Glass spectrum, excess wing phenomenon, and master curves in molecular glass formers: A multi-method approach

View Online   Export Citation   CrossMark

Ernst A. Rössler[a] (ID) and Manuel Becher (ID)

AFFILIATIONS

Nordbayerisches NMR Zentrum, Universität Bayreuth, 95440 Bayreuth, Germany

[a] Author to whom correspondence should be addressed: ernst.roessler@uni-bayreuth.de

ABSTRACT

The relaxation spectra of glass formers solely displaying an α-peak and excess wing contribution collected by various methods are reanalyzed to pin down their different spectral evolution. We show that master curve construction encompassing both α-peak and emerging excess wing works for depolarized light scattering (DLS) and nuclear magnetic resonance (NMR) relaxometry. It reveals the self-part of the slow dynamics' spectrum. Master curves are to be understood as a result of a more extensive scaling covering all temperatures instead of strict frequency–temperature superposition. DLS and NMR display identical relaxation spectra; yet, comparing different systems, we do not find a generic structural relaxation at variance with recent claims. Dielectric spectroscopy (DS) spectra show particularities, which render master curve construction obsolete. The DS α-peak is enhanced or suppressed with respect to that of DLS or NMR, yet, not correlated to the polarity of the liquid. Attempting to single out the excess wing from the overall spectrum discloses a stronger exponential temperature dependence of its amplitude compared to that below T_g and a link between its exponent and that of the fast dynamics' spectrum. Yet, such a decomposition of α-peak and excess wing appears to be unphysical. Among many different glasses, the amplitude of the excess wing power-law spectrum is found to be identical at T_g, interpreted as a relaxation analog to the Lindemann criterion.

INTRODUCTION

The orientational dynamics of glass forming liquids has been extensively investigated by dielectric spectroscopy (DS),[1,2] depolarized light scattering (DLS),[2–4] optical Kerr effect,[5,6] and, recently, also by field cycling (FC) nuclear magnetic resonance (NMR) relaxometry.[7,8] Still, the extent of universality characterizing the structural α-relaxation is debated and comparing the relaxation spectra as probed by the different methods has only started. Recent studies suggest that FC NMR and DLS yield a similar relaxation stretching, which varies only weakly among the glass forming liquids and resembles that found in DS, provided that the liquid is nonpolar.[8–13] For polar liquids, the dielectric spectra were found to be narrower. Later on, it was even stated that various systems display a "generic structural relaxation" when studied by DLS, whereas the corresponding DS spectra varied largely.[12] Attempting to understand the particularities of the dielectric spectra of polar liquids, cross-correlation effects were suggested.[10–12,14] This is supported by

recent molecular dynamics simulations.[15–17] In the case of DLS and NMR, it was argued that such collective effects can be ignored.[8–11]

The observation of a generic structural relaxation refers to temperatures close to the glass transition temperature T_g.[12] It is well established that at high temperatures the stretching parameter varies among the systems.[18] This raises the question how the relaxation stretching changes with temperature and up to what extent it reflects individual molecular properties possibly showing up only at high temperatures.[19] Many studies discuss the shape of the main (or, likewise, α-) relaxation peak neglecting, however, its high-frequency contribution, the "excess wing."[1,20–24] Any attempt, yet, to isolate the α-relaxation is elusive in this regard as the result depends on the fitting range covering more or less of the excess wing contribution.[9] Although our analysis will disclose a common spectral evolution of α-relaxation and excess wing, the excess wing has to be distinguished from the α-peak itself: The corresponding fluctuations do not reflect full reorientations of the molecules as is the case for those in the frequency regime of α-peak.[25]
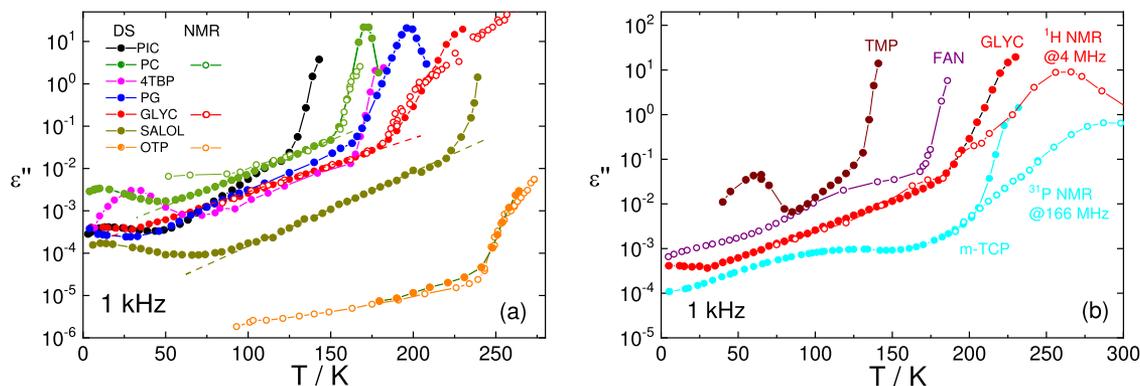
11 February 2025 06:39:18

Often the excess wing is obscured by a β-relaxation.[21,26] Consequently, one may distinguish glass formers that virtually display no discernible β-peak (type-A systems) from those showing a distinct β-relaxation (type-B systems).[21] The excess wing persists as a power-law contribution in the dielectric spectra of the glass ($T < T_g$) and its amplitude increases exponentially with temperature,[22,24] it appears that there is a certain "generic" behavior in the glass state either.[23,24] The excess wing phenomenon gained new interest due to its identification in computer simulations.[27,28] In the present contribution we reiterate the idea that the excess wing phenomenon is a generic feature of glass forming liquids and central to the understanding of the spectral evolution above T_g.

Starting with reconsidering the spectra below T_g, we turn to their evolution above T_g up to temperatures higher than T_m. Although innumerous broadband spectra were measured, and although many approaches were published[20,29–37] no full understanding of the spectral evolution has been established so far. Often, master curves are constructed by applying what is called frequency–temperature superposition (FTS), actually challenging the idea of a changing stretching parameter. Application of FTS usually refers to the α-peak alone, but it appears that the excess wing emerging only close to T_g may be included in a master curve construction by FC NMR in terms of $\chi''(\omega \tau_\alpha)$.[7–9] FTS in its conventional form assumes a susceptibility $\chi''(\omega)$ not changing its spectral shape with temperature. Thus, FTS seems to fail at low temperatures due to the emergence of an excess wing at frequencies between those of the α-relaxation peak and the fast dynamics. How then one has to understand constructed master curves when it is possible to include the excess wing?[7,8]

Attempting to further pin down the discrepancy reported by the different techniques and to understand the spectral features of the excess wing and the role of FTS, we scrutinize DS, DLS, and NMR relaxation spectra as reported by our group and by literature, in particular, by the authors of the work of Lunkenheimer et al.;[1,38] the latter authors report the rare case of dielectric spectra covering α-peak, excess wing, and fast dynamics spectra over the full temperature range. We extend our analyses to the GHz–THz regime encompassing the fast dynamics' spectrum. We will demonstrate that master curves including excess wing constructed from DLS and FC NMR [as well as single-frequency (SF)] data agree, and they have to be understood as resulting from an envelope scaling. We do not find, however, a generic relaxation stretching. In contrast,

whether polar or nonpolar liquids are considered, DS spectra show particularities that render master curve construction obsolete.

RELAXATION SPECTRA OF GLASS FORMING LIQUIDS BELOW AND ABOVE T_g

To highlight differences and common features of relaxation spectra probed by DS, DLS, and NMR, we display in Fig. 1 the relaxation spectra of three type-A glass formers: glycerol, o-terphenyl (OTP), and m-tricresyl phosphate (m-TCP) collected mainly in our group. The DLS data were measured by combining a double monochromator with a tandem Fabry–Pérot interferometer (TFPI/DM)[39] together with photon correlation spectroscopy (PCS),[3] and the FC ^{1}H NMR spectra were obtained by transforming the spin-lattice relaxation rate into the susceptibility representation.[7,8,40,41] As the amplitudes of the spectra probed by the different techniques cannot be directly compared, the different data sets were scaled to achieve a similar height of α-relaxation maxima.

All relaxation spectra display an α-relaxation peak, an excess wing, and a fast dynamics spectrum associated with a susceptibility minimum in the GHz regime. As the excess wing emerges upon cooling, simple FTS does not hold regarding the full slow dynamics' spectrum. Below T_g, the excess wing persists as a well-defined power-law spectrum covering at least 6 decades in frequency with an exponent γ indicated in Fig. 1 (values may differ somewhat from previous ones[23,24]). Its amplitude decreases exponentially upon cooling as demonstrated in Fig. 2(a), where the data of other molecular glasses are included. A flat spectrum is also probed by FC ^{1}H NMR extending up to some 10 MHz,[43] and traces of an excess wing contribution may even be recognized in the TFPI/DM spectra: The relaxation minimum becomes flatter at lowest temperatures. While an excess wing is recognized in the dielectric data of nonpolar OTP measured with a high-precision (HP) bridge (so far unpublished) and also is revealed by FC ^{1}H NMR,[45] the spectra reported in Ref. 47 [included in Fig. 1(b)] do not cover low enough amplitudes to disclose an excess wing. Likewise, our Fourier-transformed PCS data do not reach sufficiently low amplitudes. In the case of m-TCP, all techniques indicate an excess wing; yet, at high frequencies the dielectric spectrum is obscured by the emergence of a β-relaxation. Importantly, the DS spectra are significantly narrower compared to those by DLS and NMR while those of OTP appear similar.

