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Evolution of dynamic susceptibility in molecular glass formers—a critical assessment

A Brodin, C Gainaru, V Porokhonsky and E A Rössler

Experimentalphysik II, Universität Bayreuth, D-95444 Bayreuth, Germany

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Abstract

Dielectric, depolarized light scattering (LS) and optical Kerr effect (OKE) data are critically discussed in an attempt to achieve a common interpretation of the evolution of dynamic susceptibility in molecular glass formers at temperatures down to the glass transition T_g . The so-called intermediate power-law, observed in OKE data below a certain temperature T_x , is identified with the excess wing, long since known from dielectric spectroscopy, with a temperature-independent exponent. This is in contrast with several recent analyses that concluded a considerable temperature dependence of spectral shapes. We introduce a new approach to disentangle α -peak and excess wing contributions in the dielectric spectra, which allows for frequency–temperature superposition (FTS) of the α -process at all temperatures above T_g . From the LS spectra we conclude, in particular, that FTS holds even at temperatures well above the melting point, i.e. in normal equilibrium liquids. Attempting to correlate the fragility and stretching, our conclusions are opposite to those made previously. Specifically, we observe that a high fragility is associated with a less stretched relaxation function.

1. Introduction

Super-cooling a liquid below the melting point results in a strong continuous increase in the viscosity. The viscosity changes by many orders of magnitude within a relatively small temperature interval. Eventually, the viscous flow becomes so slow that the system can be regarded as a solid body. Conventionally, the glass transition temperature T_g is defined as the temperature where the viscosity reaches 10^{12} Pa s. Upon cooling a liquid through T_g , the relaxation time quickly exceeds the timescale of a typical experiment, leading to quite an abrupt change in many physical properties, such as a step-like behaviour of the heat capacity. Well below T_g , structural relaxation does not occur any longer, and the system is trapped in a non-ergodic state. Molecular liquids are of particular interest, since there the glass transition can be studied using a large variety of experimental techniques. Moreover, they are models of van der Waals liquids that are often examined in molecular dynamics simulations and theoretical approaches.

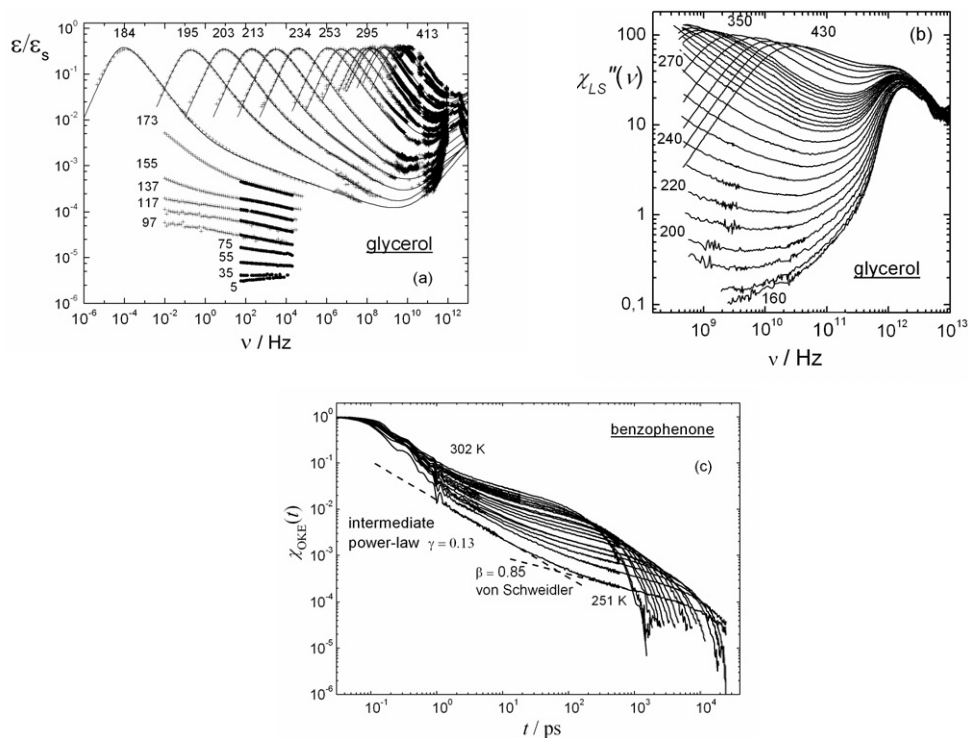


Figure 1. (a) The dielectric spectra of glycerol at indicated temperatures, obtained by Lunkenheimer *et al* [6], Kudlik *et al* [12] and Gainaru *et al* [9], normalized by the static permittivity [11]. Fitted curves (solid lines) above T_g were obtained by applying a special distribution of relaxation times for the slow dynamics (α -peak and excess wing) and a power-law for the fast dynamics [11]. (b) Depolarized light scattering spectra of glycerol as compiled by Brodin and Rössler [7]. (c) Optical Kerr effect data of benzophenone measured by Cang *et al* [8], representing a pulse-response function.

One of the properties of glasses not found in crystals is the occurrence of molecular motion on virtually all timescales. In the super-cooled liquid state, the primary α -relaxation of the structure towards thermal equilibrium slows down from picosecond times at $T \gg T_g$ to about 100 s near T_g . The relaxation is markedly non-exponential, which is known as *relaxation stretching* that concerns the long-time ultimate decay of structural fluctuations. At short times, relaxation sets in as oscillation de-phasing with typical frequencies in the THz range at all temperatures. Hence, upon cooling a liquid, a large gap, extending near T_g over more than 14 decades in time and frequency, opens up between the timescales of the α -relaxation and microscopic dynamics, in which there emerge so-called secondary relaxation processes. Despite important experimental progress in the last two decades [1–6], a generally accepted phenomenological view of the evolution of dynamic susceptibility is still missing. Moreover, the spectra obtained by different techniques appear to show different relaxation features. It is the aim of the present paper to discuss the relaxation features of the most complete data sets compiled up to date by dielectric spectroscopy (DS), depolarized light scattering (LS) and optical Kerr effect experiments (OKE), in an attempt to achieve a common understanding.

