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Abstract
We discuss dielectric and light scattering susceptibility spectra of simple glass formers at temperatures above as well as below the critical temperature of the mode coupling theory (MCT). Close to T_g the systems are characterized by the presence of a pronounced excess wing (type A glass formers). The data are analysed within a phenomenological approach, on the one hand, and within MCT, on the other. Among other work we present a complete interpolation of the dielectric data for glycerol (Lunkenheimer *et al* 2000 *Contemp. Phys.* **41** 15). The crossover temperature T_x, defined by the emergence of the excess wing upon cooling, is extracted from the phenomenological analysis and found to agree well with the critical temperature T_c, extracted from the MCT analysis at high temperatures. Below T_x the evolution of the susceptibility is characterized by a universal appearance of the excess wing. No difference is observed for the non-fragile system with respect to fragile glass formers provided that the wing parameters are studied as a function of the correlation time τ_α. Finally, a generalized scaling for the susceptibility minimum is proposed which is a phenomenological extension of that of MCT but now also includes the data below T_c.

1. Introduction

Understanding the evolution of the dynamic susceptibility when a simple liquid transforms into a glass is still a great challenge. Upon supercooling, the molecular motion of a liquid slows down significantly and two-step correlation functions emerge. The long-time decay defines the timescale of the structural relaxation (α-process) whereas the fast decay defines some local, spatially highly restricted motion. The shape of the long-time decay is non-exponential, and for a long time it has been known that this stretching is essentially temperature independent.

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This is cast in the form of the frequency–temperature superposition (FTS) principle; i.e., re-scaling the relaxation functions by the relaxation time τ_α should lead to a master curve. Around the glass transition temperature T_g the time constant τ_α is of the order of some 100s and at somewhat lower temperatures structural relaxation is arrested. From an experimental point of view, monitoring the molecular dynamics of such highly supercooled liquids has to cover many decades in time or frequency. Thus, 0–1 THz spectroscopy is needed to address the evolution of the dynamic susceptibility. From the theoretical side, the mode coupling theory (MCT) provides a clear description of the evolution of the two-step correlation functions at high temperatures above a critical temperature T_c [1]. The latter can be extracted within a scaling analysis of the susceptibility data. Thus, MCT in its idealized version is concerned with the onset of the glass transition, and the scenario has been verified in many experiments as well as in molecular dynamics simulations [1, 2]. However, below T_c the experimental and the theoretical situation are less clear.

In the last decade many experimental methods have tackled the challenge of carrying out 0–1 THz spectroscopy and significant progress has been made. First of all, dielectric spectroscopy is now able to cover a frequency range 10^{-6}–10^{13} Hz [3]. Quasi-elastic light scattering may monitor the fast dynamics with high precision (10^8–10^{13} Hz) [4–9] and neutron scattering experiments have compiled the q-dependence [10, 11]. Given this technical progress, further relaxational features have been identified, and the question of whether the FTS principle is indeed valid has been re-addressed [12–16]. Two processes are discussed, namely the excess wing showing up on the high-frequency side of the α-process susceptibility, and the Johari–Goldstein (JG) β-process, the latter being identified by a separate relaxation peak in the kilohertz regime ($T \cong T_g$) and known of for a long time [17]. Both processes emerge above T_g and persist also below T_g and they exhibit features of a secondary relaxation process. Whereas a well distinguished β-relaxation peak is not always observed, it appears that the excess wing is found in most glass formers provided that it is not hidden by a strong β-process [13]. We have proposed calling such simple systems showing no discernible β-process type A glass formers, in contrast to type B glass formers with a more or less pronounced β-relaxation peak [13]. Up to now, how the emergence of these relaxation processes is related to the anticipated change of the dynamics around T_c has not been understood; nor do there exist theoretical predictions concerning their evolution.

Regarding the slow response of type A systems, several attempts have been made to find a universal scaling procedure, but none of these has been generally accepted, and most of the currently applied phenomenological susceptibility functions do not properly take into account, e.g., the excess wing contribution. Hence, any statement concerning the validity of the FTS principle is not well founded, since the results depend more or less on the fitting interval. One purpose of this contribution is to propose such a complete description for type A systems, which finally leads to a generalized scaling procedure for the low-frequency part of the susceptibility minimum which converges with that of MCT at high temperatures. As no generally accepted theoretical predictions are available for the susceptibility spectra below T_c and close to T_g, any approach has to rely on a phenomenological description, which finally may trigger further theoretical progress. Our major point is that in type A systems the excess wing emerges upon cooling close to the critical temperature T_c and this terminates the high-temperature scenario of MCT. Describing the evolution of the wing close to T_g allows us to extract a dynamic crossover temperature T_x which agrees well with T_c found by a MCT analysis from the high-temperature data. In order to substantiate our approach, we discuss recently published light scattering spectra [8, 9] as well as broad-band dielectric spectra [3, 13, 15, 16]. New data for the glass former trimethyl phosphate are presented.
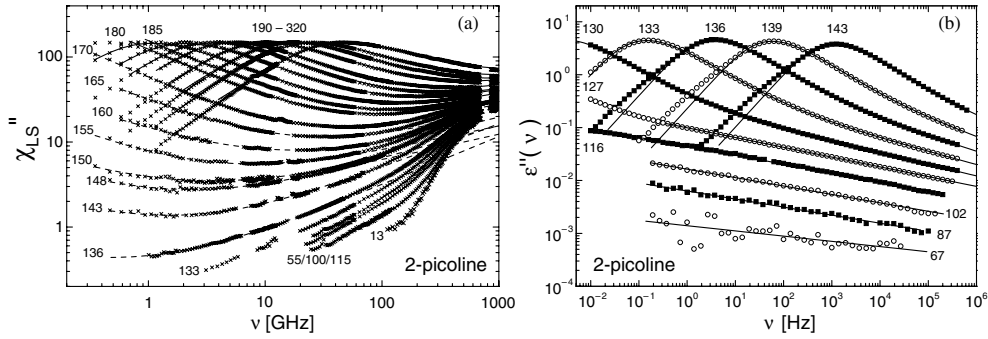
Figure 1. (a) Light scattering spectra of 2-picoline for different temperatures [9]; solid curves: fits of the data above 170 K ($T = 180$, 185, 190, 200, 210, 220, 240, 260, 280, and 320 K) applying the CD susceptibility with $\beta_{CD} = b_{mct} = 0.64$ and a power law contribution for the fast dynamics with $a_{mct} = 0.327$; dashed curves: fits of the data below 180 K by a superposition of two power laws with an exponent γ taken from figure 5(a) (the low-frequency part of the minimum), and an exponent a freely fitted (the high-frequency part of the minimum). (b) Corresponding dielectric data; solid curves: fits interpolating the α-relaxation peak and excess wing by applying the GGE distribution, equation (1).

