Molecular Cross-correlations Govern Structural Rearrangements in a Nonassociating Polar Glass Former

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Self- and cross-correlation dynamics of deeply supercooled liquids were recently identified using photon correlation spectroscopy on the one hand and dielectric investigations on the other. These results fueled a controversial discussion whether the "generic" response identified by photon correlation spectroscopy, or rather the nonuniversal dielectric response, reflect the liquid's structural relaxation. The present study employs physical aging and oscillatory shear rheology to directly access the structural relaxation of a nonassociating glass-forming liquid and reveals that collective equilibrium fluctuations of simple liquids and not single-particle dynamics govern their structural relaxation. The present results thus challenge recent views that the glassy response of polar supercooled liquids can generically be decomposed into a Debye-type, supramolecular response and a single-particle dynamics with the latter reflecting the "true" structural relaxation. Furthermore, the current findings underscore the pivotal role dielectric spectroscopy plays in glass science as one of the rare molecular-level reorientation techniques that senses dynamical cooperativity directly.

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A popular notion regarding glasses holds that they are liquids fallen out of time, i.e., structurally disordered solids with thermally arrested dynamics. The most salient features of the structural dynamics of glass-forming liquids can be summarized with reference to their nonexponential, nonlinear, and non-Arrhenius nature—succinctly coined the three "nons" [1]. Yet, the microscopic origin of these well-established, practically universally observed characteristics of supercooled liquids remains a source of fruitful controversy. The most important debate centers on the nature of the structural relaxation itself and explores whether or not vitrification can be regarded as a collective phenomenon. In viscous liquids, the coupling among structural subunits was considered early on [2] and ever since remained an inspiring idea in the search for evidence unraveling the collective nature of viscous liquid dynamics [3]. In this vein, indications for molecular cooperativity were reported based on nuclear magnetic resonance (NMR) investigations [4], confinement studies [5], and atomic force measurements of dielectric noise [6]. More recently, theoretical work [7] inspired nonlinear dielectric studies [8,9] that relate the emergence of "humps" in higher-order susceptibilities to a collective, multiparticle behavior, an assignment that is, however, not uncontested [10,11].

Several classes of glass-forming liquids exhibit well-recognized collective relaxation modes already in their linear responses. Here, polymer melts come to mind, in which concerted motions within the macromolecular backbone, the well-known normal modes, relax slower than the structural, segmental modes [12]. A wealth of nonpolymeric glass formers, many of them featuring hydrogen bonds, also display clear spectral signatures of supramolecular relaxations. Prominent examples include the monohydroxy alcohols, for which the timescale of their so-called Debye-like process is sometimes more than 1000 times slower than their structural relaxation [13]. The collective nature of the main dielectric response of these materials has been rationalized with reference to the large contrast between the dielectric and NMR relaxometry timescales reflecting their cross-correlation (collective) and self-correlation (single-particle) molecular motions, respectively [14].

Even for much smaller spectral separations, and aided by photon correlation spectroscopy (PCS), a decomposition of the total response in terms of single- and multiparticle dynamics was demonstrated not only for the dielectric spectra of monohydroxy alcohols [15], but also suggested for the prototypical H-bonded glassformer glycerol [16]. This decomposition was motivated by the observation that the main relaxation process probed by PCS (often understood to reflect single-particle dynamics [17,18]) is significantly faster than the dielectric relaxation [19] and that the PCS spectra display a "generic shape" which then necessarily is temperature independent. Avoiding the complexities inherent in the physics of hydrogen-bonded liquids, this decomposition was recently demonstrated also for tributyl phosphate (TBP) [17], a moderately polar, nonassociating liquid [20] featuring a calorimetric glass transition temperature T_g near 141 K [21].

The finding of a generic shape for the main (reorientational) relaxation thus identified by PCS for a large number of glass formers contrasts with the multitude of spectral shapes detected by deuteron NMR [22] or the variation of widths found from dielectric susceptibility spectra near T_g [23]. The latter was shown to correlate well with the dielectric relaxation strength $\Delta\varepsilon$ [24] was and rationalized in terms of changes in the intermolecular potential [25]. Thus, currently one faces the situation that in numerous simple (nonassociating and nonpolymeric) liquids, PCS is reported to probe a generic dynamics, which can be significantly different from that revealed, e.g., by dielectric spectroscopy. The central question arises: Which of these methods that probe different equilibrium fluctuations reflects the structural rearrangements within these materials most closely? Should, following recent suggestions [17], the structural relaxation be associated with the generic single-particle dynamics? Or can one demonstrate that the collective, dielectrically detected modes govern the timescale of the structural fluctuations in simple liquids? In related terms, do the generic spectra obtained by PCS really probe the structural relaxation of liquids in the vicinity of the glass transition? It is clear that the existence of even a single counterexample will cast serious doubts on the given interpretation [17] that the spectral shape of the structural relaxation itself is truly generic.