Figure 1 shows some representative data, obtained by DS, LS and OKE techniques [6–8]. The dielectric data for glycerol, shown in figure 1(a), reveal in a sense a complete picture of

the evolution of glassy dynamics in this system, in that they cover an enormous range of 18 decades in frequency. (We note in passing that, by using high-precision impedance bridges, the dielectric loss can be measured down to cryogenic temperatures (see figure 1(a)) reaching even the tunnelling regime [9].)

Qualitatively, one can distinguish four regimes of spectral evolution, corresponding to different states of a glass forming liquid:

- (i) a low-density fluid at very high temperature, where relaxation and microscopic dynamics have essentially merged,
- (ii) a liquid of moderate viscosity (10^{-3} – 10^{-1} Pa s) with its characteristic two-step relaxation and a stretched long-time part,
- (iii) a highly viscous liquid close to T_g where additional, slow secondary relaxations have emerged, such as the extra power-law contribution seen in figure 1(a), and
- (iv) the glassy state below T_g .

In the glass, structural relaxation is arrested, so that the susceptibility spectra reflect vibrational and secondary relaxation dynamics. The double-peaked spectrum, corresponding to a two-step relaxation function with a stretched α -relaxation part (the stretching reflected in an asymmetric broadening of the primary relaxation peak in figures 1(a) and (b)), is often taken as characteristic of glassy dynamics. It will be shown that such a dynamic pattern generally sets in significantly above the melting point.

In the following, we will focus our attention on universal and non-universal properties of the dynamic susceptibility of molecular liquids, and will attempt to answer several long-standing questions. To what extent does the frequency temperature superposition (FTS) hold? From the very beginning of glass science, FTS was regarded as an essential feature of ‘glassy dynamics’. However, in recent years there have appeared indications that it might fail close to T_g [6]. The concept of fragility has long been used to classify different types of relaxation behaviour in different glass forming systems, such as in molecular versus network forming glasses. There have been numerous approaches to try and find a connection between relaxation features and fragility, addressing specifically the following questions: (i) does the shape of the α -peak correlate with the degree of fragility and (ii) is there a commonly accepted way to separate the α -peak and secondary spectral features, so that the extent of relaxation stretching can be unambiguously determined? In this paper we will discuss a new approach to these problems. Another important question concerns the existence of a critical temperature. More than 20 years since the advent of the mode coupling theory (MCT) that suggested a dynamic crossover at a critical temperature well above T_g [4, 10], there is still no consensus as to whether such a crossover exists. Can we unambiguously identify a crossover temperature? It turns out that definitive answers to these questions do not exist, as quite dissimilar approaches apparently describe the experimental susceptibility equally well. This calls, of course, for further theoretical support, which, regarding the role of slow secondary relaxations, is unfortunately not in sight.

We mainly focus on the so-called type A glass formers [12], whose dielectric spectra do not exhibit a discernible secondary (β) relaxation peak but rather show the so-called excess wing, which can be formally considered as a kind of secondary relaxation of as yet unknown microscopic origin. We critically re-assess the data from different techniques, compiled by several research groups; as a result, the paper partly takes the form of a review. Refraining from looking into details of various phenomenological models, we rather demonstrate the scaling properties of the experimental susceptibility of molecular liquids that are being supercooled towards T_g .

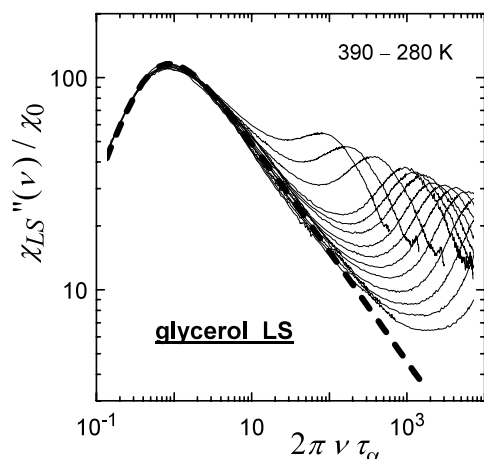


Figure 2. Normalized depolarized light scattering spectra of glycerol, plotted versus reduced frequency. The α -peaks overlap on a master curve. (Data taken from [7].)

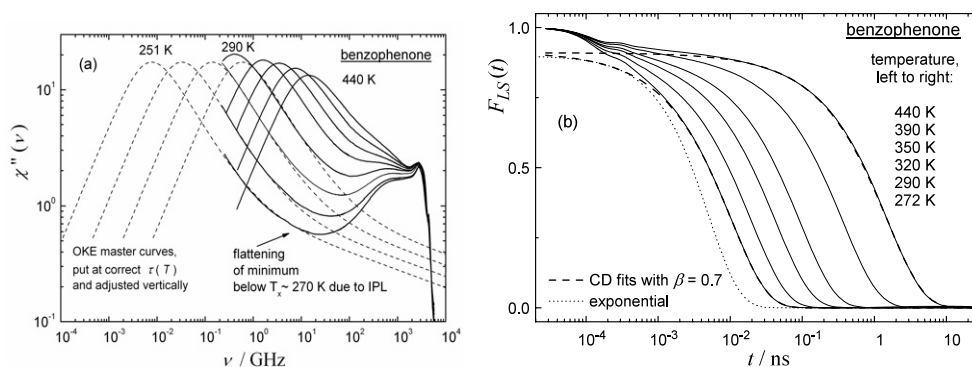


Figure 3. (a) Depolarized light scattering spectra of benzophenone (solid lines) together with those expected from the optical Kerr effect data in figure 1(c) (dashed lines). At low temperatures the susceptibility minimum flattens, signalling the emergence of an intermediate power-law (IPL), namely the excess wing (cf [22]). (b) Step response functions of benzophenone, obtained by Fourier-transforming the LS spectra in (a). The data fit well to the Cole–Davidson (CD) function (dashed lines) with a temperature-independent stretching parameter $\beta = 0.7$.