2. Results

2.1. Dielectric and light scattering spectra

Figure 1(a) presents our light scattering (LS) spectra of 2-picoline ($T_g \cong 133$ K) [9] and figure 2 displays the best currently available dielectric loss spectra $\varepsilon''(\omega)$ for glycerol ($T_g \cong 186$ K) measured by Lunkenheimer *et al* [3]. The LS spectra are restricted to frequencies above 0.3 GHz whereas the dielectric spectra of glycerol cover an extremely broad frequency range, $10^{-6} < \nu < 10^{13}$ Hz. In order to analyse the data for glycerol we have normalized the susceptibility data by the static permittivity ε_s extracted from the real part of $\varepsilon(\omega)$. This was not done in a previous analysis of the data [18]; however, it is crucial for valid MCT as detailed below. The LS spectra of 2-picoline demonstrate that quasi-elastic contributions may well be identified even down to temperatures of 13 K, and a susceptibility minimum is observed also at temperatures close to T_g. Figure 1(b) shows our dielectric results for 2-picoline which are only measured in a small frequency range, partly due to the fact that 2-picoline exhibits a high tendency to crystallize in a metal capacitor. Inspecting the dielectric spectra, it is clear that both glycerol and 2-picoline belong to the group of type A glass formers since the only spectral change of the susceptibility found is given by the emergence of the excess wing close to T_g. Finally, in figure 3 we show the dielectric data of trimethyl phosphate (TMP; $T_g = 137$ K). This system exhibits (in addition to an excess wing) a JG process (seen for low temperatures at highest frequencies), the former being well separated from the α-process, and therefore one can study both secondary processes. Between 150 and 180 K we were unable to collect data for TMP because of its strong tendency to crystallize. Regarding the spectra of all these glass formers, it becomes evident that the question of whether the FTS principle actually works is intimately connected with the question of whether we find a complete phenomenological description of the data which may allow us to quantify possible deviations from the FTS.

3. Analysis of the spectra

In order to describe both the α-peak and the excess wing, Kudlik *et al* [13] have introduced an extension of the generalized gamma distribution (GGE). As is demonstrated by Blochowicz
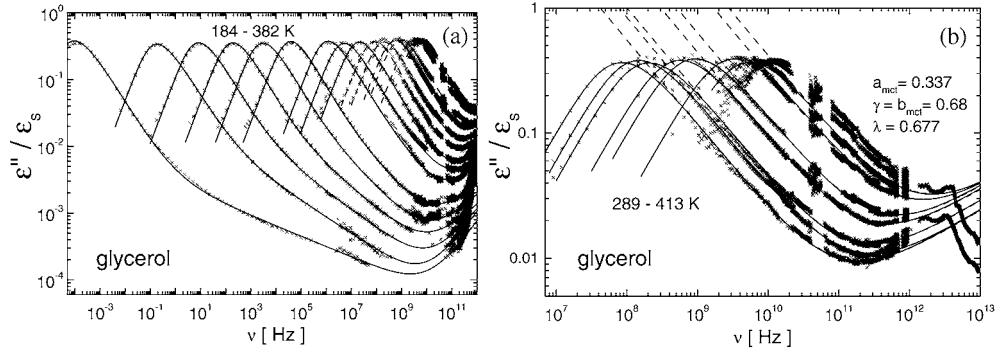
Figure 2. (a) The imaginary part of the dielectric permittivity of glycerol (taken from Lunkenheimer *et al* [3]) scaled by the static permittivity for various temperatures $\varepsilon''/\varepsilon_s$; temperature from left to right (in K): 184, 195, 204, 213, 223, 234, 253, 263, 273, 289, 303, 323, 333, 363, and 382 K; dashed curves: interpolations at high temperatures ($T \geqslant 289$ K) of the α-process applying the GGE distribution with the constraint (CD limit) of equation (4), with $\gamma = 0.68$, together with a power law contribution, ν^a, for the fast dynamics with $a = 0.337$; solid curves: applying the same procedure without any constraints at $T < 289$ K, equation (7). (b) High-temperature data for glycerol only (289, 295, 303, 323, 333, 363, 382, 403, 413 K) fitted with the GGE distribution applying the constraint (CD limit) of equation (4), with $\gamma = 0.68$, together with a power law contribution, ν^a, for the fast dynamics with $a = 0.337$ (solid curves), and minimum interpolation by the asymptotic law of MCT, equation (7) (dashed curves); note the high scatter and different point densities of the data which make fits and judgement difficult.
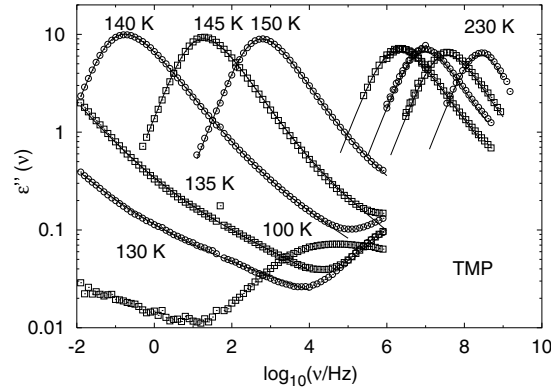

