at four temperatures measured for a field of 375 kV/cm. The arrows indicate the α -peak frequencies. The lines are guides for the eyes.



In Fig. 11, for cyclo-octanol in addition to the modulus shown in Fig. 10(a), the real and imaginary parts of the third-order harmonic susceptibility (times E^2) are presented. This should be compared to the corresponding spectra as found for the supercooled liquids glycerol and 1-propanol [19]. In the latter, the spectra of both quantities could be well described by exclusively considering saturation effects of the polarization at high fields [73], as already treated in very early works on nonlinear dielectric spectroscopy [71,72]. In 1-propanol, cooperativity seems to be absent for the main relaxation process due to the well-known peculiarities of the relaxational dynamics of most monohydroxy alcohols [102,103]. However, in glycerol, the real and imaginary

parts of χ_3 showed clear qualitative deviations from the behavior predicted for entirely saturation-induced nonlinearity, which was ascribed to cooperativity effects [19]. For cyclo-octanol, the spectra of Fig. 11 in many respects resemble those of glycerol and also clearly do not follow the behavior predicted for a purely saturation-dominated system such as 1-propanol. Especially, just as for glycerol, the well-pronounced negative minima, occurring in both the real and the imaginary part not far from ν_α , together generate the hump observed in the modulus of χ_3 [Fig 10(a)], which is taken as signature for cooperative glassy dynamics [28]. The negative real part of χ_3 found at low frequencies [Fig. 11(a)] can be assumed to arise from the entropy effects [39] discussed above, in contrast to the saturation effect dominating the low-frequency response in glycerol. At low frequencies, i.e. on long time scales, the liquid flow (directly related to the α relaxation) should destroy glassy correlations [27], leaving room for additional nonlinear contributions becoming dominant, which in the PCs predominantly seem to be entropy effects.

Within the model by Bouchaud and Biroli [36,37], a hump observed in the third-order susceptibility χ_3 , as documented for the PCs cyclo-octanol and 60SN-40GN in Fig. 10, should be related to the number of correlated molecules N_{corr} . Especially, the dimensionless quantity $X_3^{(3)}$, defined by [23]

$$X_3^{(3)} = \frac{k_B T}{\varepsilon_0 (\Delta\chi_1)^2 a^3} \chi_3^{(3)},$$

which corrects χ_3 for trivial temperature dependences, should be directly proportional to N_{corr} . (In this equation, $\Delta\chi_1$ is the dielectric strength and a^3 the volume taken up by a single molecule.) Figure 12(b) presents the temperature dependence of the peak value of this quantity for three supercooled liquids [26] and for the two PCs for which χ_3 data are available (symbols; left scale) [28,31]. At the peak, $X_3^{(3)}$ should be dominated by the cooperativity contribution to χ_3 and thus correspond to $N_{\text{corr}}(T)$ in arbitrary units. As revealed by Fig. 12(b) [26,28,31], for all these systems N_{corr} increases with decreasing temperature, implying a growth of correlation length scales. This is in accord with the notion that the glass transition is related to an underlying thermodynamic phase transition [43,59].

The temperature dependence of N_{corr} for the two PCs, shown in Fig. 12(b) (closed symbols) fully matches the general scenario found for the supercooled liquids [26] (open symbols): Simply spoken, the more fragile the material, the stronger is the temperature dependence of its N_{corr} . To illustrate their significantly different

fragilities, Fig. 12(a) shows an Angell plot of the relaxation times τ of the same materials as in Fig. 12(b). As discussed above, the fragility of a glass former quantifies the degree of deviation of its temperature-dependent relaxation time from Arrhenius behavior. In Fig. 12(a), these deviations are revealed to be weakest for glycerol and strongest for the two other glass-forming liquids. Indeed, with fragility parameters $m \approx 53$ (glycerol [104]), 90 (3-fluoroaniline), and 104 (propylene carbonate [104]), the supercooled liquids in this plot vary considerably between intermediate and high fragility. Correspondingly, glycerol has significantly weaker temperature dependence of N_{corr} than the other two glass formers [Fig. 12(b)]. As pointed out in Ref. [26], this finding well corroborates the notion that the non-Arrhenius behavior of supercooled liquids arises from increasing molecular cooperativity at low temperatures.