FIG. 1. Relaxation spectra of glycerol (a),[7,37,42,43] o-terphenyl (b),[44,45] and m-tricresyl phosphate [m-TCP; (c)][3,37,46] as measured by DS (black circles; high-precision bridge: gray lines), by FC ^{1}H NMR (blue lines), and by DLS (TFPI/DM: red lines, PCS: red circles); for o-terphenyl, dielectric data of Ref. 47 are added (open black circles); numbers indicate temperatures in K, dashed straight lines interpolate power-law spectra at $T < T_g$ with corresponding exponent γ.

FIG. 2. (a) Imaginary part of the dielectric constant ε'' at 1 kHz as a function of temperature for type-A glass formers measured by applying a high-precision bridge:[23,24] α-picoline (PIC), propylene carbonate (PC), propylene glycol (PG), glycerol (GLYC), 4-tertbutyl pyridine (TBP), salol, and o-terphenyl (OTP; so far unpublished); scaled ^{2}H NMR relaxation rates for OTP[49] and glycerol[50] at 55 MHz and for PC at 40 MHz[51] are included (open symbols); straight dashed lines: exponential fits. (b) Analog data of glass formers with a weak β-relaxation: trimethyl phosphate (TMP),[23,53] fluoroaniline (FAN),[21,53] m-tricresyl phosphate (m-TCP).[54] Data of glycerol added as reference for a type-A system together with ^{1}H NMR relaxation at 4 MHz (open red);[51] for m-TCP the rescaled ^{31}P NMR relaxation rate at 166 MHz is displayed (open turquoise).[46,54]

In Fig. 2(a), the temperature dependence of ε'' at 1 kHz is displayed for several type-A glass formers.[23,24,48] As recognized before,[23,24] an exponential temperature dependence is observed in the glassy state for a large temperature range terminated at high temperature by T_g and at low temperature by additional relaxation features. In the case of OTP,[49] glycerol,[50] and propylene carbonate (PC),[51] we added now the single-frequency (SF) ^{2}H NMR spin-lattice relaxation rates at some 10 MHz, i.e., at frequencies about four decades higher than that of $\varepsilon(1\,\text{kHz})''$. In the case of glycerol, we also added ^{1}H NMR relaxation data [cf. Fig. 2(b)].[52] Below T_g, all NMR data essentially follow the temperature dependence of ε''. The glass spectra can be described by

$$\chi''(\omega) = A_o \omega^{-\gamma} \exp(DT) \quad T < T_g. \tag{1}$$

The exponent lies in a narrow range, $\gamma = 0.1\text{–}0.2$, while the parameter D varies significantly, and A_o denotes the hypothetical amplitude of the glass spectrum at $T = 0$ K.

In Fig. 2(b), we show $\varepsilon''(T)$ data for several type-B glass formers with a more or less weak β-relaxation in addition to an excess wing contribution.[21,23,24,53] In the case of fluoroaniline, both, an excess wing and a weak β-peak, are recognized above T_g, whereas a power-law spectrum background can be anticipated well below T_g.[23] For m-TCP, a β-relaxation is only recognized at low temperatures, whereas above T_g only the excess wing with its exponential temperature dependence is seen [cf. Fig. 1(c)]. We included the SF ^{31}P NMR spin-lattice relaxation rate of m-TCP,[46,54] which shows an exponential temperature dependence close to that of ε''. For trimethyl phosphate, we display $\varepsilon''(T)$ at 0.1 Hz, which exhibits an exponential temperature dependence at high temperatures and a β-relaxation at low temperatures.

In order to determine the temperature dependence of the relaxation spectrum, one has to remove that of the dielectric relaxation strength. As an estimate, we assume a Curie behavior. Thus, in Fig. 3 we plot $T\varepsilon''(T)/(T_{\text{ref}}\Delta\varepsilon_{\text{ref}})$ as a function of the reduced temperature T/T_g, where $T_{\text{ref}}\Delta\varepsilon_{\text{ref}}$ ($T_{ref} > T_g$) is taken from Ref. 24.

In the case of OTP, we take $\Delta\varepsilon_{\text{ref}} = 2.75\cdot10^{-2}$ at 256 K, and for PC $\Delta\varepsilon_{\text{ref}} = 65$ at 212 K. The differences of the dipole density are ignored as similar values are expected for the present organic liquids, likewise any Kirkwood factor is ignored. Two groups of liquids can be distinguished.[48] The first one shows very similar exponential traces close to T_g. It can be interpolated by an exponential temperature dependence with a parameter $C \approx 7.8$ (cf. dashed line, again somewhat different from what was reported earlier due to a different scaling of ε'').[23,24] The second group shows data that lie well above the dashed straight line. Indeed, inspecting the dielectric spectra of such apparently type-A systems like picoline, 4-TBP, salol, and even glycerol (in particular under pressure[55]) in detail, one finds indications of a weak β-relaxation.[48] We take deviations from the exponential temperature behavior as a signature of the presence of a β-relaxation. Interestingly, in the case of 4-TBP and salol, the data appear to turn back to the dashed line at intermediate temperatures, suggesting that in these regimes the influence of the β-relaxation can be ignored as the spectra become very broad. In the
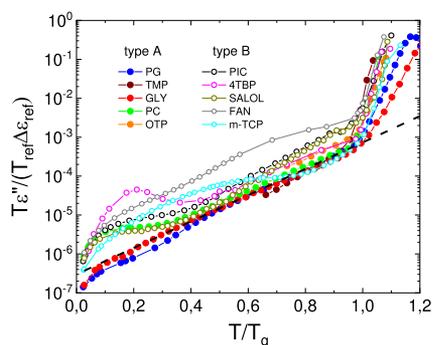

FIG. 3. Rescaled ε'' data at 1 kHz from Fig. 2 as a function of the reduced temperature T/T_g. Solid straight line suggests a generic behavior of type-A glass formers (filled symbols); type-B glasses are marked by open symbols. In the case of TMP, the dielectric spectra are extrapolated to 1 kHz.

case of m-TCP, a β-relaxation obscures the exponential behavior at low temperatures.

Generalizing and concluding, we propose that β-relaxations with a varying temperature dependence of time constants as well as amplitudes superimpose on a power-law spectrum, the latter displaying an exponential temperature dependence. A presumably generic behavior indicated by the dashed line in Fig. 3 suggests that amplitude of the power-law spectrum takes virtually a constant value at T_g. Removing the frequency dependence in Eq. (1), we can write the following expression for the amplitude at 1 Hz and at T_g:

$$A_{1Hz}(T_g) = A_o \exp(C) \approx const \quad T < T_g, \quad (2)$$

which with Eq. (1) leads to

$$C = D T_g \approx const, \quad (3)$$

i.e., the lower the value D, the higher is T_g. The dielectric fluctuations in the glass reach a certain universal level when the α-relaxation sets in on macroscopic time scale (for more, see the section entitled "Discussion").

COMPARING DIELECTRIC AND DEPOLARIZED LIGHT SCATTERING SPECTRA AT $T > T_g$

Turning to the relaxation spectrum at $T > T_g$, the glass power-law spectrum persists as excess wing; yet, it is truncated at low frequencies by the emergence of the α-process leading to a main relaxation peak. The question to address next is how does the original glass spectrum ranging from the sub-Hertz to the GHz range alter upon further heating and how if at all can it be disentangled from α-relaxation. Therefore, we reconsider DS and DLS spectra.

Some while ago, our group analyzed the dielectric spectra by applying a generalized gamma distribution extended (GGE) to include also the excess wing.[35,37] Two temperature regimes were distinguished. One refers to high temperatures, where the spectra exhibit a non-Debyeian α-peak displaying a virtually temperature-independent stretching parameter β (or high-frequency exponent), i.e., FTS holds. The second regime below some temperature T_x is characterized by the emergence of an excess wing (with power-law exponent γ) on the high-frequency flank of the α-relaxation. The parameters of the GGE distribution were found to show characteristic interdependences, indicating that the excess wing is linked to the α-relaxation in a unique way. At $T > T_x$, the exponent γ becomes temperature independent and identical with β. Although "universal relaxation patterns" were reported, their meaning remained unclear.