2. The high-temperature regime

Inspecting figures 1(a) and (b), at high temperature the α -peak of glycerol shifts with changing temperature, essentially keeping its shape. This is seen in both DS and LS data. Consequently, the α -peaks plotted versus the reduced frequency $\omega\tau_\alpha$ in figure 2 superpose well, suggesting that their width, related to the stretching of the relaxation function, is independent of temperature within experimental accuracy. Such behaviour, which is one of the characteristic features of high-temperature glassy dynamics, is occasionally discussed in the literature as ‘ α -peak scaling’. It implies nothing other than the validity of FTS.

FTS may be even better visualized in the time domain, by plotting Fourier-transformed LS data [13]. Figure 3(b) shows, as an example, the so-obtained two-step relaxation functions of benzophenone with temperature-independent stretching. Neutron scattering [14] and molecular dynamics simulation studies [15, 16] also report a two-step decay with a nearly temperature-

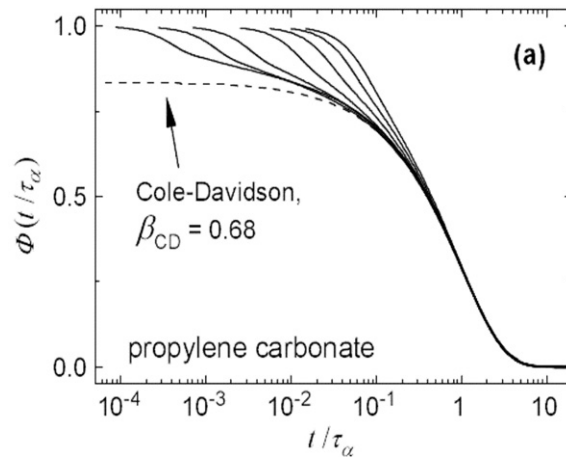


Figure 4. Step-response functions of propylene carbonate versus re-scaled time t/τ_α , obtained by Fourier-transforming the corresponding depolarized light scattering spectra at temperatures well above the melting point $T_m = 218$ K (temperatures in K: 220, 235, 255, 300, 350, 400, 445; boiling point $T_b = 523$ K). The long-time parts form a master curve, displaying the validity of frequency-temperature superposition (adapted from [13]).

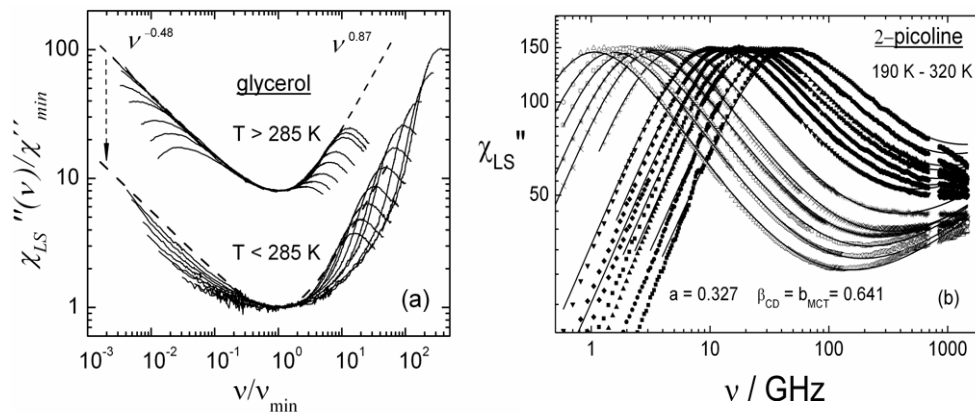


Figure 5. (a) Re-scaling the glycerol data of figure 1(b) such that their minima (ν_{\min} , χ_{\min}'') coincide [7]. Above 285 K, the spectra overlap on a master curve that is interpolated by a sum of two power-laws with exponents that are not compatible with the predictions of mode coupling theory (MCT). (b) Depolarized light scattering spectra of 2-picoline, interpolated by a sum of the Cole-Davidson (CD) function and a power-law; the shape parameters are compatible with MCT (adapted from [18]).

independent long-time shape. Consequently, plotting against the re-scaled time t/τ_α results in a master curve at $t \geq \tau_\alpha$ (see figure 4 for propylene carbonate). We emphasize that all these data (cf also figure 3) are obtained at temperatures above the melting point, in some cases even approaching the boiling point. Even the non-glass forming benzene exhibits glassy dynamics with stretched two-step relaxation up to the boiling point [17]. Thus, this relaxation behaviour appears to be typical of the stable liquid state. No crossover to a less stretched or exponential relaxation is observed in most cases. In this context, the notion ‘glassy dynamics’ appears somewhat misleading.

Another property of the high-temperature spectra is revealed when the spectra of different temperatures are rescaled such that their minima (χ''_{\min} , ν_{\min}) overlap, i.e. plotting χ''/χ''_{\min} versus ν/ν_{\min} . As an example, LS spectra of glycerol are shown in figure 5(a). At high temperatures ($T > 285$ K), the minima superpose well, suggesting that the shape of the minimum is also temperature independent and can be described by a master curve. This behaviour shall be called ‘minimum scaling’. The minimum scaling was discussed in the MCT [4, 10], where asymptotic solutions of the theory interpolate the minimum as a sum of two power-laws with characteristic temperature-independent exponents (the so-called asymptotic scaling laws). However, while experimental susceptibility minima often exhibit the scaling property, the exponents of the power-law interpolation may or may not agree with those predicted by MCT. In the case of glycerol, the asymptotic laws fail, whereas for 2-picoline they do apply (cf figure 5(b)). In the latter case, a superposition of the Cole–Davidson function and a power-law, both with temperature-independent exponents, provides an almost perfect fit [18]. Together, the α - and minimum scaling imply that the shapes of *both* the α -peak and the fast relaxation spectrum above the minimum are temperature independent, the only change of the spectrum being due to a shift of the peak.