Figure 3. Dielectric loss spectra of trimethyl phosphate (TMP); solid curves: interpolations with the GGE function.

et al [15], this distribution of correlation times allows us to almost perfectly interpolate the slow response ($\lesssim 1$ GHz) of type A glass formers (see also figures 1, 2(a) and 3). Explicitly, the distribution function is given by

$$G_{GGE}(\ln \tau) = N_{GGE}(\alpha, \beta, \gamma) \exp\left(-\frac{\beta}{\alpha}\left(\frac{\tau}{\tau_0}\right)^{\alpha}\right)\left(\frac{\tau}{\tau_0}\right)^{\beta}\left[1 + \left(\frac{\tau\sigma}{\tau_0}\right)^{\gamma-\beta}\right] \quad (1)$$

with the normalizing factor

$$N_{GGE}(\alpha, \beta, \gamma) = \alpha\left(\frac{\beta}{\alpha}\right)^{\beta/\alpha}\left(\Gamma\left(\frac{\beta}{\alpha}\right) + \sigma^{\gamma-\beta}\left(\frac{\alpha}{\beta}\right)^{\frac{\gamma-\beta}{\alpha}}\Gamma\left(\frac{\gamma}{\alpha}\right)\right)^{-1} \quad (2)$$

and the mean time constant associated with the α-process

$$\tau_\alpha = \langle \tau \rangle = \tau_0 \left(\frac{\alpha}{\beta}\right)^{1/\alpha} \frac{\Gamma\left(\frac{\beta+1}{\alpha}\right) + \sigma^{\gamma-\beta}\left(\frac{\alpha}{\beta}\right)^{\frac{\gamma-\beta}{\alpha}} \Gamma\left(\frac{\gamma+1}{\alpha}\right)}{\Gamma\left(\frac{\beta}{\alpha}\right) + \sigma^{\gamma-\beta}\left(\frac{\alpha}{\beta}\right)^{\frac{\gamma-\beta}{\alpha}} \Gamma\left(\frac{\gamma}{\alpha}\right)}. \tag{3}$$

In addition to the parameters α and β pertaining to the α-relaxation peak, there appear two parameters σ and γ which define the onset of the excess wing and its exponent in the corresponding $G(\ln \tau)$, respectively. The ratio σ/τ_0 is a measure of the frequency at which the susceptibility crosses over from the α-peak to the excess wing (provided that $\sigma \gg 1$; see below). We emphasize that the width parameters α and β can assume values $0 < \alpha, \beta < \infty$. Figure 4(a) gives an example of the gamma distribution (GG, exhibiting no wing) and the GGE distribution together with the Cole–Davidson (CD) function. In contrast to a sharp cut-off at long correlation times, as exhibited by the CD distribution, the GGE distribution provides a smoother edge at long correlation times which is specified by the parameter α. It turns out that the GGE distribution provides an excellent fit of a CD susceptibility with $\gamma = \beta_{CD}$, when a constraint $\sigma(\alpha, \beta, \gamma) = \sigma_c$ is introduced in such a way that the absolute short-correlation-time asymptotes of the GGE and CD distribution [19] become identical [15, 16]. Explicitly, one finds for this constraint

$$\sigma_c(\alpha, \beta, \gamma) = \left(\frac{\left(\frac{\beta}{\alpha}\right)^{\frac{\beta}{\alpha}} \left(\frac{\alpha\pi}{\sin(\pi\gamma)} - \left(\frac{\alpha}{\beta}\right)^{\frac{\gamma}{\alpha}} \Gamma(\gamma/\alpha)\right)}{\Gamma(\beta/\alpha)}\right)^{\frac{1}{\beta-\gamma}} \tag{4}$$

and we display this case in figure 4(b). Again, instead of a sharp cut-off as in the case of CD distribution, the so-constrained GGE distribution exhibits a smoother cut-off at long correlation times. Thus, although at $\tau/\tau_0 \ll 1$ the GGE distribution is still described by two power laws with exponents β and γ, the resulting susceptibility function is a simple peak function which is very close to a CD susceptibility and exhibits only a single power law contribution on the high-frequency side with an exponent $\gamma = \beta_{CD}$. For type A glass formers, one typically finds that, reproducing a function close to a CD susceptibility, the onset parameter σ reaches values of the order of 1, i.e. the onset of the excess wing in the GGE distribution shifts very close to the parameter τ_0, i.e. close to τ_α. Simultaneously, the parameter β becomes >1. This is demonstrated in detail in [15]. We note that the exact value of σ in this limit depends somewhat on the parameter α, which is often found to be constant for a given glass former. We shall call this limit—a susceptibility exhibiting no excess wing—the CD limit of the GGE distribution. Thus, the GGE distribution is able to interpolate between the two limiting cases, namely the CD limit and the strong-wing limit, and this allows us to monitor a possible emergence of a wing when a glass former is cooled from high temperatures down to temperatures close to T_g.