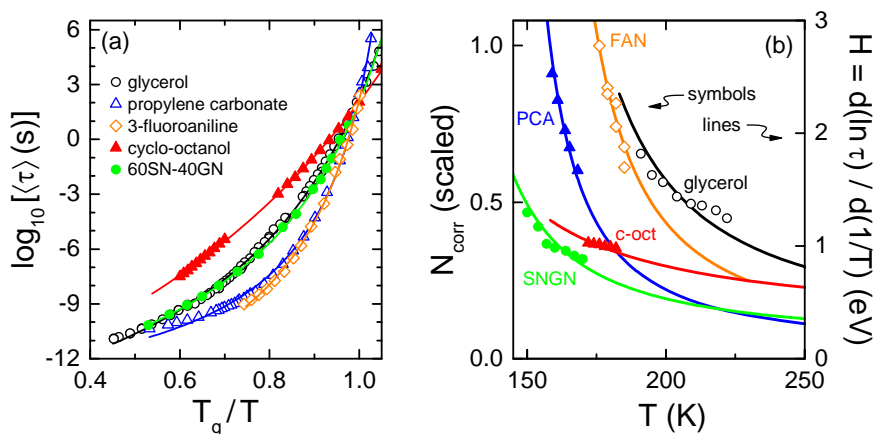


Fig. 12 (a) Temperature-dependent average α -relaxation times of three glassforming liquids and two PCs [48,50,61,91] shown in an Angell plot [52]. The lines are fits with the Vogel-Fulcher-Tammann (VFT) function [50]. (b) Comparison of the effective activation energies H (lines; right scale) with the number of correlated molecules N_{corr} (symbols; left scale) for the same materials as in frame (a) [26,28,31]. H was determined from the derivatives of the VFT fits of the temperature-dependent relaxation-times shown in frame (a). N_{corr} , shown in arbitrary numbers, was determined from χ_3 (see text). To match the $H(T)$ curves, N_{corr} was multiplied by separate factors for each material (glycerol: 1.15, propylene carbonate (PCA): 0.72, 3-fluoroaniline (FAN): 1.30, cyclo-octanol: 0.19, 60SN-40GN (SNGN): 1.05). Note that both ordinates start from zero, implying direct proportionality of both quantities.

Concerning the PC results included in Fig. 12, cyclo-octanol is known to be a rather strong glass former ($m \approx 33$), which is quite common for this class of glasslike materials [1,45]. In Fig. 12(a), this immediately becomes obvious from the fact that its τ curve is only weakly bended and, for $T > T_g$, lies above the data points of all the other shown materials. Figure 12(b) reveals that, just as for the supercooled liquids, this strong dynamics of cyclo-octanol is nicely mirrored by the very weak temperature dependence of its N_{corr} as determined from the χ_3 measurements. Thus it seems that, for this PC, a temperature-dependent variation of cooperativity also is the main factor determining its non-Arrhenius behavior. A crucial test to support this idea is provided by the results on 60SN-40GN. This is one of the very few examples [45,47,48], where a relatively *high* fragility ($m \approx 62$) is realized in a PC. Indeed, in Fig. 12(a) its $\tau(T)$ curve is similarly bended as for the intermediately fragile glycerol. Therefore, for 60SN-40GN the number of correlated molecules should increase significantly stronger than for cyclo-octanol. In fact, this is observed in Fig 12(b). Within the theoretical framework by Bouchaud and Biroli [36,37], these results allow to conclude that the origin of the non-Arrhenius behavior in PCs is the same as for structural glass former, namely an increase of cooperativity when approaching the glass transition under cooling.

