Anomaly of the non-ergodicity parameter and crossover to white noise in the fast relaxation spectrum of a simple glass former

S. V. Adichtchev, 1 St. Benkhof, 1 Th. Blochowicz, 1 V. N. Novikov, 1 E. Rössler, 1 Ch. Tschirwitz, 1 and J. Wiedersich 1, 2

1 Physikalisches Institut EP II, Universität Bayreuth, 95440 Bayreuth, Germany
2 Technische Universität München, Lehrstuhl für Physik Weihenstephan, Vöttinger Str. 40, 85350 Freising, Germany
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We present quasi-elastic light scattering (LS) and dielectric (DS) spectra of the glass former \(\alpha\)-picoline \((13 \, \text{K} < T < 320 \, \text{K})\). At high temperatures the evolution of the susceptibility minimum is well described by mode coupling theory (MCT) yielding a critical temperature \(T_c = 162 \, \text{K} \pm 5 \, \text{K}\). At \(T_c < T < 162 \, \text{K}\) the excess wing of the \(\alpha\)-process is rediscovered in the DS spectra and characterized by a power-law exponent \(c\) is rediscovered by DS data of several glass formers, the fast dynamics spectrum is singled out, allowing to determine the non-ergodicity parameter \(f(T)\). The latter shows the predicted cusp-like anomaly identifying \(T_c\) as well. Another discontinuous change of \(f(T)\) is observed at \(T_c\). The fast dynamics spectra exhibit a crossover to “white noise” \((T < T_c)\). Concerning the fast dynamics, we conclude that idealized MCT predictions hold even below \(T_c\).

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The molecular slowing-down in glass forming liquids has been investigated by neutron (NS) and light scattering (LS) as well as by dielectric spectroscopy (DS) \(1\), and the predictions of mode coupling theory (MCT) have been found to hold above the critical temperature \(T_c\), the latter being about 20% above the glass transition temperature \(T_g\). Below \(T_c\) the situation is less clear. Concerning the temperature dependence of the non-ergodicity parameter \(f(T)\), which is expected to show a cusp-like behavior, agreement is less convincing and a matter of debate \(1, 2\). Related to this is the prediction of a “knee” in the fast dynamics spectrum, i.e. a power law behavior with exponent \(a\) changing from \(a \approx 0.3\) at high frequencies to \(a = 1.0\) at low frequencies. A crossover to a “white noise” spectral density is predicted upon cooling towards \(T < T_c\). However, up to now no such behavior has been confirmed. The frequency window of, e.g., LS techniques is restricted to frequencies \(\nu \gtrsim 0.5\, \text{GHz}\), and one could argue that the knee cannot be identified unambiguously. Recent MCT analyses indeed have shown that the experimental data are compatible with the presence of a knee \(3\). In addition, below \(T_c\) the analysis is hampered by the fact that the time constant \(\tau_{\alpha}\) of the \(\alpha\)-process actually does not diverge at \(T_c\) as presumed by idealized MCT. Hence, contributions from the \(\alpha\)-process have to be taken into account to evaluate the fast dynamics spectrum. However, there is no generally accepted way to do this.

The aim of this contribution is to perform an analysis of the susceptibility spectra of a simple glass former as obtained by tandem Fabry-Perot interferometry (TFPI) and by DS in the temperature range \(2.5 \, T_g > T > 0.1 \, T_g\). Most LS measurements reported so far do not include the temperature range below \(T_g\). We carefully apply additional interference filters in order to suppress contributions from higher orders in the TFPI spectra, as is required to obtain reliable LS spectra \(3, 4, 5\). In particular, we address the question of how the susceptibility minimum evolves below \(T_c\). We will demonstrate that the excess wing of the \(\alpha\)-process, identified in dielectric experiments, is also observed in LS spectra.

We have studied the glass former \(\alpha\)-picoline (cf. Fig. 1), which has the same molecular weight and a similar structure as toluene but a significantly higher dipole moment. Picoline has a smaller tendency to crystallize and allows us to compile more LS data at \(T_g < T < T_c\) \(3\). By DSC \(T_g\) is found to be at 133 K.