Independent of any fitting, a derivative analysis suggests that the excess wing can be described also above T_g by a distinct power law.[37] In Fig. 4, the temperature dependence $\gamma(T)$ is shown as revealed by applying a GGE distribution (crosses) analyzing the glycerol spectra reported in the work of Lunkenheimer et al.[1] [cf. Fig. 9(a)].[37] A steep increase is recognized in the temperature regime $T_g < T < T_x$, a behavior also confirmed by other studies,[56] while at $T > T_x$ $\gamma = \beta = const.$ holds. Below T_g, γ becomes virtually constant as shown above. A scenario as depicted in Fig. 4 was revealed for many type-A glass formers.[37] We added the results for picoline[37] and PC.[37]

To corroborate these findings, we present a possibility to estimate $\gamma(T)$ without relying on a specific fitting routine. Figure 5(a)
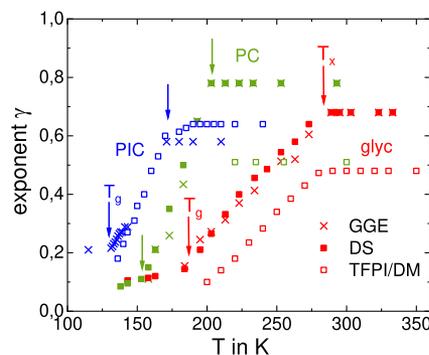
FIG. 4. Excess wing exponent $\gamma(T)$ ($=\beta$ for $T > T_x$) of glycerol ($T_x \approx 275$ K), propylene carbonate (PC; $T_x \approx 205$ K), and picoline (PIC; $T_x \approx 172$ K)[57] provided by different approaches: from dielectric (filled squares) and TFPI/DM (open squares) generalized minimum scaling and from applying a GGE distribution interpolating the dielectric spectra (crosses);[37] T_g and T_x are marked.

displays a minimum scaling[58] of the dielectric spectra of glycerol;[1] height and position of the spectral minimum in the GHz range are scaled to one. At high temperatures ($T > T_x$; black symbols), all spectra are described by a temperature-independent envelope of the minimum with a low-frequency flank following a power law with exponent $\beta = 0.68$ and a high-frequency flank with an exponent a reflecting the fast dynamics' spectrum. Such a scenario is well documented[3,4,59,60] and forecast by the mode coupling theory.[60,61]

At $T < T_x$, the minimum broadens on its low-frequency flank due to the emergence of excess wing. Next, we plot $(\chi''/\chi''_{min})^{\beta/\gamma}$ vs ω/ω_{min} by choosing γ such that the excess wing slope matches that of the high-temperature minimum envelope [cf. main Fig. 5(a)]. Thereby, an estimate of $\beta/\gamma = f(T)$ is obtained. Moreover, a common envelope encompassing the high-frequency flank of the α-peak and excess wing emerges. For the present purpose, we call this "generalized minimum scaling." We do not claim that it is necessarily an exact description, yet, it allows to distinguish DS from DLS relaxation spectra, see the following discussion. The resulting model-free $\gamma(T)$ values are included in Fig. 4 together with those of PC (Sec. S1 of the supplementary material)[1] and picoline.[57] They agree well with the values obtained by GGE fits, corroborating the latter approach of parametrization.

Such a generalized minimum scaling, however, cannot be constructed from the TFPI/DM spectra as is best seen in the case of OTP in Fig. 5(c) but also recognizable for glycerol in Fig. 5(b). The lower traces present the data in terms of minimum scaling, i.e., (χ''/χ''_{min}) vs ω/ω_{min}. At high temperatures, evolution of the minimum (gray lines) follows again a master curve, which can be interpolated by a sum of two power laws (solid line). This, however, does not work below T_x (colored lines): As in the case of dielectric spectra, the minimum becomes progressively flatter upon cooling. Yet, attempting to match the apparent slope of the excess wing at the minimum with that of the high-temperature spectra by displaying $(\chi''/\chi''_{min})^{\beta/\gamma}$, one can map the spectra only in a narrow frequency range onto the high-temperature master curve [upper traces in Fig. 5(b) and 5(c)]. At low frequencies, an overshoot is observed, i.e., there is no extended region that can be described by a distinct power law. Nevertheless, such determined $\gamma(T)$
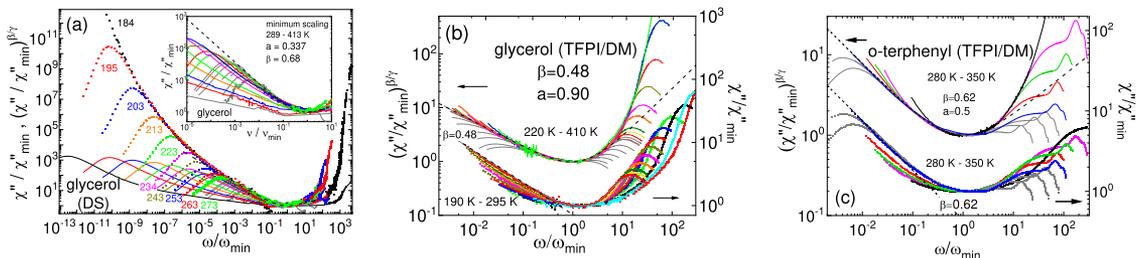
FIG. 5. (a) Minimum scaling of the dielectric spectra of glycerol[1] (gray lines: $T > T_x$, colored lines: $T < T_x$) and rescaled along plotting $(\chi''/\chi''_{min})^{\beta/\gamma}$ to agree with the high-temperature minimum envelope (colored points); inset displays blow-up of minimum region. (b) and (c) Depiction of corresponding scaling of the TFPI/DM spectra of glycerol[42] and o-terphenyl[44] (gray lines: $T > T_x$, colored lines: $T < T_x$); bottom: minimum scaling at $T \leq T_x$; top: plotting $(\chi''/\chi''_{min})^{\beta/\gamma}$; dashed lines in panels (a)–(c) denote interpolation by a sum of two power laws with exponents β and a as indicated.

values, defining only a narrow spectral range close to the minimum, are similar for glycerol and PC, whereas they are somewhat higher for picoline (see Ref. 62); in contrast, the dielectric $\gamma(T)$ values of glycerol and PC are much higher (cf. Fig. 4).

The difference between DS and DLS spectra is most clearly seen when plotting the susceptibility as a function of $\omega\tau_\alpha$, see Fig. 6(a). The dielectric spectra of glycerol do not superimpose on the high-frequency flank and the width of the α-peak itself broadens upon cooling. These features are similarly observed for PC.[37] In all respect, master curve construction fails for the dielectric spectra ($T < T_x$). In contrast, the TFPI/DM spectra suggest a superimposed structure of the relaxation pattern encompassing α-peak and excess wing, which is more and more disclosed the more spectra at lower temperatures are included. Since strict FTS is not fulfilled here, we suggest the naming of generalized FTS as the master curve construction includes the emerging excess wing. The resulting full spectrum, in particular, its high-frequency shape, can be reconstructed by taking points at such frequencies for which the influence of the fast dynamics' spectrum can be assumed to be negligible [red dashed-dotted line in Fig. 6(a)]. It represents the spectrum of the slow dynamics at lowest temperatures close to T_g. The recently published PCS data taken at much lower temperatures (dark yellow crosses, $T \approx T_g$)[11] perfectly

follow this reconstructed TFPI/DM spectrum including the excess wing. Virtually no broadening of the α-peak with temperature is observed in the DLS spectra.

Up to now, only a few further liquids exist for which PCS spectra at low temperatures can be directly compared to those collected by TFPI/DM at high temperatures. In Fig. 6(b), $\chi''(\omega\tau_{DLS})$ spectra of m-TCP are shown as probed by DLS and DS.[3,37] Again, the spectral shape of the high-temperature α-peak (by TFPI/DM) agrees well with that at low temperatures (by PCS[11]), and the glycerol TFPI/DM spectrum perfectly provides an envelope also for m-TCP slow dynamics' spectrum. In contrast, the dielectric spectra taken close to T_g are again significantly narrower.

Figure 7(a) presents $\chi''(\omega\tau_{DLS})$ of OTP obtained from TFPI/DM and a PCS spectrum taken close to T_g.[44] Again, the spectral shape of the α-peak does not change with temperature and an emerging excess wing is observed. The PCS spectrum shows some broadening and signs of artifacts on the low-frequency flank, probably a result of time instability of the PCS setup. Anticipating the discussion of the NMR master curves (next section), we include the single-frequency (SF) ^{2}H relaxation rate $R_1(\tau_{DLS}(T))$ (blue symbols) converted to a susceptibility representation $\omega R_1(\omega\tau_{DLS}(T))$, which
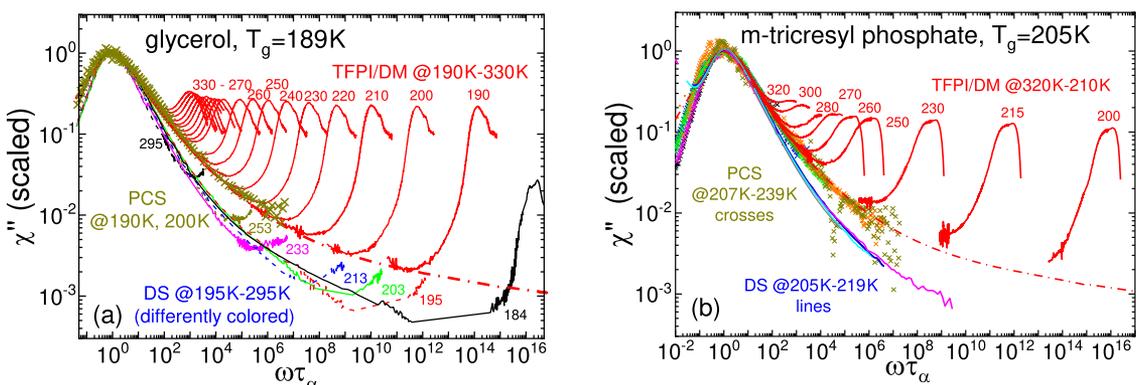

FIG. 6. Rescaled dielectric (differently colored) and TFPI/DM spectra (red dots) plotted in terms of $\chi''(\omega\tau_\alpha)$ vs $\omega\tau_\alpha$: (a) glycerol[1,11,42] and (b) m-tricresyl phosphate;[3,37] numbers indicate temperature in K; added in (a)[11] and (b):[3] corresponding PCS data[3,12] (dark yellow crosses) and reconstructed TFPI/DM slow dynamics' spectrum of glycerol (red dashed-dotted line).

