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Mode-coupling crossover in viscous toluene revealed by neutron and light scattering

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Abstract. The dynamics of supercooled toluene, studied in a GHz–THz range by incoherent neutron and depolarized light scattering, is found to be in full accord with mode coupling predictions. Around the susceptibility minimum, neutron spectra are wavenumber independent and proportional to light scattering data; the fast β-relaxation scaling law applies; amplitude and frequency diverge with power laws that extrapolate towards a crossover temperature $T_c = 143$ K.

PACS. 61.25.Em Molecular liquids – 61.12.-q Neutron diffraction and scattering – 78.35.+c Brillouin and Rayleigh scattering; other light scattering

Mode coupling theory [1] has suggested that much of the phenomenology of glass formation can be understood by considering in detail the microscopic dynamics around a critical (or cross-over) temperature T_c, situated well above the caloric glass transition temperature T_g. On cooling towards T_c, the slow α relaxation (responsible for viscous flow) starts to separate from the vibrational THz motion. Testable predictions are made in particular for an intermediate frequency range, now labelled the fast β relaxation regime, where the dynamic susceptibility, by no means a mere superposition of vibrational contributions and α relaxation, is predicted to follow nontrivial scaling laws.

These scaling predictions have been confirmed to different extent in a couple of model systems by scattering of neutrons [2] and of light [3]. Systematic comparisons of both scattering techniques, however, are sparse: so far, they are most often restricted to the low-frequency wing of the vibrational spectra [4]; in the few cases where the comparison covered the susceptibility minimum only moderate accord was found [5,6].

Here we present a parallel neutron and light scattering study of viscous toluene, a very fragile [7] glass former with $T_g = 118$ K, $T_m = 178$ K. In ^{2}H-NMR T_1 dispersion experiments [8,9] toluene was found to behave significantly different from orthoterphenyl, a prototypical fragile glass former: while NMR-data on orthoterphenyl are consistent with a fast β relaxation on a psec scale [10], the toluene measurements were interpreted in terms of a much slower local process of the Johari-Goldstein type [9]. The primary aim of our scattering experiments was therefore to observe the nsec–psec motion in toluene more directly and to see whether the microscopic glass transition dynamics deviates from the mode coupling scenario observed in other fragile liquids [2,3]. There is also some practical interest in toluene because as a solvent it plays an important rôle in the dynamics of polymer solutions [11].

Inelastic neutron scattering has been measured on the time-of-flight spectrometer Mibémol at the Laboratoire Léon Brillouin, Saclay, with an incident neutron wavelength of 8.5 Å, corresponding to a resolution of 8.4 GHz. In order to concentrate on the incoherent signal from the phenyl ring protons, the methyl group was hidden by using partially deuterated toluene-d$_3$ (euriso-top). As in our work on orthoterphenyl [12], the sample liquid was filled into thin capillaries which prevented crystallization down to 80 K. On further cooling towards 4 K, several tubes cracked so that the 80 K run had to be taken for normalization.

The raw data were reduced along the lines of reference [13]. Passing from the scattering law $S(2\theta, \omega)$ through constant wavenumber spectra $S(q, \omega)$ we obtained susceptibilities $\chi''(q, \omega) = \omega S(q, \omega)$. In order to safely exclude wings of the elastic line, we analyse only data above 35 GHz, except at the highest temperatures where $S(q, \omega)$ is so much broadened that resolution effects are negligible.

The vibrational maximum is located at a relatively low frequency of 600–700 GHz, and in contrast to most other glasses, the slope of the low-frequency wing of

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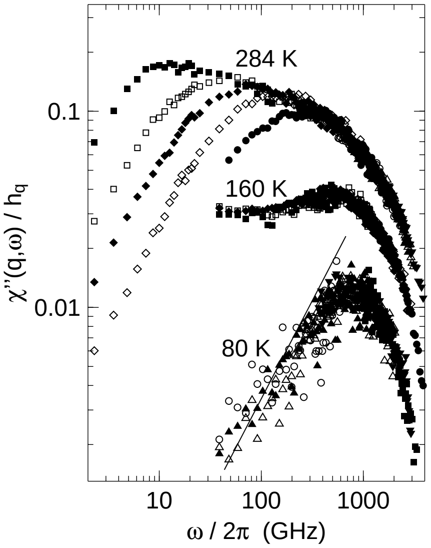

Fig. 1. Dynamic susceptibility $\chi''(q,\omega) = \omega S(q,\omega)$ from incoherent neutron scattering in toluene-d$_3$ for three selected temperatures. The data are rescaled by a factor h_q in order to demonstrate that the spectral lineshape is independent of wavenumber — except in the low-frequency α-relaxation limit where long-ranged transport leads to a strong q dependence. The straight line across the low-temperature data indicates a slope ω^1: toluene belongs to the few glasses which have no "boson" peak in $S(q,\omega)$.

the low-temperature susceptibilities is throughout smaller than ω^1, *i.e.*, toluene is one of the few glasses in which the scattering law shows no "boson peak".