It is well established that at high temperatures MCT describes the evolution of the susceptibility minimum in the GHz regime (see figures 1 and 2) [1]. For the asymptotic limit of MCT this minimum is interpolated by a sum of two power laws; explicitly,

$$\chi'' = \chi''_{min}[b_{mct}(\nu/\nu_{min})^{a_{mct}} + a_{mct}(\nu/\nu_{min})^{-b_{mct}}]/(a_{mct} + b_{mct}) \tag{5}$$

where ν_{min} and χ''_{min} are the frequency and amplitude of the minimum, respectively. The exponents a_{mct} and b_{mct} determine the low-frequency behaviour of the fast dynamics and the high-frequency part of the α-process. They are fixed by a single parameter, the exponent parameter λ, which depends on the given interparticle potential, and thus are not independent. In practice, λ is usually regarded as a fit parameter. The temperature dependence of ν_{min}, χ''_{min} and the timescale τ_α are expected to be given by

$$\chi''_{min} \propto \varepsilon^{1/2}, \qquad \nu_{min} \propto \varepsilon^{1/2a_{mct}}, \qquad \tau_\alpha \propto \varepsilon^{-\gamma_{mct}} \qquad T > T_c \tag{6}$$
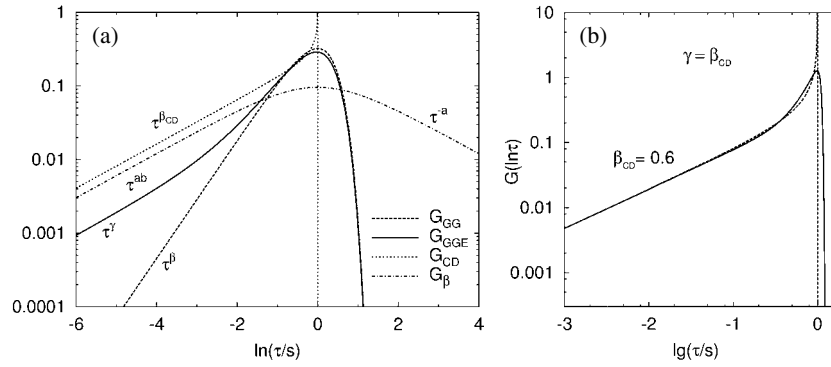
Figure 4. (a) Distributions of correlation times $G(\ln \tau)$: the CD distribution (G_{CD}), the generalized gamma function (G_{GG}), the extension of the generalized gamma function (G_{GGE}) exhibiting a second power law at short correlation times. (b) The GGE distribution (solid line) optimized to interpolate the CD distribution (dashed line) applying the constraint of equation (4).

with $\varepsilon = T - T_c$. The exponent γ_{mct} is related to the exponents a_{mct} and b_{mct} via $\gamma_{mct} = 1/(2a_{mct}) + 1/(2b_{mct})$. Usually, from $\chi''_{min}(T)$, $\nu_{min}(T)$, and $\tau_\alpha(T)$, the critical temperature T_c is extracted, and several publications have demonstrated that a consistent T_c can indeed be identified [1–9].

In the phenomenological approach, in order to account for the fast dynamics, we add a power law contribution to the GGE susceptibility $\chi''_{GGE}(\nu)$:

$$\chi''(\nu) = A\chi''_{GGE}(\nu) + B\nu^a. \tag{7}$$

The resulting susceptibility has a minimum, the shape of which is asymptotically identical to the minimum described with MCT by equation (5) when $a = a_{mct}$ and $\gamma = b_{mct}$.

Analysing the slow response of type A glass formers close to T_g by performing free fits with the GGE function, it is found (see figure 2(a)), as will be shown below, that the excess wing contribution disappears in the sense that only a simple peak susceptibility survives at high temperatures. In other words, the CD limit is indeed reached. This has also been tested in recent LS studies, where it was found that a CD function is sufficient to reproduce the complete slow response above T_c [8, 9]. We once again demonstrate this in figure 1(a) where the solid curves represent fits with a sum of a CD function and a fast-dynamics contribution described by a power law (at $T > 170$ K). The corresponding exponents are fixed by $a = a_{mct}$ and $\beta_{CD} = b_{mct}$.

In order to describe the dielectric data for glycerol, we proceed as follows. We start the line-shape analysis at temperatures close to T_g with a free fit of the data to equation (7) (in particular, γ and a are treated as free parameters) and plot the distribution parameters characterizing the wing contribution as a function of $\lg \tau_\alpha$ (see figure 5). This allows one to compare data for fragile and non-fragile glass formers. When, at some high temperatures, i.e., at some characteristic correlation time, the CD limit is reached, we apply two constraints for fitting the data at higher temperatures:

 (i) A simple peak susceptibility is assumed; i.e. the constraint equation (4) is applied.
(ii) The relationship between γ and a is fixed by MCT; i.e. $a = a_{mct}$ and $\gamma = b_{mct}$, and the exponent parameter λ is optimized.