FIG. 7. (a) Dielectric (black, unpublished so far) and TFPI/DM spectra (red)[44] plotted in terms of $\chi''(\omega\tau_{DLS})$ for OTP, added: PCS data at 263 K (dark yellow),[44] ^{2}H NMR susceptibility $\omega R_1(\omega\tau_{DLS}(T))$ (blue crosses, scaled),[49] and DS master curve shifted in amplitude (gray). (b) Dielectric susceptibility (black) of glycerol[1] and PC[1] shifted in amplitude to achieve best overlap at high frequencies with the reconstructed TFPI/DM spectrum of glycerol (red dashed-dotted); added: single-frequency ^{2}H NMR susceptibility $\omega R_1(\omega\tau_{DLS}(T))$[50,51] (blue, scaled) and corresponding PCS data (dark yellow)[11,12] and TFPI/DM spectra of PC (orange)[63] numbers indicate temperatures in K.

follows the TFPI/DM/PCS spectra. In other words, NMR relaxation data probed at a *single* frequency completely reproduces the full spectrum as probed by DLS. This is a proof that independent of whether measured as a function of ω or τ_{DLS}, one gets the same function $\chi''(\omega\tau_{DLS})$, the essential of conventional FTS, however, now including the emerging excess wing. For OTP, being a liquid with a low polarity, a comparison with dielectric HP data [cf. Fig. 1(b)] is of interest. We plotted the rescaled dielectric spectrum $\chi''(\omega\tau_{DLS})$ (black symbols). A master curve results; however, it is quite different from that provided by DLS. The overall width of the α-peak is significantly larger; yet, the excess wing resembles that of the DLS spectra: Appropriately shifted in amplitude (gray symbols), the high-frequency flank of the DS curve provides an interpolation of the DLS and ^{2}H NMR data, albeit a lower amplitude of the main relaxation peak. Clearly, the discrepancies between DS and DLS/NMR spectra do not disappear in nonpolar OTP.

The dielectric data of glycerol[1] and PC,[1] similarly shifted at high frequencies as for OTP to match the reconstructed TFPI/DM spectrum of glycerol, also show wide overlap, see Fig. 7(b). The

reported PCS spectrum of PC taken close to T_g[12] does not indicate significant change of the relaxation peak compared to the TFPI/DM spectrum at high temperatures (orange symbols)[63] and the excess wing coinciding with that of glycerol (see Ref. 62). Thus, the DLS spectra of both liquids (and of m-TCP) virtually agree including the excess wing. In contrast, the DS α-peak of PC (as well as that of glycerol) is strongly enhanced compared to the DLS peak and it changes spectrally with temperature. For OTP, the opposite is observed. Finally, we added in Fig. 7(b) the SF ^{2}H NMR susceptibility of PC[1] (and of glycerol). They well reproduce the reconstructed TFPI/DM spectrum. In the next section, we demonstrate that this agreement can also be expanded to frequency-dependent ^{1}H NMR data.

NMR MASTER CURVES INCLUDING α-RELAXATION AND EXCESS WING

In the case of FC ^{1}H NMR relaxometry, the relaxation rate $R_1(\omega)$ may be monitored over 3–6 decades,[7,8,64–67] and master curve

FIG. 8. FC ^{1}H NMR master curves (a) of glycerol-h_5;[8] added: single-frequency (SF) ^{2}H NMR data,[50] reconstructed TFPI/DM spectrum [see Fig. 6(a); dashed-dotted line, scaled] and DS spectra[37] (black solid line, scaled) and (b) of OTP-d_{14};[45] added: SF ^{2}H NMR data at two frequencies[49] and TFPI/DM spectrum (all scaled). Note: equally colored points refer to the same frequency.

construction along $\chi''(\omega\tau_\alpha)$ can be attempted as follows. The ^{1}H relaxation rate $R_1(T)$ measured at different frequencies is plotted in terms of the susceptibility representation $\chi'' = \omega R_1$ as a function of the time constant $\tau_\alpha(T)$,[13] i.e., $\chi''(\tau_\alpha) = \omega R_1(\tau_\alpha)$ where $\tau_\alpha(T)$ is taken from DLS experiments ($\tau_\alpha \equiv \tau_{DLS}$).[18,42,44] Then, the τ_α-axis is rescaled by the corresponding NMR frequency ω. Hence, adjacent points in the spectrum assume differently colored symbols. Importantly, eliminating the explicit temperature dependence by considering $R_1(T)$ as a function of $\tau_{DLS}(T)$ a direct comparison of the spectral shape of the NMR susceptibility with that of other methods becomes possible. As demonstrated in Figs. 6 and 7, this procedure can also be done for SF ^{2}H relaxation data. It assumes that the time constants of DLS and NMR are at least proportional to each other. The case of m-TCP appears to be more involved (Sec. S2 of the supplementary material).[46]

The results for glycerol and OTP are displayed in Figs. 8(a) and 8(b). Similar master curves $\chi''(\omega\tau_{DLS})$ displaying both α-peak and excess wing are recognized. A large temperature range up to well above T_m is displayed: glycerol 180–360 K and o-terphenyl 263–393 K. Up to twelve decades in frequency are effectively covered, no systematic deviations are discernible. Importantly, the master curves emerge *without shifting* the spectra, i.e., without assuming any kind of FTS to apply. Just rescaling by ω yields a collapse of the data, and no scaling of the amplitudes is applied as the NMR coupling constant exhibits a negligible temperature dependence.[68,69]

In the case of glycerol, the relaxation maximum is observed around 0.6 as is expected for ^{1}H relaxation.[68,69] This signals that the time scales probed by DLS and NMR virtually agree. In the case of OTP and m-TCP, a small difference (a factor <2) is found between τ_{DLS} and τ_{NMR}. The FC NMR findings are corroborated by SF ^{2}H relaxation data (glycerol-d$_5$ and OTP-d$_{14}$) and the corresponding TFPI/DM spectrum [cf. Fig. 5(a)] perfectly reproducing the ^{1}H NMR results. Once again, we conclude that ^{1}H and ^{2}H NMR relaxation probes the same susceptibility spectrum as DLS.

ATTEMPTING TO SEPARATE EXCESS WING FROM THE OVERALL RELAXATION SPECTRUM

The foregoing analyses suggest that below T_x, α-peak and excess wing constitute the slow dynamics' spectrum with their spectral evolution linked in a unique way, which discloses itself as a generalized FTS. This may suggest that the excess wing has to be regarded as an inseparable precursor process of the main α-relaxation. The excess wing, however, was also considered as a kind of secondary relaxation that can more or less consistently be spectrally separated from the α-relaxation (given an incomplete database).[25,70] Hence, with the estimate for $\gamma = f(T)$ from Fig. 4, we test whether the high-frequency flank of the main dielectric relaxation including excess wing and fast dynamics spectrum can be interpolated by a sum of power laws, an approach sometimes taken.[20,23,37]

We tentatively assume that above or below T_x, the normalized dielectric susceptibility $\chi_n \equiv \chi''/\Delta\varepsilon$ at $\omega\tau_\alpha \gg 1$ can be described by two or three terms, respectively,

$$\chi_n(\omega) = C(T)\nu^{-\beta} + A_o\nu^a \qquad T > T_x, \qquad (4a)$$

$$\chi_n(\omega) = C_x(T)\nu^{-\gamma} + A_o f(T)\nu^{a_x} + B(T)F(\nu) \qquad T < T_x. \qquad (4b)$$