Let us sum up some predictions of idealized MCT \(1\). The fast dynamics and the \(\alpha\)-process are separated by a minimum in the susceptibility at \(T > T_c\), which can be interpolated by

\[
\chi''(\nu) = \chi''_{\min} \left[ \frac{b (\nu/\nu_{\min})^a + a (\nu/\nu_{\min})^{-b}}{a + b} \right],
\]

where \(\nu_{\min}\) and \(\chi''_{\min}\) are the frequency and the amplitude of the minimum. The exponents \(a\) and \(b\) describe the low-frequency behavior of the fast dynamics and the high-frequency part of the \(\alpha\)-process, respectively; they are interrelated via the exponent parameter \(\lambda\) \(1\). The temperature dependences are given by \(\chi_{\min} \propto \sigma^{1/2}, \nu_{\min} \propto \sigma^{1/2}\) for the amplitude and the frequency of the minimum and \(\tau_{\alpha} \propto \sigma^{-\gamma}\) for the time scale of the \(\alpha\)-process, where \(\sigma = T - T_c\). The exponent \(\gamma\) is related to the exponents \(a\) and \(b\) via \(\gamma = \frac{1}{2a} + \frac{1}{2b}\). The critical temperature \(T_c\) can be identified by the temperature dependence of \(\chi''_{\min}(T), \nu_{\min}(T), \tau_{\alpha}(T)\).

Below \(T_c\) the fast relaxation spectrum is expected to exhibit a crossover from a power-law behavior with exponent \(a\) at high frequencies/temperatures to a white noise spectrum \((a = 1)\) at low frequencies/temperatures. As a consequence of the appearance of this “knee” a decrease of the relaxation strength is expected upon cooling and a characteristic temperature dependence is predicted for the non-ergodicity parameter \(f(T)\)

\[
f(T) = f_c, \quad T > T_c; \quad f(T) = f_c + h|\sigma|^{1/2}, \quad T < T_c.
\]

The quantity \(1 - f\) presents the fraction which decays due to processes faster than the \(\alpha\)-process and is given by the integral.
over the susceptibility of the fast relaxation $\chi''_{\text{fast}}$, $1 - f \propto \int_{-\infty}^{\infty} \chi''_{\text{fast}}(\nu) \, d\ln \nu$.

Fig. 1a shows the susceptibility spectra as obtained by LS (Fig. 1a, b) and by DS (Fig. 1c). Picoline is a type A glass former [8], since no slow $\beta$-process can be identified in the DS data. Rather a “wing” at high frequencies shows up, which degenerates to a simple power law contribution with an exponent $c \approx -0.1$ at $T < T_B$. Fig. 1a also displays MCT interpolations by Eq. (1) of the susceptibility minimum with an exponent parameter $\lambda = 0.70$ fixing $a = 0.327$ and $b = 0.641$ (dashed lines) [1]. Clearly, at high temperatures the interpolation well reproduces the minimum, whereas at low temperatures the agreement becomes worse (cf. Fig. 1b). The parameters $\chi''_{\min}, \nu_{\min}$ and $\tau_\alpha$ (cf. below) all exhibit the behavior expected from MCT at $T > T_c$ (cf. Fig. 1c). Extrapolating the scaling laws, one obtains consistently $T_c = 162 K \pm 5 K$. Thus, idealized MCT provides a very satisfying interpolation at high temperatures up to the fluid regime. However, one observes some deviations from the scaling laws at temperatures below some 180 K (cf. Fig. 2).