In Ref. [26] it was demonstrated that, in addition to the qualitative connection of the temperature variations of the α -relaxation time and N_{corr} discussed above, there also seems to be a quantitative relation of both quantities: Let us consider the explanation of the non-Arrhenius behavior of $\tau(T)$ by a temperature-dependent effective energy-barrier H governing molecular motion, as schematically indicated in Fig. 3 [12,44,105]. Within this framework, fragile and strong dynamics imply strong or weak temperature dependence of $H(T)$, respectively. Within the time-honored Adam-Gibbs theory [59], it is assumed that the temperature-dependent energy barrier is proportional to the number of molecules within a CRR, i.e. $H \sim N_{\text{corr}}$. As indicated in Fig. 3, $H(T)$ can be estimated by the derivative of the $\log \tau(1/T)$ curves in the Arrhenius representation, $H = d(\ln \tau) / d(1/T)$. (To avoid excessive data scatter, usually arising when differentiating experimental curves, derivatives of the fit curves of $\tau(T)$ instead of the experimental data points can be used.) For the materials covered by Fig. 12, the results for $H(T)$ are indicated by the lines shown in frame (b) (right scale). As demonstrated in Ref. [26] for the supercooled liquids, the $N_{\text{corr}}(T)$ data (in arbitrary units) can be reasonably scaled onto the $H(T)$ curves obtained in this way. This obviously is also well fulfilled for the two PCs [28,31]. It should be noted that both ordinates in Fig.

12 start at zero implying that, indeed, $H(T)$ and $\tau(T)$ are directly proportional to each other. Finally, we want to mention that the scaling factors, applied to match the $N_{\text{corr}}(T)$ to the $H(T)$ curves are of the order of one for the three supercooled liquids and for plastic-crystalline 60SN-40GN (see caption of Fig. 12 for the values). However, for cyclo-octanol, this factor is 0.19 and, thus, significantly smaller. The reason for this difference is not clear at present; seemingly, for the latter compound the molecular motions are less impeded by a high N_{corr} than in the others. Further nonlinear investigations of canonical PCs are necessary to check if this deviation is a common property of this material class. 60SN-40GN may be suspected to be a special case, due to its strong substitutional disorder.

4. Summary and Conclusions

In the present overview, we have demonstrated a rich variety of nonlinear dielectric phenomena occurring in PCs. We have concentrated on two typical ways of performing nonlinear dielectric experiments, namely the measurement of the 1ω and of the 3ω components of the dielectric susceptibility, both performed under high ac fields. In many respects, PCs reveal similar behavior as found for structural glass formers. Especially, high ac fields lead to an enhancement of the dielectric permittivity at frequencies $\nu > \nu_\alpha$, just as commonly found for supercooled liquids. Therefore, it seems natural to explain this phenomenon in a similar way. Just as for the latter, currently two seemingly different explanations of the nonlinear response at $\nu > \nu_\alpha$ can be invoked, namely a selective transfer of field energy into the heterogeneous regions as considered in the box model [18,20,29,69,70] or a cooperativity-related origin implying increasing length scales and "amorphous order" when approaching T_g as treated in the model by Bouchaud and Biroli [23,26,27,31,36,37,78]. It should be noted, however, that in a recent work it was proposed that these two approaches even may be compatible [78].

At low frequencies, $\nu < \nu_\alpha$, the nonlinear 1ω response of PCs and supercooled liquids seems to differ markedly. While the latter exhibit only weak nonlinearity in this frequency range, PCs probably are dominated by entropy effects [29] as considered in Johari's theory [39]. To explain this finding, we have speculated about the different relative importance of reorientational degrees of freedom for the entropy in PCs compared to canonical glasses [31] but this issue is still far from clarified.

When approaching high frequencies, in the region of secondary processes as the excess wing or the JG relaxation, for PCs, just as for the supercooled liquids, a gradual

reduction of nonlinearity is observed. Within the cooperativity-related framework, this implies less cooperative motions as often assumed for such processes [83,91,92].