3. The low-temperature regime

The low-temperature dynamics of molecular glass forming liquids is characterized by the appearance of secondary relaxation processes, such as the excess wing and secondary relaxation peaks. In the present discussion, we mostly consider (type A) glass formers that do not exhibit a discernible β -peak but only the excess wing, such as glycerol in figure 1(a) [12]. As a consequence of the emerging excess wing, the central scaling properties, found at high temperatures (α - and minimum scaling), appear not to hold any longer in this low temperature regime. The failure of the minimum scaling is demonstrated in figure 5(a) for the LS data of glycerol [7]. Below say 285 K, the shape of the minimum becomes temperature-dependent; an apparent flattening at low temperatures is associated with the appearance of the excess wing. Inspecting the corresponding DS spectra in figure 1(a), they obviously exhibit a similar behaviour. Thus, the excess wing phenomenon is observed in DS and LS data; it is also detected by NMR [19] and OKE spectroscopy (see below). Interpolating the minimum by a sum of two power-laws, the apparent exponent of the low-frequency side of the susceptibility minimum, related to the emerging excess wing, starts to decrease below a certain temperature [7]. In the time domain and close to T_g , the relaxation cannot be described by a simple stretched exponential any longer, as the excess wing has to be accounted for [20]. Qualitatively, the emergence of these new spectral features defines the low-temperature regime; on solely phenomenological grounds, a crossover temperature T_x , associated with the onset of the described changes in the susceptibility spectra, is easily identified. It turns out that in many cases the onset corresponds to a relaxation time $\tau_\alpha \approx 10^{-9}$ s [20–22].

Several approaches were attempted to quantitatively describe the temperature evolution of the dielectric α -peak and excess wing. Most prominently, Nagel and co-workers [23] suggested a scaling procedure that allows the spectra to be overlapped at different temperatures, including the α -peak and excess wing, on a single master curve. In many cases, the scaling works remarkably well, although its formal validity has been debated [24–26]. Alternatively, a decomposition into two separate relaxation processes was proposed [27]. The latter interpretation gained certain support due to the ageing experiments of Schneider *et al* [28], which reported subtle changes of the wing and interpreted them as being due to an emerging secondary relaxation peak. The latter authors concluded that the excess wing is just a secondary relaxation process similar to the ‘normal’ β -processes of Johari–Goldstein type [28, 30].

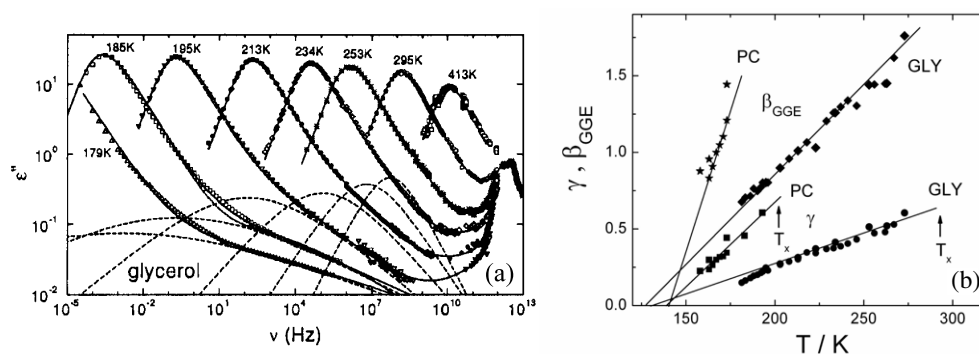


Figure 6. (a) Dielectric spectra of glycerol with interpolations of the α -peak and excess wing by a two-peak function (figure taken from [29]). Dashed lines are individual contributions of the excess wing, whose widths are strongly temperature-dependent. (b) Width parameter of the α -peak (β_{GGE}) and of the excess wing (γ) of glycerol (GLY) and propylene carbonate (PC) obtained from fitting the spectra to a special distribution of relaxation times (data from [21], fits are shown figure 1(a)); note that β_{GGE} is a width parameter of the distribution of relaxation times, and thus does not directly reflect the stretching parameter β . Clearly, both parameters strongly increase with temperature.

In the following years, several groups, including our own, analysed low-temperature susceptibility spectra of type A glass formers in terms of a two-peak function, defined either in the frequency domain (cf figure 6(a)) [29] or in the relaxation time domain (cf interpolations in figure 1(a)) [20]. These analyses concluded that both the width parameter β of the α -peak and the exponent γ of the excess wing become strongly temperature dependent below a certain T_x close to T_g . An example is presented in figure 6(b), where it is shown that both parameters change roughly by a factor of 3 [21]. Thus, the spectral shape appears to be strongly temperature-dependent, and thereby FTS is violated. It turned out that the spectral shape parameters of different systems showed similar dependences when plotted as functions of the relaxation time τ_α [20, 21]. For instance, glycerol and propylene carbonate, being quite different systems in regard to their intermolecular interactions and fragility, exhibit rather similar susceptibility spectra, when compared at the same relaxation time. This observation was recently extended in the sense that, varying both the pressure and temperature, the spectral shape appears to mainly depend on τ_α , no matter at which P and T it is reached [31].