A full description of the relaxation spectrum, including the $\alpha$-relaxation peak, is not given by idealized MCT. Hence, in order to extract the time constant $\tau_\alpha$ we choose a phenomenological approach, assuming an additive superposition of a Cole-Davidson, $\chi''_{\text{CD}}(\nu) \propto \Im(1 + i\omega\tau)^{-b}$, and a power-law, $\nu^\beta$, susceptibility for $\alpha$-process and fast dynamics, respectively. The fits for $180 K < T < 250 K$ are practically indistinguishable from those of MCT around the minimum (here the exponents are kept the same as in the MCT analysis, $\beta = \beta'$), but now include the full relaxation spectrum (cf. Fig. 1c, dotted line). The time constants $\tau_\alpha$ are plotted in Fig. 2 (insert). Including those from NS [10] and DS the full temperature range of the supercooled liquid is covered. Comparing the time constants $\tau_\alpha$ from the different techniques similar results are observed.

To unravel the origin of the deviations from MCT’s scaling laws at low temperatures (cf. Fig. 2 $T < 180 K$) we present in Fig. 3 the LS data in a way to provide a master plot for the $\alpha$-relaxation peak, i.e., $\chi''$ is plotted as a function of $\nu \tau_\alpha$, where $\tau_\alpha$ is taken from interpolating $\tau_\alpha(T)$. According to MCT, the loci of the minimum are expected to obey the relationship $\chi''_{\min}(\nu) \propto (\nu_{\min} \tau_\alpha)^{-b}$. This is indeed observed for $T > 180 K$. Below this crossover temperature subsequently called $T_{\text{crossover}}$ deviations show up. As also suggested by Fig. 2, the minima are shifted to higher frequencies $\nu_{\min}$ and to higher amplitudes $\chi''_{\min}$ as compared to MCT predictions. It appears that the minimum is determined not any longer by the high-frequency power-law of the $\alpha$-process (with exponent $b$) but rather by some additional spectral feature which only appears below $T_{\text{crossover}} \approx 180 K$. Since picoline does not exhibit a slow $\beta$-
process, the only candidate for a change in the susceptibility is the excess wing, which is clearly seen in the DS spectra (cf. Fig. [3]). From DS data of glycerol and propylene carbonate [3-4], which have been measured to higher frequencies, it is seen that the excess wing disappears at high temperatures. We conclude that the deviations of the parameter $\alpha$ when plotted as function of $\tau_\alpha$ shows a universal behaviour for both methods. Thus, let's assume that $\alpha$-peak is not described by a power-law contribution it is important to quantify the $\alpha$-process peak and the wing and to extract $c(\tau_\alpha)$ [3]. In Fig. 3 we have included such fits. Moreover, analyzing several glass formers we find that $c$ shows a universal behaviour when plotted as function of $\tau_\alpha$ (Fig. 3, insert). Contrary, the parameter $\beta_{CD}$ describing the width of the $\alpha$-peak is not universal.

These are results obtained from DS, and a priori there are no arguments that this universality also holds for the LS data. However, recent LS measurements of glycerol clearly show that the wing manifests itself in a very similar way as in DS [3-4]. Moreover, a direct comparison of DS and LS data in Fig. 3 demonstrates that the excess wing is at least similar for both methods. Thus, let’s assume that $c(T)$ is the same in both DS and LS. We further assume that the susceptibility minimum below 180 K is described by a sum of two power law contributions, $\chi''(\nu) \propto A\nu^{-c} + B\nu^{a'}$ (cf. dotted-lines-fit in Fig. 3), yielding an excellent agreement with the data. The exponent $a'$ is the exponent attributed to the fast dynamics below $T_x$. Inspecting Fig. 3 it is obvious that $a' \neq a$ at lower temperatures, e. g., $a' = 0.72$ is found at 115 K. For this low temperature ($T < T_g$), $a'$ can directly be read from the data since no interference with the wing contribution is expected. Thus, it becomes obvious that $a'$ strongly depends on temperature in the interval $T_g < T < T_x$. Fig. 4 displays the LS spectra after subtracting the contribution of the $\alpha$-process including the excess wing. In agreement with the phenomenological fit in Fig. 4, the power-law of the fast dynamics with a constant amplitude and an exponent $a = 0.327$ is rediscovered at $T > T_x$. Referring to MCT this is the critical spectrum. Below $T_x \approx 180$ K the spectra can still be described by power-laws but first their amplitude decreases and on further cooling the exponent $a'$ increases as well. The temperature dependence of $a'$ is plotted in Fig. 4 (insert). It is essentially constant at $T < T_g$, then drops above $T_g$ and finally reaches the level of $a = 0.327$ close to $T_x$. Below $T_x$ the exponent of the fast dynamics increases towards one; however, this trend stops at $T_g$.