As demonstrated in figure 2(b), this approach accounts for the salient feature of the susceptibility of glycerol at all temperatures above T_x. Inspecting the parameters of glycerol
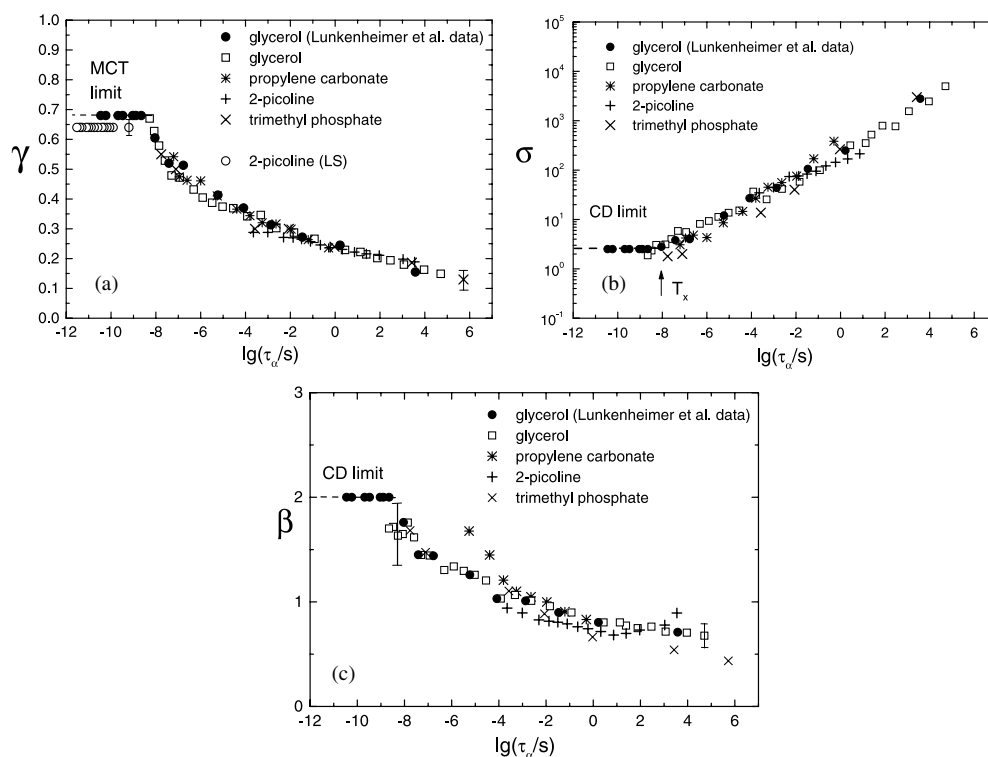
Figure 5. Fit parameters applying the GGE distribution to dielectric spectra from our work [15, 16] (see also figure 1(b)) and from Lunkenheimer *et al* [3] (see also figure 2) as a function of $\lg \tau_\alpha$: (a) the excess wing exponent $\gamma = \beta_{CD} = b_{mct}$ at high temperatures obtained from light scattering (LS) data for 2-picoline is included [9] (see also figure 1(a)); (b) the onset parameter σ; (c) the α-peak width parameter β. The CD and MCT limits, respectively, are indicated.

(see figure 5), it is indeed found that at high temperatures (or short correlation times) the data are compatible with a temperature-independent shape of the α-process susceptibility which is close to a CD function. Thus, all GGE shape parameters are temperature independent. In figure 5 we marked that regime as the 'CD limit'.

Note that the data for glycerol are characterized by very different point densities in the various frequency intervals covered by the different dielectric techniques. Also, the scatter is quite large at high frequencies. Therefore, the fits show some small systematic deviations from the data, and the analysis presented can only demonstrate that the fits at high temperatures are compatible with MCT.

In the case of the dielectric data for 2-picoline (see figure 1(b)) and TMP (see figure 3) measured in a reduced frequency range we have to restrict our analysis by omitting the fast-dynamics contribution in the fit. We note that in the case of the dielectric data for picoline some deviations from the GGE fits occur at lowest frequencies. The origin of this has not been understood so far, since this feature is not observed in other glass formers and does not show up in the LS spectra of picoline.

4. Discussion and conclusions

Figure 5 presents the parameters of the GGE function (obtained from the fits in figures 1–3), namely the wing exponent γ, the wing onset σ, and the α-peak width parameter β, as a function