To address these questions, we study the nonassociating liquid TBP for which PCS and dielectric investigations, even close to T_g, revealed significantly different dynamics. Performing shear rheology and physical aging for this glassformer, we demonstrate that near T_g its microscopic flow and its structural recovery persist on timescales significantly longer than those identified by PCS. Moreover, based on its equilibrium dielectric behavior, we successfully estimate the timescale of its nonlinear aging response which is highly relevant for the glassy behavior of this material. While a decomposition of the dielectric spectra into contributions reflecting single-particle and multiparticle dynamics was suggested also for a few other polar liquids [17,19,26], to our knowledge TBP is the only of those for which dielectric *and* PCS measurements are available and for which clearcut interpretations are not hampered by complexities associated with hydrogen bonding.

Dielectric and PCS spectra of TBP for $T = 140$ and 147 K taken from Ref. [17] are shown in Fig. 1. The shapes of the PCS spectra adapt themselves perfectly to the high-frequency parts of the dielectric losses. The dielectric spectrum at $T = 137$ K is from the present work; experimental details are given as Supplemental Material [27]. The inset of Fig. 1 illustrates that a Debye-type low-frequency contribution remains after subtracting the suitably normalized PCS susceptibility from the dielectric loss ε'', with the colored areas highlighting how the various contributions can give rise to the overall dielectric spectrum.

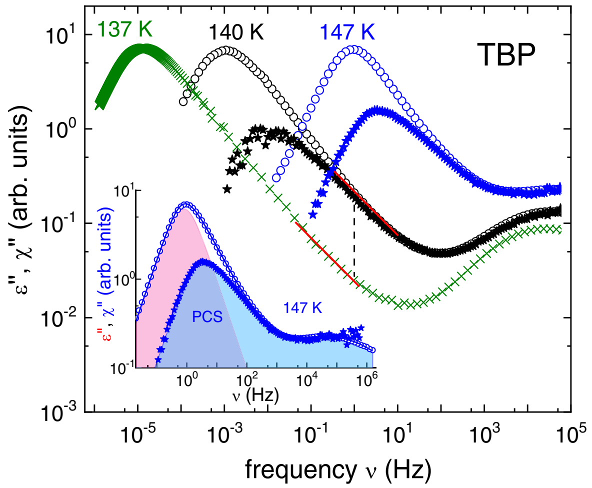

FIG. 1. The dielectric and PCS susceptibility spectra probed for TBP at 140 and 147 K are taken from Ref. [17]. The dielectric spectrum recorded at 137 K after the sample was equilibrated at this temperature for about 3×10^5 s is from the current work. The solid red lines indicate a power law $\varepsilon'' \propto \nu^{-0.48}$ for the dielectric susceptibility near the aging detection frequency (1 Hz, as indicated by the vertical line). Note that at 140 K, the PCS and dielectric susceptibility peaks are separated by a factor of 10. The inset adapted is from Ref. [17] and was used there to suggest that the dielectric response of TBP exhibits an additional slow Debye process (highlighted in red) with respect the PCS susceptibility (highlighted in blue).

To decide among the two above scenarios, it is mandatory to properly identify the structural relaxation by experimental means that provide direct access to it. Calorimetry and viscometry are recognized as suitable probes for TBP [21,33]. In a first step, we measured its complex shear mechanical compliance $J^* = J' - iJ''$, which represents a susceptibility function, similar to the dielectric and PCS functions considered in Fig. 1. Since the loss part of the compliance $J''(\nu)$ is severely superimposed by contributions from molecular flow, thus hampering a direct comparison with the dielectric and PCS spectra, in Fig. 2 we focus on the storage part of the compliance $J'(\nu)$. For details, see the Supplemental Material [27] where we also show that our viscoelastic results fully agree with expectations based on high-T viscosity and low-T calorimetry investigations of TBP [33]. While in its fluid and moderately supercooled regime the dielectric and PCS timescales differ considerably from those of the enthalpic and rheological responses [21], close to T_g the temperature dependence of all relaxation times is highly similar (see the Supplemental Material [27]) and, except for PCS, also their absolute values. We interpret this convergence of all (except the PCS) timescales to indicate that, when T_g is closely approached, the coupling among the various degrees of freedom generates a common cooperative behavior.