Of special interest are the results concerning the third-order harmonic susceptibility, characterizing the 3ω dielectric response [28,31]. For the two PCs for which this quantity was investigated until now, a spectral shape as predicted by the model by Biroli and Bouchaud is found. In this respect, the PCs behave very similar as various supercooled liquids [23,26,75]. The results seem to imply that a growth of molecular cooperativity and the approach of amorphous order under cooling is the origin of the non-Arrhenius behavior, not only in supercooled liquids [23,26,27] but also in PCs. As discussed in section 1, an energy-landscape scenario [57,58] was previously invoked to rationalize the commonly less fragile relaxation dynamics of PCs compared to structural glass formers [1,45,47,48]. The found indications for growing length scales when approaching T_g in PCs, based on χ_3 measurements, seem to imply that there must be a relation of this energy-landscape scenario to the cooperativity scenario. A possible rationalization of such a relation was discussed in section 1.

The present work makes clear that quite far-reaching conclusions can be drawn from nonlinear dielectric measurements of PCs, not only concerning this special class of glasslike systems but also concerning the glass transition and glassy state of matter in general. Nevertheless, one should be aware that until now only rather few PC systems have been investigated by nonlinear techniques. Clearly, a broader data base is highly desirable to reveal universalities and further help enlightening our understanding of the role of cooperativity and heterogeneity in glassy systems.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft via Research Unit FOR 1394. Stimulating discussions with S. Albert, Th. Bauer, G. Biroli, U. Buchenau, G. Diezemann, G.P. Johari, F. Ladieu, K.L. Ngai, R. Richert, R.M. Pick and K. Samwer are gratefully acknowledged.

References

1. R. Brand, P. Lunkenheimer, and A. Loidl, *J. Chem. Phys.* **116**, 10386 (2002).
2. J. Timmermans, *J. Chim. Phys.* **35**, 331 (1938).
3. N. G. Parsonage and L. A. K. Staveley, *Disorder in Crystals* (Oxford University Press, Oxford, 1978).
4. J. N. Sherwood, *The Plastically Crystalline State* (John Wiley & Sons, New York, 1979).
5. K. Adachi, H. Suga, and S. Seki, *Bull. Chem. Soc. Jpn.* **41**, 1073 (1968).