of $\lg \tau_\alpha$. The parameter α, being an additional quantity specifying the shape of the α-peak itself, may be taken to be constant for a given glass former though different for different systems. In addition to the parameters of the systems presented in figures 1–3, we included the distribution parameters of propylene carbonate and glycerol obtained previously [16]. Clearly, the data for γ (see figure 5(a)) and σ (see figure 5(b)) exhibit a universal behaviour in the entire range of $\lg \tau_\alpha$ studied. The onset parameter $\lg \sigma$ linearly increases with $\lg \tau_\alpha$ while the exponent γ decreases continuously. The parameter β (see figure 5(c)) is almost identical in the range $-3 < \lg \tau_\alpha$, and slowly increases while the structural relaxation accelerates. At $\lg \tau_\alpha < -3$ the parameter β increases more strongly and somewhat differently for the different systems. We note that β is characterized by a large error when the CD limit is reached. All the glass formers investigated show essentially the same behaviour independently of their fragility. In all cases the onset parameter σ approaches the order of 1 and in this regime the parameter β strongly increases. These findings signal that the susceptibility function resembles more and more a CD function with a high-frequency exponent defined by $\gamma = \beta_{CD}$, i.e., the high-frequency wing disappears at high temperatures. The CD limit is reached at $-\lg(\tau_\alpha/s) = 8$–9 for all the systems studied, and this defines the corresponding crossover temperature T_x. In the case of glycerol, taking $\lg(\tau_\alpha/s) = -8.5$ we find $T_x \cong 280$ K. Thus, in the case of the dielectric data for glycerol taken from Lunkenheimer *et al* [3]—which is actually one of the few data sets covering sufficient decades in frequency—we apply the two constraints (see above) at $T > T_x$ and it turns out, as already stated, that at higher temperatures all shape parameters can be kept temperature independent, and, moreover, they are compatible with the MCT scenario of the susceptibility minimum, since for the exponents $a = a_{mct}$ and $\gamma = b_{mct}$ have been introduced (see figure 2). In other words, the shapes of the α-process contribution as well as the fast-dynamics contribution are essentially temperature independent. As already said, a similar result is found from the light scattering data for 2-picoline (see figure 1(a)).

Here, we note that recently Schneider *et al* [20] fitted solely the α-peak of glycerol close to T_g by the CD function and reported a temperature-dependent width parameter β_{CD}. This appears to be at variance with our findings that the shape of the α-peak is virtually temperature independent close to T_g. However, since the CD fitting in [20] is applied for different fitting intervals, this discrepancy is not a surprise and stresses the fact that only if well adapted susceptibility functions are applied can the question of whether or not the FTS holds be addressed.

We note that in figure 5 we included also the distribution parameters for trimethyl phosphate, which exhibits both an excess wing and a comparatively fast JG process. Also for this glass former the wing parameters turn out to be very similar to those of the other systems studied. This confirms our picture in which the relaxation features of type A glass formers also show up in type B glass formers provided that they are not obscured by the presence of a strong or less separated JG process [13]. Fluoro aniline (FAN) is another example for which the two processes are clearly discernible [13]. However, in the case of FAN it turns out that the wing parameters are somewhat different as compared to those in figure 5, probably because the JG process interferes, since in FAN it is significantly slower than in the case of TMP and thus less separated from the α-peak [15].

Regarding the evolution of the susceptibility, the phenomenological approach provides clear evidence for the existence of a high-temperature and a low-temperature regime with a crossover at a characteristic correlation time (and at a temperature T_x). For the high-temperature regime the asymptotic laws of MCT are rediscovered. The crossover temperature T_x is defined as the point of emergence of the excess wing upon cooling. On the other hand, applying an analysis within the idealized MCT, i.e., applying the asymptotic law, equation (5), we have recently shown that the critical temperature T_c of glycerol is identified at 288 K [16].
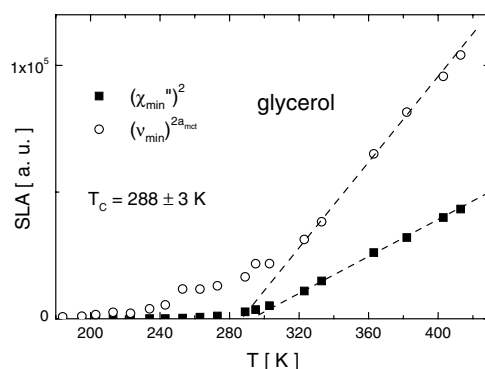
Figure 6. Testing scaling laws of MCT; linearized scaling law amplitudes (SLA) plotted for ν_{min} and χ''_{min}. The two points at the highest temperatures were obtained from the master curve in figure 8.

In figure 2(b) we included the MCT interpolations of the minimum (dashed curves) and in figure 6 we once again show the rectified scaling laws of the MCT analysis clearly allowing for a consistent identification of T_c. In the case of glycerol, the correlation time at T_c is found to be $\lg(\tau_\alpha/s) = -8.7$ which is very close to the onset of the CD limit in figure 5. The MCT high-temperature scenario appears to work well up to the highest temperatures. Similarly broad temperature ranges have been reported for an epoxy resin [21], toluene [8], and 2-picoline [9], a feature not theoretically expected. We note that previously Lunkenheimer *et al* [18] presented a MCT analysis of glycerol reporting $T_c = 262$ K which is significantly lower than that extracted here. We explain this discrepancy by the fact that the authors did not analyse normalized susceptibility data, and their analysis did not cover the highest temperatures which, as shown, are actually well described by MCT (see figures 2(b) and 6).