Having singled out the fast dynamics contribution we are able to determine the non-ergodicity parameter $f$. More precisely, we integrate the fast dynamics spectra and get a quantity which is proportional to $1 - f(T)$ (cf. above). The integration is performed in the frequency interval 0 – 200 GHz. Fig. 5 displays the results. Obviously, the anomaly expected by MCT is discovered: Above 180 K only a weak temperature depen-
dence of $1 - f$ is discernible; below a strong decrease is observed with decreasing temperature. This decrease can be fitted by the square root law (cf. Eq. 2). At $T \approx T_g$ the strong temperature dependence halts and only a weaker one persists at $T < T_g$.

This contribution is aimed at describing the evolution of the LS susceptibility on cooling a glass former from high temperatures ($T \gg T_x$) to temperatures in the glassy state ($T \ll T_x$). Since no simple and generally accepted predictions exist for the low temperature regime, $T < T_c$, and since the frequency window is limited, our analysis is phenomenological in nature and has to rely on certain assumptions. Nevertheless, a clear scenario is observed:

(i) Above a crossover temperature $T_x$ the susceptibility minimum is well described by the asymptotic laws of MCT, allowing to identify consistently the critical temperature $T_c \lesssim T_x$. For describing the full spectrum, including the $\alpha$-relaxation, it is sufficient to fix a single width parameter, i.e., $\beta_{CD} = b$, which defines the high-frequency power-law behavior of $\chi_a(\nu)$. This has also been observed in toluene [8].

Quite surprisingly these asymptotic predictions hold up to the fluid regime. No peculiarities are observed around the melting temperature, $T_m = 206$ K. (ii) Below $T_x$ the positions of the susceptibility minima do not follow the MCT predictions. Instead they are controlled by the appearance of the excess wing. The wing is believed to be a kind of precursor of the $\alpha$-process and/or a secondary relaxation process [14, 15]. Thus, we think including a hopping mechanism is not sufficient to understand the evolution of the susceptibility minimum below $T_x$. (iii) Within a phenomenological approach one is able to single out the fast dynamics contribution. Power-law contributions are found with an exponent being constant above $T_x$ but increasing upon further cooling. This we take as an indication that the susceptibility crosses over to a white noise spectrum similarly as predicted by MCT. This trend is impossible to follow to a temperature at which $\alpha' = 1$ holds, since the glass transition at $T_g$ interferes, resulting in a temperature independent exponent $\alpha'$ at $T < T_g$. (iv) The spectra of the fast dynamics allow to determine the non-ergodicity parameter, which clearly displays the anomaly predicted. In contrast to what has been reported from NS experiments a further change of its temperature dependence is observed at $T_g$, i.e., the evolution of the fast dynamics is altered when the supercooled liquid’s structure freezes. The discrepancy of LS and NS data may be explained by the fact that the usual determination of $f(T)$ by NS includes also harmonic contributions and, as a consequence, the change of $f(T)$ around $T_g$ (and $T_c$) is smeared out.

We conclude that the fast dynamics in picoline is well described by idealized MCT even well above $T_c$ and even below the crossover temperature $T_x$. The crossover to a white noise spectrum is ultimately related to the prevalence of the anomaly of $f(T)$. Why actually no “knee” appears and why the crossover to “white noise” is rather observed as a function of temperature than as a function of frequency is an open question. Finally, we note that the crossover temperature $T_x$, where first deviations from the MCT predictions appear, is somehow higher than $T_c$ as obtained from extrapolating the scaling laws. This may explain certain discrepancies in identifying $T_c$ found in the literature.

* corresponding author

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