-
6. U. T. Höchli, K. Knorr, and A. Loidl, *Adv. Phys.* **39**, 405 (1990).
 7. A. Loidl and R. Böhmer, in *Disorder Effects on Relaxational Processes*, edited by R. Richert and A. Blumen (Springer, Berlin, 1994), p. 659.
 8. M. D. Ediger, C. A. Angell, S. R. Nagel, *J. Phys. Chem.* **100**, 13200 (1996).
 9. H. Sillescu, *J. Non-Cryst. Solids* **243**, 81 (1999).
 10. M. D. Ediger, *Annu. Rev. Phys. Chem.* **51**, 99 (2000).
 11. P. Lunkenheimer, U. Schneider, R. Brand, and A. Loidl, *Contemp. Phys.* **41**, 15 (2000).
 12. J. C. Dyre, *Rev. Mod. Phys.* **78**, 953 (2006).
 13. D. L. Leslie-Pelecky and N. O. Birge, *Phys. Rev. Lett.* **72**, 1232 (1994).
 14. M. A. Ramos, S. Vieira, F. J. Bermejo, J. Dawidowski, H. E. Fischer, H. Schober, M. A. González, C. K. Loong, and D. L. Price, *Phys. Rev. Lett.* **78**, 82 (1997).
 15. R. Brand, P. Lunkenheimer, U. Schneider, and A. Loidl, *Phys. Rev. Lett.* **82**, 1951 (1999).
 16. F. Affouard and M. Descamps, *Phys. Rev. Lett.* **87**, 035501 (2001).
 17. P.-J. Alarco, Y. Abu-Lebdeh, A. Abouimrane, and M. Armand, *Nature Mater.* **3**, 476 (2004).
 18. R. Richert, *J. Phys.: Condens. Matter* **29**, 363001 (2017).
 19. P. Lunkenheimer, M. Michl, Th. Bauer, and A. Loidl, *Eur. Phys. J. Special Topics* **226**, 3157 (2017).
 20. R. Richert and S. Weinstein, *Phys. Rev. Lett.* **97**, 095703 (2006).
 21. L.-M. Wang, R. Richert, *Phys. Rev. Lett.* **99**, 185701 (2007).
 22. A. Drozd-Rzoska, S.J. Rzoska, and J. Ziolo, *Phys. Rev. E* **77**, 041501 (2008).
 23. C. Crauste-Thibierge, C. Brun, F. Ladieu, D. L'Hôte, G. Biroli, and J.-P. Bouchaud, *Phys. Rev. Lett.* **104**, 165703 (2010).
 24. L. P. Singh and R. Richert, *Phys. Rev. Lett.* **109**, 167802 (2012).
 25. Th. Bauer, P. Lunkenheimer, S. Kastner, and A. Loidl, *Phys. Rev. Lett.* **110**, 107603 (2013).
 26. Th. Bauer, P. Lunkenheimer, and A. Loidl, *Phys. Rev. Lett.* **111**, 225702 (2013).
 27. S. Albert, Th. Bauer, M. Michl, G. Biroli, J.-P. Bouchaud, A. Loidl, P. Lunkenheimer, R. Tourbot, C. Wiertel-Gasquet, and F. Ladieu, *Science* **352**, 1308 (2016).
 28. M. Michl, Th. Bauer, P. Lunkenheimer, A. Loidl, *Phys. Rev. Lett.* **114**, 067601 (2015)
 29. B. Riechers, K. Samwer, and R. Richert, *J. Chem. Phys.* **142**, 154504 (2015).
 30. S. Samanta and R. Richert, *J. Chem. Phys.* **142**, 044504 (2015).
 31. M. Michl, Th. Bauer, P. Lunkenheimer, and A. Loidl, *J. Chem. Phys.* **144**, 114506 (2016).
 32. B. Schiener, R. Böhmer, A. Loidl, and R. V. Chamberlin, *Science* **274**, 752 (1996).
 33. S. Weinstein and R. Richert, *Phys. Rev. B* **75**, 064302 (2007).
 34. G. P. Johari and M. Goldstein, *J. Chem. Phys.* **53**, 2372 (1970).
 35. P. Lunkenheimer and A. Loidl, in *Broadband Dielectric Spectroscopy*, edited by F. Kremer and A. Schönhals (Springer, Berlin, 2002), chapter 5.
 36. J.-P. Bouchaud and G. Biroli, *Phys. Rev. B* **72**, 064204 (2005).
 37. M. Tarzia, G. Biroli, A. Lefèvre, and J.-P. Bouchaud, *J. Chem. Phys.* **132**, 054501 (2010).