From Fig. 2 it is obvious that the frequency position of the clearly resolved inflection point in $J'(\nu)$ is close to the

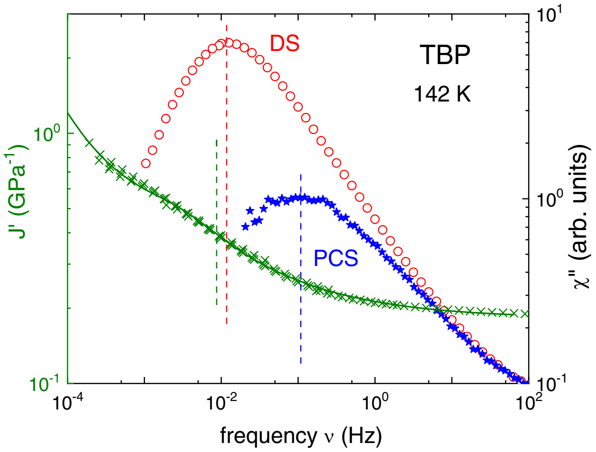

FIG. 2. Master plot of the shear susceptibility spectra of TBP. The reference temperature was chosen as 142 K in order to facilitate comparison with dielectric spectroscopy (DS) and PCS experiments carried out at the same temperature. The vertical lines indicate the characteristic frequencies of the different isothermally probed susceptibilities. Note that the peak separation between the PCS and the dielectric susceptibility is about a factor of 10. The absence of a low-frequency plateau in $J'(\nu)$ corresponding to the recoverable compliance is due to low-torque artifacts. The solid line reflects a fit with a Cole-Davidson function [34] augmented by a power law accounting for the latter.

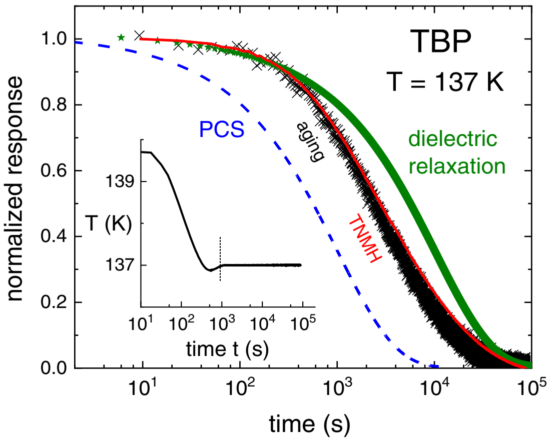

FIG. 3. The normalized equilibrium dielectric response of TBP probed at 137 K (green solid stars) is compared with the normalized 1 Hz dielectric aging data (black crosses) probed at the same base temperature and the expectation of the equilibrium PCS response at 137 K (blue dashed line). The latter was estimated assuming the same one decade for the timescale difference between the PCS and dielectric responses, obvious from the results presented in Fig. 1 (at 140 K) and Fig. 2 (at 142 K). The solid red line is calculated using the TMNH formalism; see the Supplemental Material [27]. The inset depicts the temperature variation prior and during the acquisition of the dielectric aging results. The vertical line indicates a possible choice for the starting condition in this experiment, another one is discussed in the Supplemental Material [27].

characteristic frequency of the dielectric loss peak but differs significantly from that of the PCS susceptibility, which at 142 K indicates an about 10 times faster relaxation. Although one may argue that comparisons of the results from different techniques are prone to suffering from differences in the experimental conditions, temperature readings, and other circumstances, this observation nevertheless confirms that the dielectric, and not the light-scattering experiment, provides direct access to the viscoelastically detected structural relaxation.

Then, how can the structural relaxation be monitored in a way that is independent of the specific probe? The most popular means is to exploit physical aging experiments: These are classically based on inducing a change of the liquid's structural state, e.g., by a temperature step, and to detect its subsequent evolution by means of techniques as diverse as neutron detected vibrational spectroscopy [35], dilatometry [36,37], shear-mode monitoring [38], and not the least dielectric spectroscopy [39,40]. Common to all these techniques is that the largely varying dynamics to which these methods are primarily sensitive are all driven by or intimately coupled to the same structural state within the liquid and its temporal evolution. A drawback of the aging diagnostics, by whatever technique, is that it is necessarily nonlinear in the sense that its outcome depends on the direction and magnitude of the externally applied temperature perturbation. The consequences of this circumstance were recognized early on [36] and can adequately be captured within the well-known Tool-Narayanaswamy-Moynihan-Hodge (TMNH) [41] or Kovacs-Aklonis-Hutchinson-Ramos models [42].