In view of the absence of a theory to describe the full susceptibility spectrum and its temperature evolution, an empirical fitting to a suitable two-component function with a subsequent analysis of the temperature dependence of the fit parameters appears to be a valid phenomenological approach. It has, however, to be realized that the empirical fit parameters as such have no physical significance, so that assigning them a physical meaning requires due caution. For instance, the strong variation of the shape parameters by a factor of about 3 with temperature, seen in figure 6(a), may be misleading in the sense that it suggests a strong temperature dependence of the spectral shape, which is not observed in the actual spectra. Indeed, rescaling the spectra so that their peaks overlap (see figure 7) shows that the spectral shape is nearly temperature independent. Moreover, the high-frequency flanks of the spectra in figure 7, constituting the excess wing, appear to be parallel, implying a temperature-independent wing exponent. Thus, the strong temperature dependence of the shape parameters of the fits, observed in figure 6(b), may be an artefact of the fitting procedure used and thereby lack physical significance. It thus appears entirely possible that the apparent failure of FTS, concluded from the empirical fitting analyses discussed above, is a mere artefact of the two-peak interpolation model and/or limited fitting range.

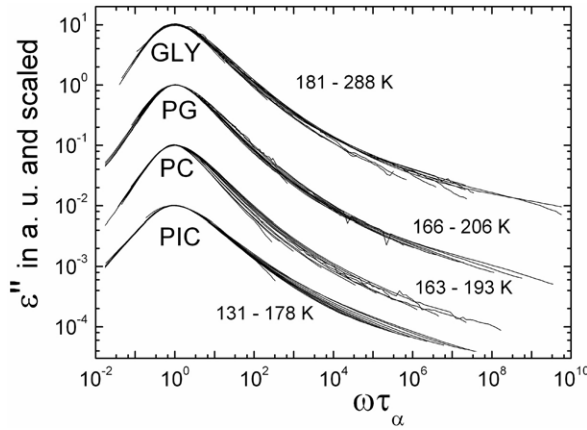


Figure 7. Dielectric spectra, re-scaled so that their peaks overlap, of glycerol (GLY), propylene glycol (PG), propylene carbonate (PC) and 2-picoline (PIC) (cf [12, 20, 21]).

Next, we discuss the optical Kerr effect (OKE) results, in particular those recently reported by Fayer and co-workers [8] (cf also [32]). The OKE signal, obtained with sufficiently short laser pulses, is a pulse-response function $F_{\text{OKE}}(t)$ that is related to the usual step-response (relaxation) function $F_{\text{LS}}(t)$ through $F_{\text{OKE}}(t) = -dF_{\text{LS}}(t)/dt$. As an example, OKE data of benzophenone [8] are shown in figure 1(c). The authors of [8] observed that, quite universally, the ultimate α -decay is preceded by a temperature-independent ‘intermediate power law’ (IPL) $t^{\gamma-1}$ with a positive γ being usually close to zero. If γ is identically zero, such power law corresponds to a logarithmic decay of the corresponding relaxation function and to a flat susceptibility spectrum (constant loss). Explicitly, the OKE data were interpolated by the following function:

$$F_{\text{OKE}}(t) = [E(t/\tau_\alpha)^{\gamma-1} + D(t/\tau_\alpha)^{\beta-1}] \exp(-t/\tau_\alpha). \quad (1)$$

The two terms describe IPL and the main α -relaxation with relative amplitudes E and D , respectively [8]; the power law $t^{\beta-1}$ corresponds to the von Schweidler law of the onset of α -relaxation. (Technically, the model of equation (1) is an additive two-peak model, as in the frequency domain it corresponds to two Cole–Davidson peaks with the same relaxation time.) The Fayer group interpreted the IPL phenomenon, which apparently contradicts the standard MCT results, as a manifestation of higher-order singularities that appear as special solutions to MCT equations. Later, Götze and Sperl interpreted the same results as non-generic features within a schematic MCT model [33], thus rebuffing the recourse to unrealistic higher-order singularity scenarios.

The OKE decay curves of figure 1(c) exhibit an interesting property that is not immediately recognized [22]. If the curves are re-scaled so that their α -relaxation parts overlap, they form a master curve that covers both the von Schweidler and IPL parts (see figure 8(a)). This means that the *whole* spectrum, including the main α -relaxation *and* IPL, is subject to FTS. Transforming now the DS data of glycerol of figure 7 into the pulse-response representation in the time domain (see figure 8(b)) and comparing them with the OKE data in figure 8(a), one immediately recognizes an unmistakable similarity. The DS data of figure 8(b) also fall onto a master curve, just as the OKE data in figure 8(a) do, moreover with the intermediate power law exponent $\gamma = 0.16$, rather similar to $\gamma = 0.185$ of figure 8(a). In the dielectric data of glycerol in figure 8(b), it is clear that the first power-law is nothing other than the excess wing in the frequency domain (cf figure 1(a)). Hence, we are led to conclude that IPL and the excess wing

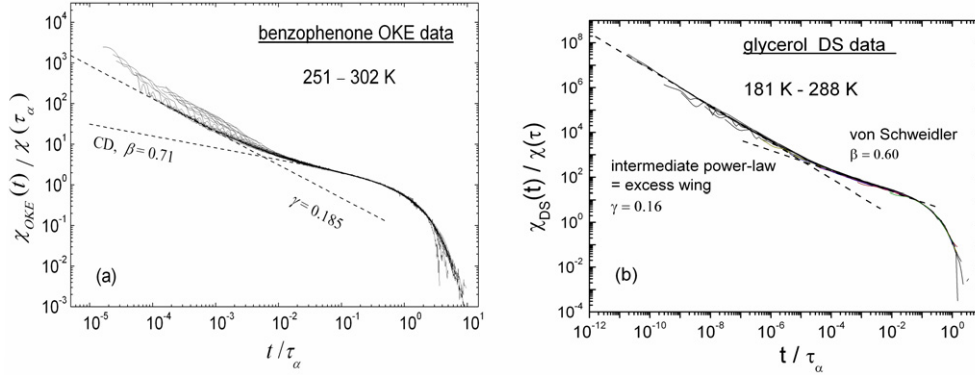


Figure 8. (a) Optical Kerr effect data of benzophenone [8] (cf also figure 1(c)), re-scaled so that their α -relaxation parts overlap. The curves then fall onto a master curve that covers both the von Schweidler and intermediate power-laws with exponents as indicated. (b) Dielectric data of glycerol [20] in pulse-response representation (adapted from [22]). A master curve with a similar IPL exponent as in (a) is found.