-
38. C. Brun, F. Ladieu, D. L'Hôte, M. Tarzia, G. Biroli, and J.-P. Bouchaud, *Phys. Rev. B* **84**, 104204 (2011).
 39. G. P. Johari, *J. Chem. Phys.* **138**, 154503 (2013).
 40. G. P. Johari, *J. Chem. Phys.* **145**, 164502 (2016).
 41. M. Winterlich, G. Diezemann, H. Zimmermann, and R. Böhmer, *Phys. Rev. Lett.* **91**, 235504 (2003).
 42. G. P. Johari and J. Khouri, *J. Chem. Phys.* **137**, 104502 (2012).
 43. T. R. Kirkpatrick and P. G. Wolynes, *Phys. Rev. B* **36**, 8552 (1987).
 44. P. G. Debenedetti and F. H. Stillinger, *Nature* **310**, 259 (2001).
 45. F. Mizuno, J.-P. Belieres, N. Kuwata, A. Pradel, M. Ribes, and C. A. Angell, *J. Non-Cryst. Solids* **352**, 5147 (2006).
 46. C.A. Angell, in *Relaxation in Complex Systems*, edited by K. L. Ngai and G. B. Wright (Office of Naval Research, Washington DC, 1985), p. 3.
 47. L. C. Pardo, P. Lunkenheimer, and A. Loidl, *J. Chem. Phys.* **124**, 124911 (2006).
 48. Th. Bauer, M. Köhler, P. Lunkenheimer, A. Loidl, and C. A. Angell, *J. Chem. Phys.* **133**, 144509 (2010).
 49. M. Götz, Th. Bauer, P. Lunkenheimer, and A. Loidl, *J. Chem. Phys.* **140**, 094504 (2014).
 50. P. Lunkenheimer, S. Kastner, M. Köhler, and A. Loidl, *Phys. Rev. E* **81**, 051504 (2010).
 51. P. Lunkenheimer, M. Köhler, S. Kastner, and A. Loidl, in *Structural Glasses and Supercooled Liquids: Theory, Experiment, and Applications*, edited by P.G. Wolynes and V. Lubchenko (Wiley, Hoboken, 2012), chapter 3, p. 115.
 52. C. A. Angell and W. Sichina, *Ann. N.Y. Acad. Sci.* **279**, 53 (1976).
 53. D. J. Plazek and K. L. Ngai, *Macromolecules* **24**, 1222 (1991).
 54. R. Böhmer and C. A. Angell, *Phys. Rev. B* **45**, 10091 (1992).
 55. A. Srinivasan, F. J. Bermejo, A. de Andrés, J. Dawidowski, J. Zúñiga, and A. Criado, *Phys. Rev. B* **53**, 8172 (1996).
 56. R. Brand, P. Lunkenheimer, U. Schneider, and A. Loidl, *Phys. Rev. B* **62**, 8878 (2000).
 57. C. A. Angell, *J. Phys. Chem. Solids* **49**, 863 (1988).
 58. R. Böhmer and C. A. Angell, in *Disorder Effects on Relaxational Processes*, edited by R. Richert and A. Blumen (Springer, Berlin, 1994), p. 11.
 59. G. Adam and J. H. Gibbs, *J. Chem. Phys.* **43**, 139 (1965).
 60. D. L. Leslie-Pelecky and N. O. Birge, *Phys. Rev. Lett.* **72**, 1232 (1994).
 61. R. Brand, P. Lunkenheimer, and A. Loidl, *Phys. Rev. B* **56**, R5713 (1997).
 62. M. Shablakh, L. A. Dissado, and R. M. Hill, *J. Chem. Soc. Faraday Trans. II* **79**, 369 (1983).
 63. O. Anderson and R. G. Ross, *Mol. Phys.* **71**, 523 (1990).
 64. H. Forsmann and O. Anderson, *J. Non-Cryst. Solids* **131-133**, 1145 (1991).
 65. L. P. Singh and S. S. N. Murthy, *Phys. Chem. Chem. Phys.* **11**, 5110 (2009).
 66. P. Lunkenheimer and A. Loidl, *J. Chem. Phys.* **104**, 4324 (1996).