From figure 5 it appears that the crossover to the CD limit is always observed at a very similar correlation time, $-\lg(\tau_\alpha/s) = 8$–9; comparing the so-defined T_x with T_c as obtained by a conventional MCT analysis, we find a strong correlation. This is most easily demonstrated by plotting the temperature at which a correlation time of the order of $\lg(\tau_\alpha/s) = -8$ is found against the reported critical temperature T_c [4, 5, 8, 9, 22, 23]. This is tested in figure 7. A satisfying correlation is found. A small systematic deviation is observed which may be explained by assuming that in most cases T_c is somewhat lower than T_x since it is extracted from a high-temperature scenario; conversely, T_x may be somewhat too high since it is extracted from an analysis at low temperatures. This actually explains the difference in the case of picoline between $T_c \cong 162$ K and the first temperature ($T \cong 170$ K; see figure 1) for which the asymptotic laws of MCT do not apply any longer upon cooling [9]. We conclude that the emergence of the excess wing terminates the high-temperature scenario which actually is well described by the asymptotic laws of MCT, and this crossover occurs at a correlation time which is similar to that discussed already by Goldstein for the expected crossover from a liquid-like to a solid-like behaviour of the molecular dynamics [24]. Essentially no difference is found on comparing fragile (2-picoline) and non-fragile (glycerol) glass formers.

The MCT predictions concerning the interpolation of the susceptibility minimum, equation (5), may be recast in a form for which, upon re-scaling the minimum by ν_{min} and χ''_{min}, a master curve for the minimum envelope is expected to result. Indeed, this is what is observed in the case of glycerol (DS data); see figure 8. In order to demonstrate the changes of the shape of the minimum while passing through T_x, we have included all the data available for glycerol irrespectively of whether the temperature is above or below T_x. The data represented
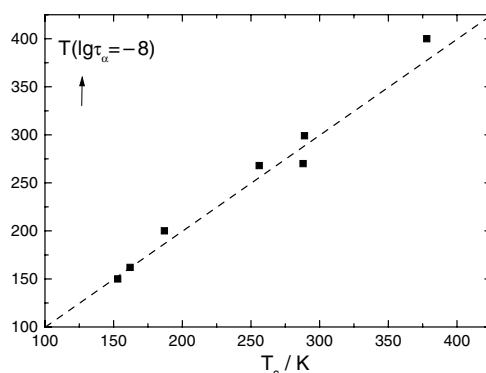
Figure 7. The correlation between the temperature $T(\lg \tau_\alpha = -8)$ at which $\tau_\alpha \cong 10^{-8}$ s and the critical temperature T_c reported by an idealized MCT analysis [4, 5, 8, 9, 22, 23]; dashed line: straight line with slope one.
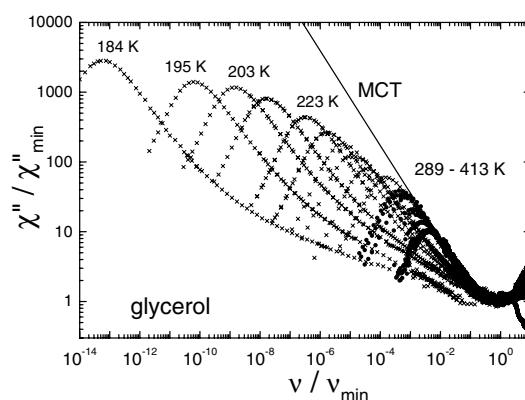

Figure 8. Dielectric data for glycerol re-scaled by ν_{min} and χ''_{min}; solid circles: data $\geqslant 289$ K; crosses: data below 289 K; straight line: interpolation by MCT master curve.

with solid symbols are above T_x whereas crosses indicate the data below T_x. Clearly, all curves above $T_x \cong 280$ K can be collapsed onto a master curve for the envelope which is well interpolated by the MCT expression (see equation (5)), whereas below T_x deviations show up, namely the minimum becomes broader and more asymmetric with lowering temperature. This feature reflects nothing else than the appearance of the excess wing below T_x. Again, it appears that the emergence of the excess wing terminates the high-temperature scenario of MCT ($T_x \cong T_c$) and thus allows us to identify unambiguously the crossover temperature from such a representation of the data.

Inspecting once again the GGE distribution parameters below T_x (see figure 5), it is obvious that at least for the systems investigated all the parameters depend in a unique way on the time constant τ_α, demonstrating that the excess wing co-evolves with the α-peak. Moreover, it follows that below T_x, in addition to τ_α, a single parameter is needed to completely describe the evolution of the susceptibility function. We choose the excess wing exponent γ. This parameter shows up directly in the data, and thus can be easily determined. As is shown in figure 5(a), γ decreases from a value $\gamma = \gamma_c \cong b_{mct}$ at high temperatures (and short correlation times τ_α) to quite low values close to T_g. If we re-scale the data in figure 8 by multiplying
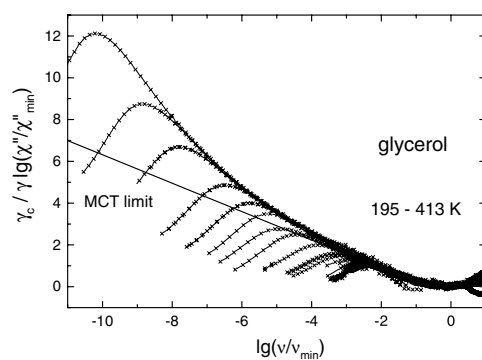
Figure 9. Generalized scaling of the glycerol data at temperatures above as well as below the crossover temperature T_c.

the ordinate by the scaling factor γ_c/γ, at least the high-frequency excess wing is expected to collapse to the data at high temperature, i.e. to the master curve of MCT. This is indeed observed in figure 9. In fact, not only does the excess wing fall onto a master curve, but also the entire low-frequency side of the susceptibility minimum follows a master curve with a high-frequency part interpolated by the MCT master curve. In other words, the proposed re-scaling provides a generalized scaling which includes temperatures above as well as below T_c. It is a phenomenological extension of the MCT scaling down to temperatures close to T_g. Inspecting the re-scaled data in figure 8, the data below T_c are easily identified, since they exceed the MCT master curve (the MCT limit in figure 9). Note that this procedure is not expected to collapse data at $\nu/\nu_{min} > 1$ at $T < T_x$.