are essentially identical phenomena, albeit manifested in different domains. Thus, the OKE experiments do not reveal a new feature, but rather re-discover the long since known excess wing in the time domain. The presence of an excess wing in the LS data is, however, less clear because of the low-frequency limit of the technique of only ~ 200 MHz. As we discussed above, the wing in the available LS spectral window manifests itself as a flattening of the susceptibility minimum (cf figures 1(b) and 5(a)). To show how this comes about, and also to demonstrate the equivalence of the frequency- and time-domain data, we added to the LS data of benzophenone in figure 3(a) Fourier transforms of the OKE master curve of benzophenone from figure 8(a) (dashed lines), whose characteristic time was adjusted to match the relaxation times of the LS data in figure 3(a), which are known from the OKE results. It is seen in figure 3(a) that the dashed lines, reflecting the OKE data, match perfectly the corresponding LS spectra, and that as soon as the excess wing ‘enters’ the explored frequency range at the two lowest temperatures, the susceptibility minimum starts to flatten. We thus reiterate the conclusion that both techniques reveal essentially the same features [22].

Even though the IPL of the time-domain data is identical with the excess wing in the frequency domain and, in general, time- and frequency-domain representations are in essence just different representations of the same data, each representation may still possess specific benefits. It seems that the excess wing (namely IPL) and, in particular, its exponent, are more easily identified in the time domain pulse-response representation. In figure 9 we show frequency-domain representations of dielectric data for five different systems close to T_g ; the curves are re-scaled vertically to match at short times. It appears that even though the curves are different at $t \sim \tau_\alpha$, their IPLs (\equiv excess wings) at short times are essentially the same, with the exponent $\gamma \sim 0.2$ (see the straight line). Thus, it appears that the wing (IPL) exponent is not only temperature independent, but also has nearly the same numerical value for different systems.

4. Alternative scenario for the evolution of dynamic susceptibility

We have seen that qualitative and model-independent analyses of dielectric and OKE data suggest the approximate validity of FTS at all temperatures down to T_g . We thus propose a

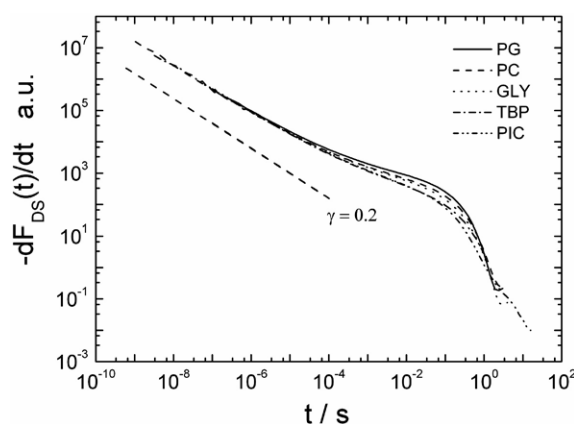


Figure 9. Pulse-response representation of the dielectric data at temperatures close to T_g , re-scaled to match at short times, of five glass formers: propylene glycol (PG), propylene carbonate (PC), glycerol (GLY), 4-tert-butyl pyridine (TBP), 2-picoline (PIC). Time constants of the datasets are similar. The dashed line represents an intermediate power-law (excess wing) with exponent $\gamma = 0.2$ (data from [12, 20, 21]).

model for describing the evolution of susceptibility, which incorporates FTS *from the outset*, in which respect it is at variance with all other phenomenological approaches known to us [34]. We thus assume that FTS holds for all temperatures above T_g . The stretching parameter β of the α -relaxation peak is thus assumed to be temperature independent, and its value determined from the spectra at sufficiently high temperatures, where they are not obscured by secondary relaxations. We assume that the excess wing exponent γ is temperature independent, too, and that its value can generally be fixed at $\gamma \approx 0.2$ (see figure 9). In order to account for minor changes of the spectral shape with temperature, as recognized in figure 7, we allow the relative magnitude of the wing to be temperature dependent. Mathematically, we fit the spectra to a convolution of a power-law and the Cole–Davidson function, with the exponents fixed as explained above. The model thus has only three free parameters, the time constant τ_α , the relative relaxation strength $1 - S_{\text{ex}}$ of the excess wing, and the overall magnitude of the dielectric spectra. It might seem that the imposed constraints will make it impossible to achieve good fits. It turns out that the fits are close to perfect, without any detectable systematic deviation from the data (see figure 10). The relaxation strength $1 - S_{\text{ex}}$ decreases with increasing temperature, which is opposite to what is observed for β -processes. Assuming a linear temperature dependence, $1 - S_{\text{ex}}$ extrapolates to zero close to the crossover temperature T_x that separates the high- and low-temperature regimes, as discussed in the previous sections.

The present approach also allows for an explanation of the ageing experiments of Schneider *et al* [28] that is different from theirs, specifically assuming the existence, in addition to the excess wing, of a very weak β -peak that is only discernible at $T \leq T_g$ [34]. An additional appearance of a small β -process contribution may also explain that in some cases a curvature is observed in the spectra measured at $T \leq T_g$ in the frequency range of the excess wing, and this may also lead to an apparent smaller value exponent γ . The approach can be further extended to analyse the pressure-dependent data, based on the observation of Ngai *et al* [31] that the overall spectral shape depends on the pressure and temperature only implicitly, through the dependence of $\tau_\alpha = \tau_\alpha(P, T)$. Within our approach, it would mean that the effect of pressure is to only change the relaxation strength $1 - S_{\text{ex}}$. Unfortunately, an actual analysis of the pressure data to test our approach is hampered by the fact that the pressure data lack the necessary quality,