In accordance with previous studies,[3,18,57,59,70–73] we assume that the susceptibility minimum above T_x results from an interplay of a fast dynamics spectrum with an amplitude A_o and a power-law exponent a, both being temperature independent, and a high-frequency flank of an α-peak with a constant stretching parameter β. Due to a shifting α-relaxation, its amplitude changes along $C(T) \propto (2\pi\tau_\alpha(T))^{-\beta}$. Below T_x, we take recourse to a superposition of three terms. The first term of Eq. (4b) corresponds to the excess wing power law with exponent γ and amplitude $C_x(T)$, the second to that of the fast dynamics' spectrum with a possibly temperature-dependent exponent a_x and amplitude $f(T)$ [with $f(T \geq T_x) \equiv 1$], and the third $F(\nu)$ to an α-relaxation of yet unknown spectral shape and amplitude $B(T)$. Instead of displaying $\chi_n(\omega) - C_x(T)\nu^{-\gamma}$ ($T < T_x$), we carry out the spectral separation by plotting

$$\left(\frac{1}{C(T)}\chi_n\nu^\beta - 1\right)C(T) = A_o\nu^{a+\beta} \qquad T > T_x, \qquad (5a)$$

$$\left(\frac{1}{C_x(T)}\chi_n\nu^\gamma - 1\right)C_x(T) = A_o f(T)\nu^{a_x+\gamma} + B(T)F(\nu)\nu^\gamma \qquad T < T_x. \qquad (5b)$$

This will allow to discover some relations between the excess wing contribution and the fast dynamics' spectrum. The result for glycerol is displayed in Fig. 9(a). The top curves show the original spectra.[1] In addition, the excess wing power laws are displayed taking $\gamma(T)$ from Fig. 4 and fixing thereby $C_x(T)$ at $T < T_x$. These power laws appear to intersect at a common frequency in the THz range, which could be interpreted as the high-frequency end of the excess wing spectrum. The curves in the middle display the result after removing the excess wing along Eq. (5).

The following is observed: (i) At $T > T_x$, the fast dynamics' spectra coincide in amplitude and exponent $\varepsilon = a + \beta = 0.84$, i.e., indeed $A_o = const.$, and with $\beta = 0.68$ one finds $a = 0.16$ (significantly smaller than in previous analyses.[58]). (ii) Below T_x, the amplitude of the fast dynamics' spectra strongly decreases, yet, its exponent [in the representation given by Eq. (5)] remains virtually the same as above T_x, i.e., $\varepsilon = a_x(T) + \gamma(T) = 0.84$. As $\gamma(T)$ decreases upon cooling, a_x increases. (iii) The high-frequency flank of the α-relaxation left after subtracting the excess wing can be described by a power law ($\omega\tau_\alpha \gg 1$) with an apparent exponent $b(T) - \gamma(T) = const = 0.46$, again not changing with temperature. Thus, the high-frequency wing of the α-peak and the excess wing can indeed in some approximation be interpolated by two power laws, with temperature-dependent exponents $b(T)$ and $\gamma(T)$, respectively. However, since $\gamma(T)$ of glycerol goes up to $\gamma_x = \beta = 0.68$, the exponent of the α-peak becomes larger than 1, which is not acceptable for an independent relaxation process.

Regarding the bottom traces of Fig. 9(a), a factor $f(T)$ (reflecting the amplitude of the fast dynamics' spectrum) is applied that collapses the fast dynamics spectrum with that at $T > T_x$. The temperature dependence of $f(T)$ is plotted in Fig. 9(b) together with that of amplitude $C_x(T)$ of the excess wing. Above T_x, $f(T) \equiv 1.0$ while $C(T)$ weakly grows along $C(T) \propto (2\pi\tau_\alpha)^{-\beta}$. Below T_x, both quantities, $f(T)$ and $C_x(T)$, follow the same exponential temperature dependence [as demonstrated by plotting $C_x(T)/f(T)$ in Fig. 9(b)]. Amplitude of the excess wing increases with temperature exponentially as is the case below T_g, yet, the extent is much larger, and
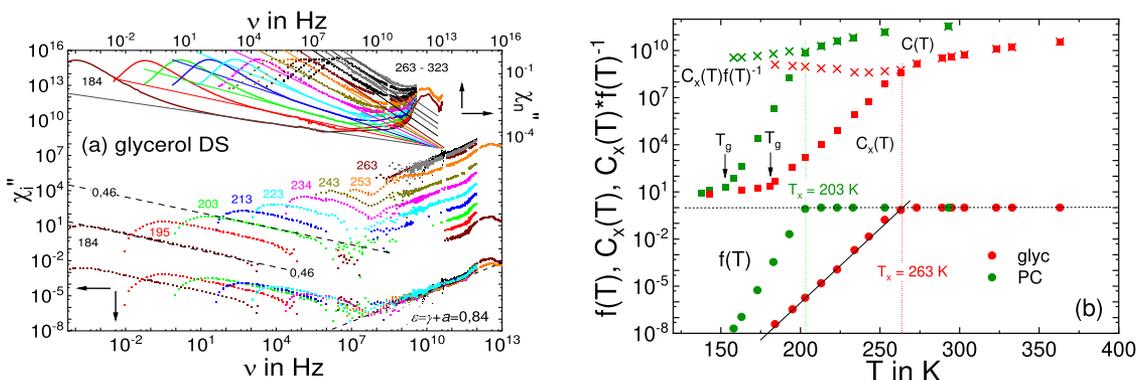
FIG. 9. (a) Top: original spectra of glycerol;[1] middle: removing the excess wing contribution along Eq. (5); bottom: rescaling the data to provide a master curve of the fast dynamics' spectrum (note different frequency scales). (b) Amplitude of the fast dynamics' spectrum $f(T)$, of the excess wing $C_x(T)$, and the product $C_x(T)f(T)^{-1}$ for glycerol and propylene carbonate [note $C_x = C(T)$ at $T > T_x$]; transition temperatures T_g and T_x are marked. In the case of glycerol, the value of T_x differs somewhat from that in Fig. 4.

this is accompanied by virtually the same exponential increase of the fast dynamics' spectrum. Both appear to be part of a common relaxation pattern. Similar results are found for PC (Sec. S3 of the supplementary material) and included in Fig. 9(b). Moreover, the chosen analysis along Eq. (5) directly suggests that there is a connection between the exponent of the excess wing γ and that of the fast dynamics' spectrum a_x.

Finally, within the present approach the amplitude $B(T)$ of the (residual) α-peak decreases toward zero when approaching T_x from low temperatures; above T_x, the amplitude is zero as the excess wing contribution appears to become the main relaxation. The situation displays some similarity to the merging of β- and α-relaxation.[21,25,74] Yet, our tentative analysis demonstrates that the overall spectrum of the slow dynamics cannot be consistently separated in two independent relaxation processes.

DISCUSSION

Below T_g, the dielectric spectrum of type-A glasses exhibits a power-law characteristic extending from the sub-Hertz to the THz range with an exponential temperature dependence of its amplitude, features described before,[24] and now also identified by NMR relaxation. Removing the effect of different dipole moments, a universal trace is revealed as a function of T/T_g. Macroscopic flow and α-relaxation appear to set in when a certain value of the amplitude of the glass spectrum is reached.

Applying the Lindemann criterion is one of the concepts of interpreting the glass transition phenomenon.[75–77] Explicitly, for different glasses, the ratio of the root mean square atomic displacement to the mean interatomic distance turns out to be virtually of constant value at T_g (as is the case in crystalline systems at T_m). When the ratio reaches a certain value, instability of the disordered lattice sets in and structural relaxation becomes possible. The present study also suggests that the amplitude of the dielectric power-law *relaxation*, reflecting a certain level of highly restricted molecular motion,[25] reaches a distinct value at T_g provided it is not obscured by some β-relaxation: a relaxation analog to the Lindemann criterion.

Above T_g, the dielectric glass spectrum manifests itself as excess wing of the main (α-) relaxation peak and its exponent γ increases with temperature such that a high-frequency cutoff in the THz range may be anticipated. This may mark its spectral "end" since it is not expected that it extends into the optical frequency range. As the exponent γ changes with temperature and as the α-peak itself broadens, any attempt to construct master curves from dielectric data fails. A separation of the excess wing from the overall spectrum, an approach often taken[20,22,37,70] but rarely covering the full temperature/frequency range, yields an exponential increase of its amplitude with temperature – as below T_g - yet, the increase is much stronger. It goes along with virtually the same exponential increase of the amplitude of the fast dynamics' spectrum. Moreover, a connection between the corresponding exponents γ and a_x is revealed, suggesting that both relaxations have to be regarded as of common origin. Within this decomposition approach, the amplitude of the excess wing grows upon heating, leaving less and less polarization relaxed by the α-relaxation. Finally, at $T > T_x$, the excess wing spectrum seems to become the main relaxation. There is a similarity with the merging of α- and β-relaxation in type-B glass formers:[21,25,74] The amplitude of β-relaxation increases strongly above T_g at the expense of that of α-relaxation. However, although reflecting qualitatively different orientational fluctuations, the attempted decomposition indicates that a clear-cut spectral separation of excess wing and α-relaxation peak into independent processes is not possible, as already revealed by the GGE analysis.[37]

In stark contrast, the DLS relaxation spectra display different characteristics. Although an excess wing contribution is recognized, there is no extended frequency range that can be attributed to a distinct power law. Instead, the slow dynamics spectrum evolves in such a way that the spectrum at the lowest temperature provides the most extended spectrum including both α-peak and excess wing. Upon heating this low-temperature spectrum is more and more truncated by a disappearing excess wing, yet, the shape of the main relaxation peak remains unaltered, i.e., while at high temperatures there is no excess wing it emerges close to T_g. The possibility to

construct such DLS/NMR master curves including the excess wing is a more extensive spectral feature than conventional FTS and we suggest to call it generalized FTS. The excess wing can be regarded as a generic precursor process of a single-peak α-relaxation and has to be associated with highly restricted reorientational fluctuations as suggested by NMR investigations.[25] Such fluctuations persist below T_g as a power-law spectrum displaying a characteristic exponential temperature dependence leading to a universal amplitude at T_g.