At high temperatures, structural relaxation is so much stronger than the vibrations that the latter nearly disappear below the relaxational α-peak. Only in a small intermediate temperature range around 160 K, the susceptibility is seen to pass through a flat minimum.

Around the susceptibility minimum, mode coupling theory predicts that the β line shape is asymptotically the same for all experimental observables which couple to density fluctuations; thus *a fortiori* it must be the same for incoherent neutron susceptibilities measured at different wavenumbers q. A factorization of neutron spectra is also expected for harmonic vibrations in a disordered medium. To test this property, in Figure 1 we show rescaled susceptibilities $\hat{\chi}''_q(\omega) = \chi''(q,\omega)/h_q$ where the h_q have been calculated such that the $\hat{\chi}''_q$ for neighbouring q maximally overlap [14]. Depending on ω, wavenumbers between 0.5 and 1.8 Å^{-1} are included. Well around the susceptibility minimum, and up to the vibrational peak, the factorization is fully confirmed: all $\hat{\chi}''_q(\omega)$ coincide within a ±5% band except at the lowest temperature where count rates are low and statistical errors largely exceed 5%. At high temperatures and low frequencies, the factorization breaks down when $\chi''(q,\omega)$ bends over to the α peak: structural relaxation, as a nonlocal motion, depends strongly on q.

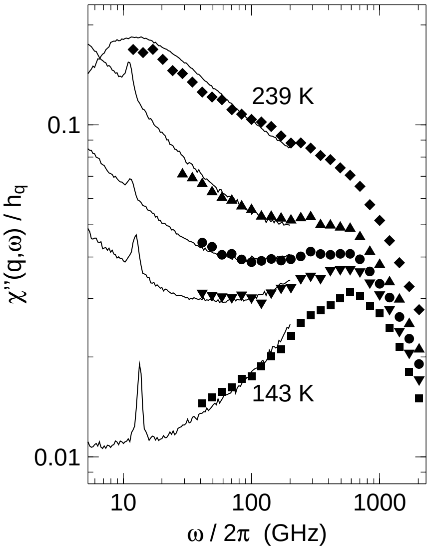

Fig. 2. Symbols show the susceptibility from incoherent neutron scattering, restricted to frequencies for which the line shape does not depend on wavenumber, and arbitrarily rescaled to $q = 1$ Å^{-1}. Solid lines show the susceptibility from depolarized light scattering, arbitrarily rescaled in intensity (the peaks around 12–15 GHz are due to the longitudinal acoustic mode leaking through the polarizer). In the β relaxation regime around the susceptibility minimum, both techniques are in full accord.

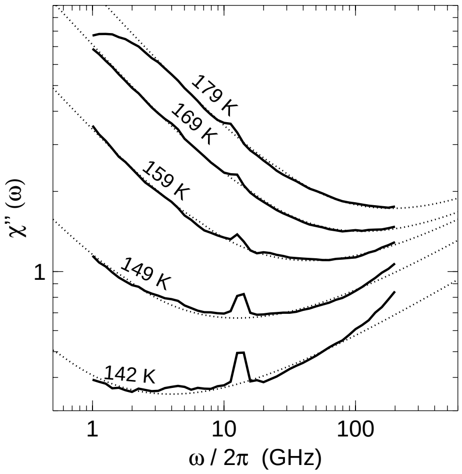

Fig. 3. Susceptibility from depolarized light scattering (solid lines) fitted by the asymptotic scaling function (1) of mode coupling theory.

Light scattering was measured using a 532 nm YAG laser at 150 mW and a Sandercock tandem interferometer in a set-up similar to that employed by other groups working in the field [15]. We choose depolarized 180° geometry in order to eclipse acoustic lines. For each temperature, scans taken with 9 different mirror spacings could be combined to cover frequencies between 1 and 200 GHz. In all scans, elastic scattering was suppressed by a mechanical shutter; no instrumental resolution effects have to be corrected for.