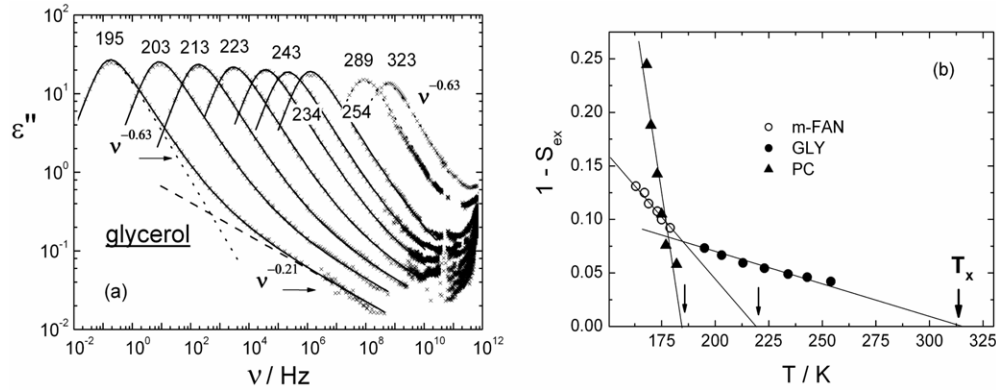


Figure 10. (a) Dielectric permittivity spectra of glycerol [6] with fits (solid lines, see text for details). (b) Relaxation strength of the excess wing versus temperature for *m*-fluoroanilin (m-FAN), glycerol (GLY) and propylene carbonate (PC); linear extrapolation yields crossover temperature T_x (arrows).

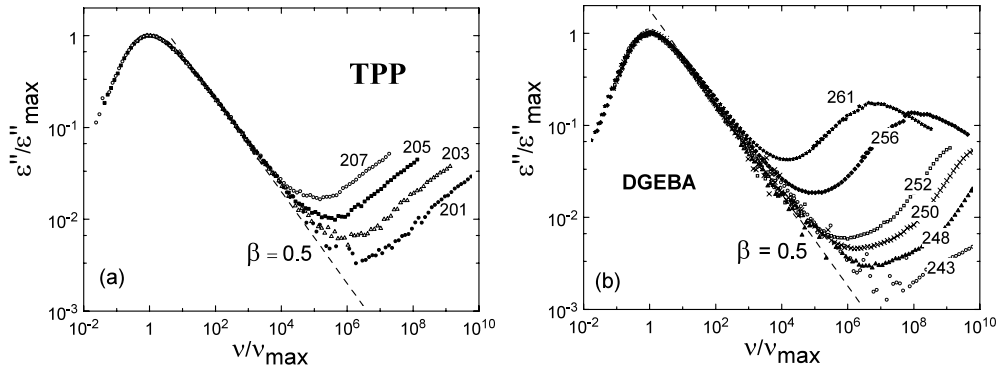


Figure 11. Dielectric spectra of (a) triphenyl phosphate (TPP) and (b) diglycidyl ether of bisphenol A (DGEBA) [36], both exhibiting a strong β -peak, rescaled so that the α -peak maxima overlap. The α -peaks are rather broad ($\beta \approx 0.5$) and superpose well, demonstrating FTS.

covering in particular too limited a frequency range. In fact, even at normal ambient pressure, the dielectric data that cover a sufficiently broad range of frequencies and temperatures to test the applicability of our approach, only exist to date for two systems, glycerol and propylene carbonate [6].

To conclude the section, we briefly discuss the related α -relaxation behaviour of glass formers that exhibit a clearly discernible β -relaxation peak on the high-frequency side of the α -peak (such systems are sometimes classified as type B). The α -peak in these systems is usually broad, with a typical stretching exponent $\beta \approx 0.5$, at least in the cases where the β - and α -peaks are sufficiently separated, so that the shape of the α -peak can be unambiguously determined. In these cases, no excess wing is recognized, and the α -peak usually follows FTS, as noticed by Olsen *et al* [35]. In figure 11, we show examples of such behaviour. On a closer examination of figure 11(b) of DGEBA, at low temperatures (≤ 252 K) an excess wing seems to emerge from underneath the well-separated β -peak. Thus, the excess wing may also be found in those type B systems which exhibit a broad α -peak.

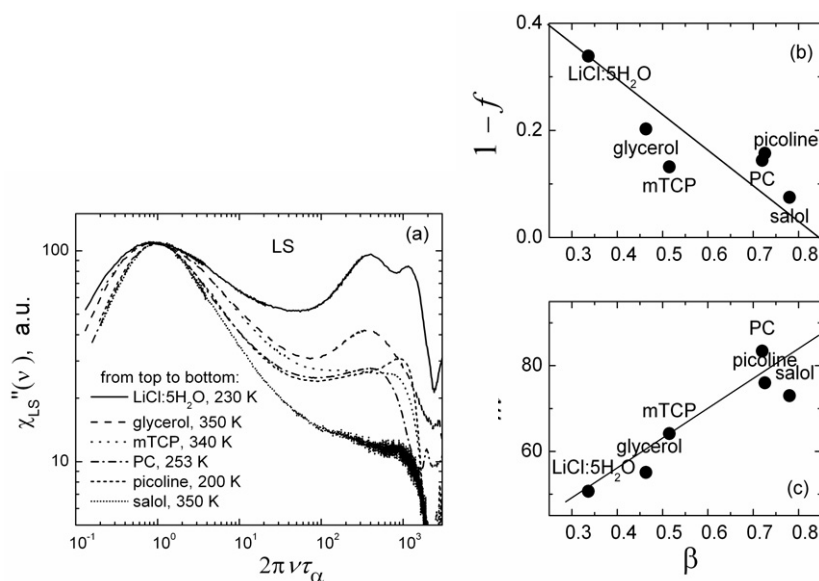


Figure 12. (a) Depolarized light scattering spectra of different liquids (m-TCP, *m*-tricresyl phosphate; PC, propylene carbonate) versus re-scaled frequency $2\pi\nu\tau_\alpha$; the amplitudes are adjusted so that relaxation maxima overlap. (b) Relaxation strength $1 - f$ of the fast dynamics (above the susceptibility minimum) as a function of stretching parameter β . (c) Fragility m versus stretching parameter β .