Several publications discuss the difference between DLS and dielectric spectra.[8–12] They suggest that DS spectra of polar liquids are narrower compared to those measured by DLS. Cross correlation may yield an additional contribution on top of a broader single-particle α-peak while the excess wing remains virtually unchanged.[10–12] Furthermore, a "generic structural relaxation" probed by PCS is claimed to hold at temperatures close to T_g[12] while dielectric spectra vary strongly.[9] Yet, it is well established that at high temperatures the TFPI/DM stretching parameter β varies among the liquids.[18] Hence, a generic DLS relaxation at T_g would imply failure of strict FTS (regarding solely the α-peak) when reaching high temperatures. However, as demonstrated by our DLS and NMR data covering relaxation data up to high temperatures, we do not find indications of such a change of the width of main relaxation, a feature also recognized when DLS data of methyl tetrahydrofuran or dimethyl phthalate are considered in the time domain.[78] Thus, our survey challenges the idea of a generic structural DLS relaxation at T_g[12] as well as the idea of a failure of conventional FTS (regarding the main relaxation peak) when reaching high temperatures. In other words, the DLS stretching parameter reflecting the width of the α-relaxation peak appears not to change. Interestingly, in a recent simulation work,[17] the stretching of the Legendre polynomial correlation function of second rank (probed DLS) was found virtually not to change with temperature whereas that of the first rank (probed by DS) displayed significant change. Recently, a TFPI/DM study showed that the relaxation spectra of molecules with pronounced internal dynamics may show multimodal spectra at high temperatures,[19] however, such peculiarities were not observed for the present systems.[18]

Without assuming FTS, FC ^{1}H NMR master curves $\chi''(\omega\tau_{DLS})$ including excess wing and α-peak emerge and they agree with the spectrum revealed by DLS. Even plotting single-frequency ^{2}H NMR relaxation data as a function of τ_α, the susceptibility spectrum is correctly reproduced, i.e., it does not matter whether χ'' is measured

FIG. 10. Original TFPI/DM spectra of picoline (red),[57] and reconstructed slow dynamics' TFPI/DM spectra of glycerol (blue) and of *o*-terphenyl (green).

as a function of ω or τ_α. As typical NMR frequencies are below some 100 MHz, the fast dynamics is not probed. Deuteron NMR definitely probes single-particle reorientation[69] and the identity of the relaxation spectrum with that of ^{1}H and DLS demonstrates that both techniques provide relaxation not spoiled by collective effects, it reflects the self-part of the orientational spectrum.

In Fig. 10, we summarize our results for the slow dynamics' spectra as probed by DLS and NMR relaxometry. The original TFPI/DM spectra of picoline[57] are compared to the reconstructed TFPI/DM spectrum of glycerol and OTP. In the region of excess wing, the three excess wing contributions almost perfectly overlap; yet, in the case of the spectrum of the α-peak itself, no generic shape is observed as also reported by previous TFPI/DM results.[18] For example, the α-peak of OTP is significantly narrower than that of glycerol. Remarkably, the DLS/NMR slow dynamics' spectrum of glycerol is identical with that of PC and *m*-TCP (cf. Fig. 6). Thus, for all five liquids investigated, the manifestation of the excess wing is identical suggesting that it is a generic feature of the slow dynamics' spectrum.

Concerning the dielectric spectra, the α-peak amplitude is enhanced in glycerol and PC in comparison to that of the DLS/NMR spectra, in picoline it is similar or suppressed in the case of OTP. Moreover, the dielectric enhancement changes with temperature [cf. Fig. 7(b)]. Thus, the difference between DS and DLS relaxation spectra appears not to disappear for a nonpolar liquid like OTP. We note that there are other systems where DS and DLS spectra were found to be similar in the case of nonpolar liquids.[10,11]

CONCLUSIONS

The relaxation spectra collected by dielectric spectroscopy (DS), depolarized light scattering (DLS), and FC ^{1}H NMR of glass formers displaying solely an α-peak and excess wing contribution (type-A glass formers) are reanalyzed in order to understand the difference among the temperature evolution of their relaxation spectra.

Below T_g, a generic dielectric relaxation pattern is reinspected: A power-law spectrum with an exponential temperature dependence of its amplitude is observed and confirmed by NMR relaxation. Its amplitude is found to be virtually the same at T_g for all the inspected liquids. This is interpreted as a relaxation analog to the Lindemann criterion. Above T_g, its exponent increases linearly with temperature such that a common high-frequency cutoff may be anticipated possibly marking the spectral end of the excess wing relaxation. As its exponent changes with temperature and as the α-peak itself broadens, any attempt to construct master curves fails in the case of dielectric spectra.

Extracting the dielectric excess wing contribution from the overall slow dynamics' spectrum, we find its amplitude growing exponentially with temperature, much stronger than below T_g, while that of a residual α-process decreases. A similar scenario as in the case of the merging of α- and β-relaxation is suggested. The increase in excess wing amplitude with temperature is accompanied by a similar increase in the fast dynamics' spectrum. Their temperature-dependent exponents appear to be linked. Such a spectral decomposition, yet, does not allow for a clear-cut separation of excess wing and α-relaxation into independent relaxation processes, although reflecting qualitatively different orientational fluctuations.
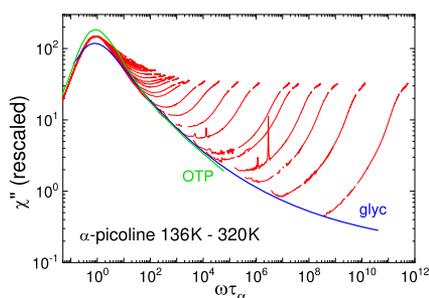
In stark contrast, the evolution of DLS spectra has to be understood as providing a master curve in terms of a slow dynamics' spectrum that includes α-peak and the emerging excess wing and that is only fully disclosed at T_g. The width of the α-peak appears not to change with temperature as demonstrated by the possibility of constructing master curves up to high temperatures. The possibility to construct such DLS/NMR master curves including the excess wing is a more extensive spectral feature than conventional FTS, which assumes a non-changing spectral shape. It may be called generalized FTS. In contrast to recent observations, we do not observe a generic DLS relaxation peak whereas the excess wing appears to be virtually the same for all five investigated liquids, possibly indicating a generic feature. The FC ^{1}H NMR master curves follow those measured by DLS. Even ^{2}H NMR relaxation measured at a *single* frequency can provide the correct susceptibility and identifies DLS and NMR as probing single-particle dynamics, i.e., does not matter whether the susceptibility is measured as function of ω or τ_α.

A direct comparison of DS and DLS/NMR spectra suggests that the difference between the first and the two other techniques regarding the manifestation of the α-peak does not disappear for a nonpolar liquid like OTP. Whereas the dielectric α-peak amplitude is enhanced in some systems in comparison to that of the DLS spectra, it is similar or even suppressed in others.

SUPPLEMENTARY MATERIAL

The supplementary material contains the generalized minimum scaling for PC, the NMR master curve of *m*-TCP, and a separation of the excess wing from the overall dielectric spectrum of PC; in addition, an attempt to separate the excess wing from the overall TFPI/DM relaxation spectrum is given.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Ernst A. Rössler: Conceptualization (lead); Data curation (equal); Funding acquisition (lead); Investigation (lead); Methodology (lead); Project administration (lead); Resources (equal); Supervision (lead); Writing – original draft (lead). **Manuel Becher**: Conceptualization (supporting); Data curation (equal); Investigation (equal); Methodology (equal); Software (equal); Writing – review & editing (equal).

DATA AVAILABILITY

Original DS, NMR, and DLS spectra are available from the corresponding author upon reasonable request.

REFERENCES

[1] P. Lunkenheimer, U. Schneider, R. Brand, and A. Loid, "Glassy dynamics," Contemp. Phys. **41**, 15–36 (2000).

[2] T. Blochowicz, A. Brodin, and E. A. Rössler, "Evolution of the dynamic susceptibility in supercooled liquids and glasses," Adv. Chem. Phys. **133**, 127–256 (2006).

[3] N. Petzold, B. Schmidtke, R. Kahlau, D. Bock, R. Meier, B. Micko, D. Kruk, and E. A. Rössler, "Evolution of the dynamic susceptibility in molecular glass formers: Results from light scattering, dielectric spectroscopy, and NMR," J. Chem. Phys. **138**, 12A510 (2013).