The introduced re-scaling was guided by the quite universal results of fitting the data with the GGE distribution. Now, knowing that a generalized master curve exists, one may proceed in a reverse way. The scaling factor may be taken as an empirical parameter for obtaining the master curve without any fitting procedure. In fact, this has been done in figure 9. In figure 10 we compare the so-found exponent γ with that obtained from the GGE fit for glycerol. Clearly, very similar results are found. Only at lowest temperatures do some deviations occur, which we attribute to experimental uncertainties of the data at the highest frequencies (see figure 2). Obviously, the scaling procedure allows us to determine the parameter γ in a model-independent way, and its dependence on temperature clearly allows us to identify the crossover temperature T_x. Of course, future experiments are needed to answer the question of whether this behaviour is typical of all glass formers or, more precisely, for glass formers where the excess wing is not obscured by the presence of a JG process being spectrally too close.

In the present contribution we have analysed what have been called type A glass formers, i.e. ones for which no discernible secondary relaxation peak is observed. Recently, Schneider *et al* [25] showed that the excess wing develops some deviations from a simple power law wing when sufficiently long ageing is allowed somewhat below T_g, and the authors claimed that the wing is actually a secondary relaxation process of JG type [12]. Clearly, below T_g the excess wing contribution has characteristics of a secondary relaxation process, and also above T_g it may not necessarily be interpretable as a part of the α-process. However, we think that the wing contribution is well distinguished from a JG secondary process for the following reasons:

(i) Above T_g there are no indications that for describing the excess wing more than a power law contribution is needed.
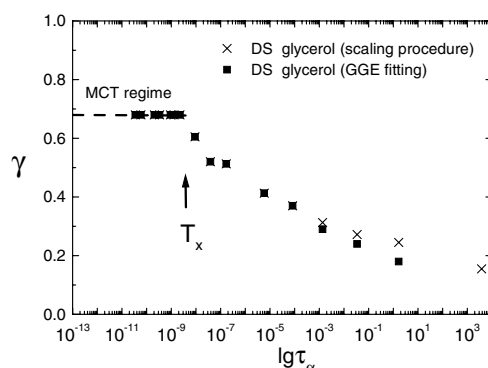
Figure 10. The exponent γ obtained from the generalized scaling procedure; for comparison, the same exponent obtained by means of fits with the GGE distribution function is also shown.

(ii) Often the excess wing is present in both type A and type B systems (see TMP and FAN). Thus, it may even be possible that, in the case of glycerol also, both the excess wing and JG process are present, the latter with such a small relaxation strength that it is only observable after ageing.

(iii) Its universal evolution presented in our analysis suggests that the excess wing is a distinct process.

(iv) In dielectric experiments under pressure, the excess wing and JG process behave quite differently [26].

(v) If the excess wing is indeed described in terms of a JG process, then it is obvious that its correlation times are much longer than those of a JG process ($T \cong T_g$), and, as shown by Döss *et al* [27], in such an analysis the attempt times may become extremely long and thus cannot be attributed to any local process.

(vi) Independently of any detailed analysis, it is obvious that the relaxation strength of the excess wing with respect to that of the α-process is essentially the same for all the systems, whereas the strength of the JG process may vary substantially.

We note that Schneider *et al* [25] did not give a clear definition of the JG process, and the excess wing exhibits features which, e.g., have not been reported as typical of a JG process by Johari and Goldstein [12] themselves.

Another remark may be worth making. In polymers or more complex low-molecular-weight glass formers, the secondary relaxation process is often attributed to some side-group motion. Here care should be taken, since proving that a side group is involved does not prove that the side group is the cause of the secondary relaxation. In most cases, the main chain has to be involved to enable the relaxation of an asymmetric side group. Williams and Watts [28] have already suggested that main-chain motion might enhance or even enable large motion of side groups; similar arguments were discussed recently by Vogel and Rössler [29]. In other words, it is not strictly proven that the β-process in such systems is not a JG process.

Finally, we note that, in order to demonstrate the validity of the generalized scaling, one needs susceptibility data including the high-frequency minimum in the GHz regime since the scaling starts from data for which the minimum is already scaled by ν_{min} and χ_{min}. Currently, such data are only available for a few systems and only from dielectric experiments. It is an open question whether the scaling procedure can be recast in such a form as to allow a direct scaling of experimental data not including the GHz regime. Another question is whether a similar evolution of the excess wing is observed by means of other techniques, for example, light

scattering. In figure 1(a) we have demonstrated for the light scattering spectra of 2-picoline that taking $\gamma(\lg \tau_\alpha)$ from the dielectric spectra, i.e., from figure 5(a), one is indeed able to interpolate the susceptibility minimum below T_c also [9]. Thus, it appears possible that very similar evolution of the excess wing is probed by all techniques.

Acknowledgments

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    Here, an error in quoting equation (1) (present paper) appeared after proofreading; therefore see also
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