5. Correlations with fragility

The concept of fragility is often invoked in the attempt to correlate properties of different glass forming systems. It is rather commonly believed that the relaxation stretching is stronger for systems that are more fragile [37]. Certain caution is, however, required in determining the stretching parameter. Recalling the discussion above, the numerical value of the stretching parameter β of the α -peak close to T_g depends on the fitting model being used to extract it, while there is currently no consensus as to what model should be favoured. We have in particular seen that different phenomenological models provide very different conclusions about the behaviour of relaxation stretching. Moreover, stretching depends on the probing technique, so that one can only consistently compare stretching parameters obtained by the same experimental method. Turning now to glycerol and propylene carbonate, we recall that these two systems, having very different fragility, exhibit quite similar dielectric spectra when compared at the same relaxation time. A still closer inspection suggests that the spectrum of the less fragile glycerol is more stretched, which is against the rule mentioned above. Overall, it appears that correlating fragility and spectral parameters according to [37] lacks justification and is obsolete.

In the alternative approach introduced in the preceding section, the degree of relaxation stretching is not changing upon cooling, and thus it may be determined at sufficiently high temperature, where the α -peak is not obscured by secondary relaxation. Good quality high-temperature (and thus high-frequency) dielectric relaxation data are rather difficult to obtain. In contrast, they can be conveniently acquired by light scattering. Figure 12(a) shows some of our LS spectra of several disparate systems. Clearly, the widths of the α -peaks are quite different, as also are the relative magnitudes $1 - f$ of the fast dynamics, given by the spectral integral

over the fast dynamics above the minimum. Figures 12(b) and (c) show the fast dynamics strength $1 - f$, respectively fragility (steepness index) m [37], versus the stretching parameter β , obtained from the spectra in figure 12(a). Indeed, we find a trend. Low fragility appears to correspond to a smaller β , i.e. to a stronger stretching. This is the exact opposite to the conclusions of Böhmer *et al* [37]. In addition, lower m is associated with a lower $1 - f$. This agrees with the findings of Sokolov *et al* [38] that the boson peak is stronger in non-fragile systems.

6. Conclusions

To date, all the proposed approaches to quantitatively describe the evolution of the spectral response of molecular glass formers close to T_g have no firm theoretical foundation. Moreover, depending on the chosen procedure to separate the spectra into the primary α -process and secondary relaxations, such as the excess wing, quite different physical conclusions may follow. Still, the emergence of the excess wing in type A glass formers allows us to clearly identify, on phenomenological grounds, a crossover temperature T_x , at which the high-temperature regime with its α - and minimum scalings breaks down upon cooling. Below T_x , the conclusions on the temperature evolution of spectral shape vary greatly according to the model used. To achieve a certain consistency and meaningfulness of the results, one therefore has to impose physically plausible constraints that follow from separate, preferably model-independent analyses. One such model-independent result is the temperature and system independence of the intermediate power law (IPL) of the pulse-response function obtained by optical Kerr effect (OKE), and of the equivalent excess wing of the corresponding frequency-domain data, which we show to be different manifestations of the same phenomenon. Moreover, inspecting dielectric relaxation data in the pulse-response representation strengthens our conclusion about the near temperature and system independence of the IPL (\equiv excess wing) exponents. Using this as a constraint, and assuming in addition strict validity of frequency-temperature superposition (FTS) of the α -relaxation spectrum, we are able to obtain virtually perfect fits to the dielectric data of, e.g., glycerol and propylene carbonate with only three fit parameters—the relaxation time, the relative magnitude of the excess wing and the overall spectral magnitude. Our fits are at least as good as those obtained in other approaches with more fitting parameters, while also being consistent with qualitative analyses of the spectra. Thus, in our new approach, the FTS of the α -process turns out to be valid at *all* temperatures, starting from equilibrium low-viscosity liquid and down to T_g . These physically plausible results allow us to conclude in favour of our approach over other phenomenological analyses attempted so far, although we do not find it possible to judge on the general validity of these different approaches.

Attempting to find a relation between stretching and fragility, we argue that the stretching exponent is best obtained at sufficiently high temperatures above T_x where it is not obstructed by secondary relaxations. We indeed find a relation, which is, however, opposite to the one commonly accepted. In particular, we find that a higher fragility index m is associated with less stretched (higher stretching parameter β) relaxation. The same conclusion follows from comparing the dielectric data of glycerol and propylene carbonate.

Our analyses are purely phenomenological and do not address the question of the nature of the excess wing. Yet we briefly note that, according to our NMR experiments [39], the wing dynamics is manifested in the orientational motions of essentially all molecules as a restricted motion, being a precursor of the ultimate α -relaxation. However, concerning the kind of restricted motion, the difference to a typical β -process appears difficult to specify.

Commenting on the recent analyses of the OKE data in terms of the so-called two-correlator model of the mode coupling theory (MCT) [33, 40, 41], the authors' main conclusion

is that the intermediate power, and thus the excess wing, can be successfully reproduced as a non-generic result of the theory at temperatures above the MCT critical temperature T_c . However, since the excess wing is observed at sufficiently low temperatures down to T_g , the critical temperature T_c extracted from these analyses is bound to be lower than in previous MCT analysis, and to approach T_g . On the other hand, traditional MCT analyses in most cases yielded a T_c significantly above T_g and close to T_x [5, 11, 18]. We believe that it is impossible to reconcile the results of the recent and of more traditional MCT analyses. Whether or not the recent MCT analyses of OKE data are correct and valuable, it is still a challenge to the theory to explain the characteristic temperature evolution of dynamic susceptibility close to T_g , which is similarly revealed in the results of *all* probing techniques, in particular, in the most extended and complete dielectric spectroscopic data sets.

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