[4] H. Z. Cummins, G. Li, Y. H. Hwang, G. Q. Shen, W. M. Du, J. Hernandez, and N. J. Tao, "Dynamics of supercooled liquids and glasses: Comparison of experiments with theoretical predictions," Z. Phys. B **103**, 501–519 (1997).

[5] R. Torre, P. Bartolini, and R. M. Pick, "Time-resolved optical Kerr effect in a fragile glass-forming liquid, salol," Phys. Rev. E **57**, 1912–1920 (1998).

[6] G. Hinze, D. D. Brace, S. D. Gottke, and M. D. Fayer, "A detailed test of mode-coupling theory on all time scales: Time domain studies of structural relaxation in a supercooled liquid," J. Chem. Phys. **113**, 3723–3733 (2000).

[7] M. Flämig, M. Hofmann, N. Fatkullin, and E. A. Rössler, "NMR relaxometry: The canonical case glycerol," J. Phys. Chem. B **124**, 1557–1570 (2020).

[8] M. Becher, A. Lichtinger, R. Minikejew, M. Vogel, and E. A. Rössler, "NMR relaxometry accessing the relaxation spectrum in molecular glass formers," Int. J. Mol. Sci. **23**, 5118 (2022).

[9] T. Körber, R. Stäglich, C. Gainaru, R. Böhmer, and E. A. Rössler, "Systematic differences in the relaxation stretching of polar molecular liquids probed by dielectric vs magnetic resonance and photon correlation spectroscopy," J. Chem. Phys. **153**, 124510 (2020).

[10] F. Pabst, A. Helbling, J. P. Gabriel, P. Weigl, and T. Blochowicz, "Dipole-dipole correlations and the Debye process in the dielectric response of nonassociating glass forming liquids," Phys. Rev. E **102**, 010606 (2020).

[11] J. P. Gabriel, P. Zourchang, F. Pabst, A. Helbling, P. Weigl, T. Böhmer, and T. Blochowicz, "Intermolecular cross-correlations in the dielectric response of glycerol," Phys. Chem. Chem. Phys. **22**, 11644–11651 (2020).

[12] F. Pabst, J. P. Gabriel, T. Böhmer, P. Weigl, A. Helbling, T. Richter, P. Zourchang, T. Walther, and T. Blochowicz, "Generic structural relaxation in supercooled liquids," J. Phys. Chem. Lett. **12**, 3685–3690 (2021).

[13] M. Becher, Th. Körber, A. Döß, G. Hinze, C. Gainaru, R. Böhmer, M. Vogel, and E. A. Rössler, "Nuclear spin relaxation in viscous liquids: Relaxation stretching of single-particle probes," J. Phys. Chem. B **125**, 13519–13532 (2021).

[14] M. Paluch, K. Koperwas, and Z. Wojnarowska, "Determination of self and cross contributions to the dipole–dipole correlations function from analysis of dielectric measurements," J. Mol. Liq. **382**, 121907 (2023).

[15] K. Koperwas and M. Paluch, "Computational evidence for the crucial role of dipole cross-correlations in polar glass-forming liquids," Phys. Rev. Lett. **129**, 025501 (2022).

[16] T. Böhmer, R. Horstmann, J. P. Gabriel, F. Pabst, M. Vogel, and T. Blochowicz, "Origin of apparent slow solvent dynamics in concentrated solutions," Macromolecules **54**, 10340–10349 (2021).

[17] M. Henot, P.-M. Dejardin, and F. Ladieu, "Orientational dynamics in supercooled glycerol computed from MD simulations: Self and cross contributions," Phys. Chem. Chem. Phys. **25**, 29233–29240 (2023).

[18] B. Schmidtke, N. Petzold, B. Pötzschner, H. Weingärtner, and E. A. Rössler, "Relaxation stretching, fast dynamics, and activation energy: A comparison of

molecular and ionic liquids as revealed by depolarized light scattering," J. Phys. Chem. B **118**, 7108–7118 (2014).

[19] R. Zeißler, F. Pabst, T. Böhmer, and T. Blochowicz, "Influence of intramolecular dynamics on the relaxation spectra of simple liquids," Phys. Chem. Chem. Phys. **25**, 16380 (2023).

[20] P. K. Dixon, L. Wu, S. R. Nagel, B. D. Williams, and J. P. Carini, "Scaling in the relaxation of supercooled liquids," Phys. Rev. Lett. **65**, 1108–1111 (1990).

[21] A. Kudlik, S. Benkhof, T. Blochowicz, C. Tschirwitz, and E. Rössler, "The dielectric response of simple organic glass formers," J. Mol. Struct. **479**, 201–218 (1999).

[22] U. Schneider, R. Brand, P. Lunkenheimer, and A. Loidl, "Excess wing in the dielectric loss of glass formers: A Johari-Goldstein β relaxation?," Phys. Rev. Lett. **84**, 5560–5563 (2000).

[23] C. Gainaru, R. Kahlau, E. A. Rössler, and R. Böhmer, "Evolution of excess wing and β-process in simple glass formers," J. Chem. Phys. **131**, 184510 (2009).

[24] C. Gainaru, A. Rivera, S. Putselyk, G. Eska, and E. A. Rössler, "Low-temperature dielectric relaxation of molecular glasses: Crossover from the nearly constant loss to the tunneling regime," Phys. Rev. B **72**, 174203 (2005).

[25] M. Vogel, P. Medick, and E. R. Rössler, "Secondary relaxation processes in molecular glasses studied by nuclear magnetic resonance spectroscopy," Annu. Rep. NMR Spectrosc. **56**, 231–299 (2005).

[26] K. L. Ngai and M. Paluch, "Classification of secondary relaxation in glass-formers based on dynamic properties," J. Chem. Phys. **120**, 857–873 (2004).

[27] C. Scalliet, B. Guiselin, and L. Berthier, "Excess wings and asymmetric relaxation spectra in a facilitated trap model," J. Chem. Phys. **155**, 064505 (2021).

[28] B. Guiselin, C. Scalliet, and L. Berthier, "Microscopic origin of excess wings in relaxation spectra of supercooled liquids," Nat. Phys. **18**, 468–472 (2022).

[29] R. V. Chamberlin, "Non-Arrhenius response of glass-forming liquids," Phys. Rev. B **48**, 15638–15645 (1993).

[30] A. Kudlik, S. Benkhof, R. Lenk, and E. Rössler, "Spectral shape of the α-process in supercooled liquids revisited," Europhys. Lett. **32**, 511–516 (1995).

[31] N. Menon and S. R. Nagel, "Evidence for a divergent susceptibility at the glass transition," Phys. Rev. Lett. **74**, 1230–1233 (1995).

[32] A. Kudlik, T. Blochowicz, S. Benkhof, and E. Rössler, "Reply to Comment on 'Spectral shape of the α-process in supercooled liquids revisited,'" Europhys. Lett. **36**, 475–476 (1996).

[33] R. L. Leheny, N. Menon, and S. R. Nagel, "Comment on 'Spectral shape of the alpha-process in supercooled liquids revisited,'" Europhys. Lett. **36**, 473–474 (1996).

[34] P. Viot, G. Tarjus, and D. Kivelson, "A heterogeneous picture of a relaxation for fragile supercooled liquids," J. Chem. Phys. **112**, 10368–10378 (2000).

[35] Th. Blochowicz, Ch. Tschirwitz, St. Benkhof, and E. A. Rössler, "Susceptibility functions for slow relaxation processes in supercooled liquids and the search for universal relaxation patterns," J. Chem. Phys. **118**, 7544–7555 (2003).

[36] H. Z. Cummins, "Dynamics of supercooled liquids: Excess wings, β peaks, and rotation–translation coupling," J. Phys.: Condens.Matter **17**, 1457–1470 (2005).

[37] T. Blochowicz, C. Gainaru, P. Medick, C. Tschirwitz, and E. A. Rössler, "The dynamic susceptibility in glass forming molecular liquids: The search for universal relaxation patterns II," J. Chem. Phys. **124**, 134503 (2006).

[38] U. Schneider, P. Lunkenheimer, R. Brand, and A. Loidl, "Broadband dielectric spectroscopy on glass-forming propylene carbonate," Phys. Rev. E **59**, 6924–6936 (1999).

[39] N. V. Surovtsev, J. A. H. Wiedersich, V. N. Novikov, E. Rössler, and A. P. Sokolov, "Light-scattering spectra of fast relaxation in glasses," Phys. Rev. B **58**, 14888–14891 (1998).

[40] S. Kariyo, C. Gainaru, H. Schick, A. Brodin, V. N. Novikov, and E. A. Rössler, "From a simple liquid to a polymer melt: NMR relaxometry study of polybutadiene," Phys. Rev. Lett. **97**, 207803 (2006); Erratum **100**, 109901 (2008).