To tackle the present issue, we thus aim to check whether or not the dielectrically detected and rheologically confirmed timescales truly reflect that of the structural relaxation. Therefore, we performed equilibrium electric-field-step as well as temperature-jump experiments within the same dielectric cell and setup, so as to minimize potential differences in experimental conditions. Figure 3 presents the temporal evolution of the electrical polarization that was recorded after switching the external field isothermally at 137 K. These data were Fourier transformed, combined with those probed in the frequency domain at the same temperature, and included in Fig. 1. In Fig. 3, the time-dependent polarization decay is shown in normalized form in order to facilitate comparison with the results from the aging experiment. Here, the temperature was stepped (more precisely, rapidly ramped) from 140 K down to a base temperature of 137 K; see the temperature protocol depicted in the inset of Fig. 3. In order to track the subsequent structural changes, we recorded the dielectric loss at a frequency of 1 Hz. This detection frequency was chosen because, as one recognizes from Fig. 1, it lies within a moderately broad spectral range in which the dielectric loss follows an apparent power law. Under these provisos, this high-frequency monitoring is largely equivalent to probing the time evolution of the dielectric loss peak frequency [40].

The time-dependent dielectric loss $\varepsilon''(1\ \mathrm{Hz})$ of TBP measured while the sample ages at its base temperature is shown in Fig. 3. One recognizes that this function decays faster than the dielectric polarization, thus, at first glance, supporting the implication from Ref. [17] that is illustrated in the inset of Fig. 1, which states that structural relaxation proceeds faster than inferred from the dielectric loss peak. However, based on the data in Fig. 3, such a conclusion must be considered as premature because, after a thermal downstep, the sample initially relaxes with the rate corresponding to the starting temperature. Then, although self-retardation effects evolve in the course of physical aging, the resulting aging curve necessarily appears to be faster, typically by a factor of 2–3, as compared to the response measured in thermal equilibrium [43]. If in Fig. 3 the structural rearrangements would be reflected by the PCS curve, the aging response should appear by a factor 2–3 faster than the latter, which is not the case [44].

As the red line in Fig. 3 shows, the measured aging curve is compatible with calculations (for details, see the Supplemental Material [27]) performed on the basis of the equilibrium dielectric response within the TMNH model. Interestingly, the TMNH curve [45] presented in Fig. 3 cannot be fitted satisfactorily using a one-step Kohlrausch function $\exp[-(t/\tau)^{\beta}]$, since self-retardation implies that the effective τ is not constant during aging [41]. A double-step Kohlrausch function provides, however, an almost perfect match (see the Supplemental Material [27]) despite the fact that the TMNH calculation is based on a one-step function.

Returning to the comparison of the results from the different techniques, we note that PCS data for TBP are not available for $T = 137$ K [17]. By assuming the factor-of-10 separation valid at 140 K (Fig. 1) and 142 K (Fig. 2) from Fig. 3, we see that the PCS response thus expected at 137 K is considerably faster than the measured aging curve. Thus, the present aging experiment indeed provides unequivocal evidence that it is the collective dielectric response which probes the structural relaxation and not the contribution termed "generic."

While the present findings provide a counterexample for recent PCS-based interpretations that the structural relaxation itself is generic [17,19], they are in harmony with the relevance of a coupling among the structural subunits in glass-forming liquids [3,23] which may further be linked with cross-correlation effects that prominently show up in dielectric spectroscopy [46,47].

To summarize, we performed oscillatory shear investigations and physical aging experiments on a simple glass-forming liquid for which, on the basis of PCS and dielectric responses, single- and multiparticle dynamics, respectively, were previously distinguished. Our results demonstrate that close to T_g the timescales of the molecular flow and of the structural recovery are governed by the same collective dynamics which controls the dielectric response of TBP. Stipulating that "a theory of the physics of glass formation should aim to explain [central observations] in a unified manner" [48], prior to the present study the choice was either (i) to consider the nonuniversally shaped dielectric relaxation as the starting point of such theories or else (ii) to start from single-particle relaxation identified, e.g., by PCS. The present results favor choice (i), since they clearly demonstrate that based on cross-correlated equilibrium fluctuations, but not on self-correlations, one can predict the structural relaxation of simple liquids. Thus, dielectric spectroscopy provides unrivaled information regarding the collective reorientational dynamics of glass-forming liquids.

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