In this experiment, we used ordinary toluene-d$_0$ (Sigma-Aldrich); isotope effects on the slow dynamics are not to be expected. The sample was sealed under helium atmosphere into a duran cell. The highly viscous phase

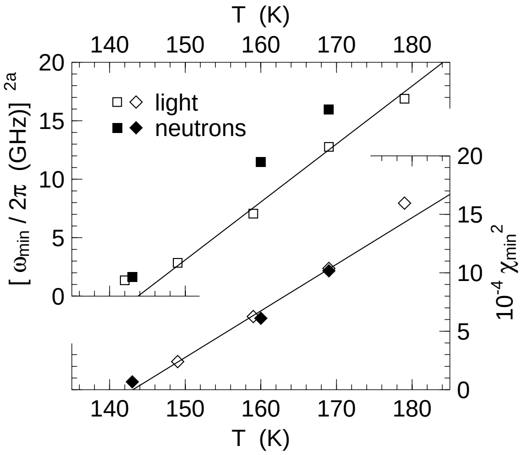

Fig. 4. Frequency $\omega_{\min}$ and amplitude $\chi_{\min}$ of the scaling function (1), linearized according to the mode coupling prediction (2). While the neutron scattering results for themselves would not allow a confirmation of theory, they are fully consistent with the light scattering data which extrapolate to a cross-over temperature $T_c = 143$ K.

between 120 and 140 K was inaccessible owing to crystallization; temperatures below 120 K could be reached by rapid quenching, but the scattering intensity was so weak that the data shall not be used for quantitative analysis. In contrast to neutron scattering, light scattering intensities are not obtained on an absolute scale; however, for temperatures between 149 and 179 K measurements were taken under strictly identical conditions so that at least some relative intensities could be determined.

We convert spectra into susceptibilities $\chi''(\omega) = \omega I(\omega)$. By arbitrary choosing intensities, the light scattering $\chi''(\omega)$ can then be directly compared to the q-independent neutron $\hat{\chi}''(\omega)$. As shown in Figure 2, around the minimum, both susceptibilities coincide; the accord is much better than in our previous study of glycerol [5]. Neutron and light scattering data combine to a consistent picture of the fast dynamics in toluene.

For a quantitative analysis, in Figure 3 the light scattering susceptibilities between 142 and 179 K are fitted with the β relaxation asymptote of mode coupling theory,

$$\chi''(\omega) = h_\sigma g_\lambda(\omega/\omega_\sigma) \qquad (1)$$

where the scaling function $g_\lambda(\tilde{\omega})$ is calculated from a tabulated expansion [16]; in an iterative procedure a line shape parameter $\lambda = 0.73 \pm 0.03$ was obtained.

In addition to λ, the fits (1) contain two adjustable parameters, h_σ and ω_σ. Mode coupling theory predicts that these parameters become singular on cooling towards T_c,

$$h_\sigma \propto \sigma^{1/2}\ , \text{ and } \omega_\sigma \propto \sigma^{1/2a} \qquad (2)$$

where σ is a reduced temperature $(T - T_c)/T_c$, and a is an exponent which depends on λ.

Figure 4 demonstrates that both parameters follow indeed (2). They consistently extrapolate to a critical temperature $T_c = 143 \pm 3$ K. Encouraged by the accord between neutron and light scattering data, we applied (1) also to the rescaled neutron susceptibilities. As shown in Figure 4, there is again good accord between neutron and light scattering; the neutron results are consistent with (2) and with $T_c \simeq 143$ K.

In conclusion, the GHz–THz dynamics of supercooled toluene turned out to be perfectly described by mode coupling theory, the asymptotic scaling laws holding better than in most other model systems. This may be correlated with the simple structure of toluene or with its high fragility: actually, the most complete experimental verification of mode coupling theory has been achieved in $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ [17] which is both a very simple and a very fragile liquid; in other, more complicated molecular liquids like glycerol [5] or salol [17] the asymptotic β region is much narrower, and the accord between neutron and light scattering is only moderate [5,6]. It may be further correlated with the strength of vibrational excitations [18]: in systems like glycerol, the high-frequency wing of $g_\lambda(\tilde{\omega})$ is mostly hidden under the boson peak which is absent in toluene, just as it is in $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ [19].

The crossover temperature 143 K is in remarkable accord with the early estimate $T_c = 1.2\,T_g$ based on a corresponding states analysis of viscosity data [20]. Even more remarkably, it is exactly the temperature below which in recent dielectric loss measurements [21] the slow (Johari-Goldstein) β process was found to separate from α relaxation.

All experimental results give a consistent picture if T_c is interpreted as the border between two distinct dynamic regimes within the viscous liquid state. Above T_c, the collective motion is captured correctly by the simplest mode coupling approximation; different glass forming systems show very similar dynamic behaviour. Below T_c, another, slower transport mechanism takes the responsibility for the long-ranged α process, leaving open an intermediate time range where different localized processes may or may not occur: in this range, at temperatures around and below T_g and with frequencies of the order of 100 MHz, the NMR relaxation experiment had seen significant qualitative differences between OTP and toluene. Most probably, on approaching T_c, these differences disappear along with the Johari-Goldstein β mode.

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