[41] S. Kariyo, A. Brodin, C. Gainaru, A. Herrmann, H. Schick, V. N. Novikov, and E. A. Rössler, "From simple liquid to polymer melt. Glassy and polymer dynamics studied by fast field cycling NMR relaxometry: Low and high molecular weight limit," Macromolecules **41**, 5313–5321 (2008).

[42] A. Brodin and E. Rössler, "Depolarized light scattering study of glycerol," Eur. Phys. J. B **44**, 3–14 (2005).

[43] C. Gainaru, O. Lips, A. Troshagina, R. Kahlau, A. Brodin, F. Fujara, and E. A. Rössler, "On the nature of the high-frequency relaxation in a molecular glass former: A joint study of glycerol by field cycling NMR, dielectric spectroscopy, and light scattering," J. Chem. Phys. **128**, 174505 (2008).

[44] N. Petzold and E. A. Rössler, "Light scattering study on the glass former o-terphenyl," J. Chem. Phys. **133**, 124512 (2010).

[45] R. Meier, R. Kahlau, D. Kruk, and E. A. Rössler, "Comparative studies of the dynamics in viscous liquids by means of dielectric spectroscopy and field cycling NMR," J. Phys. Chem. A **114**, 7847–7855 (2010).

[46] M. Becher, M. Flämig, and E. A. Rössler, "Field-cycling ^{31}P and ^{1}H NMR relaxometry studying the reorientational dynamics of glass forming organophosphates," J. Chem. Phys. **156**, 074502 (2022).

[47] H. Wagner and R. Richert, "Equilibrium and non-equilibrium type β-relaxations: d-sorbitol versus o-terphenyl," J. Phys. Chem. B **103**, 4071–4077 (1999).

[48] C. Gainaru, "Dielectric properties of molecular glass formers; from the liquid state to the tunneling regime," Ph.D. thesis, University of Bayreuth, Germany, 2008.

[49] T. Dries, F. Fujara, M. Kiebel, E. Rössler, and H. Sillescu, "^{2}H-NMR study of the glass transition in supercooled ortho-terphenyl," J. Chem. Phys. **88**, 2139–2147 (1988).

[50] W. Schnauss, F. Fujara, and H. Sillescu, "The molecular dynamics around the glass transition and in the glassy state of molecular organic systems: A ^{2}H-nuclear magnetic resonance (NMR) study," J. Chem. Phys. **97**, 1378–1389 (1992).

[51] F. Qi, K. U. Schug, S. Dupont, A. Döß, R. Böhmer, H. Sillescu, H. Kolshorn, and H. Zimmermann, "Structural relaxation of the fragile glass-former propylene carbonate studied by nuclear magnetic resonance," J. Chem. Phys. **112**, 9455–9462 (2000).

[52] Y. Akagi and N. Nakamura, "Tunnelling molecular motion in glassy glycerol at very low temperatures as studied by ^{1}H SQUID nuclear magnetic resonance," J. Phys.: Condens. Matter **12**, 5155–5168 (2000).

[53] C. Gainaru, R. Böhmer, R. Kahlau, and E. A. Rössler, "Energy landscape in molecular glasses probed by high-resolution dielectric experiments," Phys. Rev. B **82**, 104205 (2010).

[54] S. Adishchev, D. Bock, C. Gainaru, R. Kahlau, B. Micko, N. Petzold, B. Pötzschner, and E. A. Rössler, "Reorientational dynamics of organophosphate glass formers—A joint study by ^{31}P NMR, dielectric spectroscopy and light scattering," Z. Phys. Chem. **226**, 1149–1168 (2012).

[55] K. L. Ngai and M. Paluch, "Inference of the evolution from caged dynamics to cooperative relaxation in glass-formers from dielectric relaxation data," J. Phys. Chem. B **107**, 6865–6872 (2003).

[56] R. L. Leheny and S. R. Nagel, "High-frequency asymptotic shape of the primary relaxation in supercooled liquids," Europhys. Lett. **39**, 447–452 (1997).

[57] S. Adichtchev, St. Benkhof, Th. Blochowicz, V. N. Novikov, E. Rössler, Ch. Tschirwitz, and J. Wiedersich, "Anomaly of the nonergodicity parameter and crossover to white noise in the fast relaxation spectrum of a simple glass former," Phys. Rev. Lett. **88**, 055703 (2002).

[58] S. Adichtchev, T. Blochowicz, C. Tschirwitz, V. N. Novikov, and E. A. Rössler, "Reexamination of the evolution of the dynamic susceptibility of the glass former glycerol," Phys. Rev. E **68**, 011504 (2003).

[59] A. Brodin, C. Gainaru, V. Porokhonskyy, and E. A. Rössler, "Evolution of dynamic susceptibility in molecular glass formers—A critical assessment," J. Phys.: Condens. Matter **19**, 205104 (2007).

[60] W. Götze, "Recent tests of the mode-coupling theory for glassy dynamics," J. Phys.: Condens. Matter **11**, A1–A45 (1999).

[61] W. Götze and L. Sjögren, "Relaxation processes in supercooled liquids," Rep. Prog. Phys. **55**, 241–376 (1992).

[62] In Ref. 16 the authors reported the following Cole–Davidson stretching parameters by interpolating the full TFPI/DM spectra including the fast dynamics' spectrum: glycerol 0.45, m-TCP 0.41, picoline 0.65, and OTP 0.65 in fair agreement with the present results. In the case of PC a value 0.67 was reported, a rather high value in comparison to 0.51 in Fig. 4. Here, the latter value was estimated from the apparent steepest slope of the α-peak. In Fig. 7(b) one recognizes high agreement between the high-frequency flank of the PCS, NMR and TFPI/DM spectra indicating essentially the same stretching parameters.

11 February 2025 06:39:18

[63] A. Brodin and E. A. Rössler, "Universal and non-universal features of the dynamic susceptibility of supercooled liquids," J. Phys.: Condens. Matter **18**, 8481–8492 (2006).

[64] R. Kimmich and E. Anoardo, "Solid state field-cycling NMR relaxometry: Instrumental improvements and new applications," Prog. Nucl. Magn. Reson. Spectrosc. **44**, 257–320 (2004).

[65] D. Kruk, A. Herrmann, and E. A. Rössler, "Field-cycling NMR relaxometry of viscous liquids and polymers," Prog. Nucl. Magn. Reson. Spectrosc. **63**, 33–64 (2011).

[66] F. Fujara, D. Kruk, and A. F. Privalov, "Solid state field-cycling NMR relaxometry: Instrumental improvements and new applications," Prog. Nucl. Magn. Reson. Spectrosc. **82**, 39 (2014).

[67] M. Flämig, M. Hofmann, A. Lichtinger, and E. A. Rössler, "Application of proton field-cycling NMR relaxometry for studying translational diffusion in simple liquids and polymer melts," Magn. Reson. Chem. **57**, 805–817 (2019).

[68] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961).

[69] R. Böhmer, G. Diezemann, G. Hinze, and E. Rössler, "Dynamics of supercooled liquids and glassy solids," Prog. Nucl. Magn. Reson. Spectrosc. **39**, 191–267 (2001).

[70] P. Lunkenheimer and A. Loidl, "Dielectric spectroscopy of glass-forming materials: α-Relaxation and excess wing," Chem. Phys. **284**, 205–219 (2002).

[71] W. Steffen, A. Patkowski, H. Glaser, G. Meier, and E. W. Fischer, "Depolarized-light-scattering study of orthoterphenyl and comparison with the mode-coupling model," Phys. Rev. E **49**, 2992–3002 (1994).

[72] A. Aouadi, C. Dreyfus, M. Massot, R. M. Pick, T. Berger, W. Steffen, A. Patkowski, and Ch. Alba-Simionesco, "Light scattering study of the liquid–glass transition of meta-toluidine," J. Chem. Phys. **112**, 9860–9873 (2000).

[73] T. Hecksher, D. H. Torchinsky, Ch. Klieber, J. A. Johnson, J. C. Dyre, and K. A. Nelson, "Toward broadband mechanical spectroscopy," Proc. Natl. Acad. Sci. U. S. A. **114**, 8710–8715 (2017).

[74] T. Körber, F. Krohn, C. Neuber, H.-W. Schmidt, and E. A. Rössler, "Main and secondary relaxations of non-polymeric high-T_g glass formers as revealed by dielectric spectroscopy," Phys. Chem. Chem. Phys. **22**, 9086–9097 (2020).

[75] A. Heuer and H. W. Spiess, "Universality of the glass transition temperature," J. Non-Cryst. Solids **176**, 294–298 (1994).

[76] F. H. Stillinger, "A topographic view of supercooled liquids and glass formation," Science **267**, 1935–1939 (1995).

[77] D. S. Sanditov, "A criterion for the glass–liquid transition," J. Non-Cryst. Solids **385**, 000148–152 (2014).

[78] B. Schmidtke, N. Petzold, R. Kahlau, and E. A. Rössler, "Reorientational dynamics in molecular liquids as revealed by dynamic light scattering: From boiling point to glass transition temperature," J. Chem. Phys. **139**, 084504 (2013).

11 February 2025 06:39:18