-
67. O. Yamamuro, M. Hayashi, T. Matsuo, and P. Lunkenheimer, *J. Chem. Phys.* **119**, 4775 (2003).
 68. D. W. Davidson and R. H. Cole, *J. Chem. Phys.* **18**, 1417 (1950).
 69. B. Schiener, R. Böhmer, A. Loidl, and R. V. Chamberlin, *Science* **274**, 752 (1996).
 70. B. Schiener, R. V. Chamberlin, G. Diezemann, and R. Böhmer, *J. Chem. Phys.* **107**, 7746 (1997).
 71. J. Herweg, *Z. Phys.* **3**, 36 (1920).
 72. P. Debye, *Polar Molecules* (Dover Publications, New York, 1929).
 73. J. L. Déjardin and Yu. P. Kalmykov, *Phys. Rev. E* **61**, 1211 (2000).
 74. Th. Bauer, M. Michl, P. Lunkenheimer, and A. Loidl, *J. Non-Cryst. Solids* **407**, 66 (2015).
 75. P. Kim, A. R. Young-Gonzales, and R. Richert, *J. Chem. Phys.* **145**, 064510 (2016).
 76. S. Samanta and R. Richert, *J. Phys. Chem. B* **120**, 7737 (2016).
 77. R. Richert, *J. Chem. Phys.* **146**, 064501 (2017).
 78. P. Gadige, S. Albert, M. Michl, Th. Bauer, P. Lunkenheimer, A. Loidl, R. Tourbot, C. Wiertel-Gasquet, G. Biroli, J.-P. Bouchaud, and F. Ladieu, *Phys. Rev. E* **96**, 032611 (2017).
 79. F. H. Stillinger, *Science* **267**, 1935 (1995).
 80. J. S. Harmon, M. D. Demetriou, W. L. Johnson, and K. Samwer, *Phys. Rev. Lett.* **99**, 135502 (2007).
 81. C. Gainaru, O. Lips, A. Troshagina, R. Kahlau, A. Brodin, F. Fujara, and E. A. Rössler, *J. Chem. Phys.* **128**, 174505 (2008).
 82. R. V. Chamberlin, *Phys. Rev. Lett.* **82**, 2520 (1999).
 83. K. L. Ngai, *J. Phys.: Condens. Matter* **15**, S1107 (2003).
 84. W. Götze and M. Sperl, *Phys. Rev. Lett.* **92**, 105701 (2004).
 85. K. L. Ngai and M. Paluch, *J. Chem. Phys.* **120**, 857 (2004).
 86. K. L. Ngai, *Phys. Rev. E* **57**, 7346 (1998).
 87. R. L. Leheny and S. R. Nagel, *Europhys. Lett.* **39**, 447 (1997).
 88. U. Schneider, R. Brand, P. Lunkenheimer, and A. Loidl, *Phys. Rev. Lett.* **84**, 5560 (2000).
 89. K. L. Ngai, P. Lunkenheimer, C. León, U. Schneider, R. Brand, and A. Loidl, *J. Chem. Phys.* **115**, 1405 (2001).
 90. A. Döb, M. Paluch, H. Sillescu, and G. Hinze, *Phys. Rev. Lett.* **88**, 095701 (2002).
 91. A. Kudlik, S. Benkhof, T. Blochowicz, C. Tschirwitz, and E. Rössler, *J. Mol. Struct.* **479**, 201 (1999).
 92. M. Beiner, H. Huth, and K. Schröter, *J. Non-Cryst. Solids* **279**, 126 (2001).
 93. S. Samanta and R. Richert, *J. Phys. Chem. B* **119**, 8909 (2015).
 94. K. L. Ngai, *J. Chem. Phys.* **142**, 114502 (2015).
 95. S. Samanta and R. Richert, *J. Chem. Phys.* **140**, 054503 (2014).
 96. B. Roling, L. N. Patro, O. Burghaus, and M. Gräf, *Eur. Phys. J. Special Topics* **226**, 3095 (2017).
 97. C. Brun, C. Crauste-Thibierge, F. Ladieu, and D. L'Hôte, *J. Chem. Phys.* **134**, 194507 (2011).
 98. G. Diezemann, *Phys. Rev. E* **85**, 051502 (2012).

-
99. G. Diezemann, *J. Chem. Phys.* **138**, 12A505 (2013).
 100. R. M. Pick, *J. Chem. Phys.* **140**, 054508 (2014).
 101. U. Buchenau, *J. Chem. Phys.* **146**, 214503 (2017).
 102. C. Gainaru, S. Kastner, F. Mayr, P. Lunkenheimer, S. Schildmann, H. J. Weber, W. Hiller, A. Loidl, and R. Böhmer, *Phys. Rev. Lett.* **107**, 118304 (2011).
 103. C. Gainaru, R. Meier, S. Schildmann, C. Lederle, W. Hiller, E. A. Rössler, and R. Böhmer, *Phys. Rev. Lett.* **105**, 258303 (2010).
 104. R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, *J. Chem. Phys.* **99**, 4201 (1993).
 105. S. A. Kivelson and G. Tarjus, *Nature Mater.* **7**, 831 (2008).