High-frequency dielectric spectroscopy on glycerol

P. Lunkenheimer, A. Pimenov, B. Schiener, R. Böhmer(*) and A. Loidl

Institut für Festkörperphysik, Technische Hochschule Darmstadt
D-64289 Darmstadt, Germany

Abstract. – Dielectric spectroscopy has been performed on supercooled glycerol for frequencies $3\,\mu\mathrm{Hz} \leq \nu \leq 40$ GHz and temperatures between $100\ \mathrm{K} \leq T \leq 500$ K. Hence, the absorptive part of the dielectric susceptibility was measured at comparable frequencies as the dynamic susceptibility obtained by neutron and light scattering techniques. The characteristic timescales obtained from all experimental techniques essentially agree. However, the dielectric data as measured on the high-frequency wing of the loss spectra are not consistent with neutron and light scattering results which probe density fluctuations. We conclude that in glycerol at high frequencies the density fluctuations are dominated by local vibration excitations which are fully decoupled from the dipolar reorientations. The temperature dependence of the dielectric loss traces that of the spin-lattice relaxation times measured with NMR techniques and exhibits almost frequency-independent signatures near the calorimetric glass transition.

At present, the relaxation dynamics of glass-forming liquids is a matter of stimulating controversy [1]. Glycerol [$C_3H_5(OH)_3$], with a melting temperature $T_m = 291$ K and a calorimetric glass transition at $T_g \approx 185$ K, is a hydrogen-bonded material that easily can be supercooled and has been investigated in numerous attempts to test models and theories of the glass transition. Davidson and Cole [2] have introduced the phenomenological Cole-Davidson expression to fit dielectric data on glycerol. It is one of the examples used by Nagel and coworkers [3], [4] to demonstrate the universal scaling behaviour of glass-forming liquids. Dielectric data on glycerol have been used by Kremer, Schönhals and others [5], [6] to argue that the predictions of mode-coupling theory (MCT) [7] cannot be confirmed, while Wuttke *et al.* [8] and Rössler *et al.* [9] provided evidence that light scattering and neutron scattering data do qualitatively resemble the mode-coupling scenario. Finally, dielectric data on glycerol, amongst others, have been used by Menon and Nagel [10] to speculate that the static dielectric susceptibility diverges close to the Vogel-Fulcher temperature.

We investigated the complex dielectric permittivity for frequencies $3\,\mu\mathrm{Hz} \leq \nu \leq 40$ GHz, focusing on the high-frequency dispersion. The aim was to directly compare the dielectric loss, $\epsilon''(\nu, T)$, with the imaginary part of the dynamical susceptibility, $\chi''(\nu, T)$ as observed by neutron and light scattering techniques [8]. MCT [7] makes detailed predictions about density fluctuations at frequencies in between the α relaxation and the so-called microscopic peak [7].

(*) Present address: Institut für Physikalische Chemie, Johannes Gutenberg-Universität D-55099 Mainz, Germany.
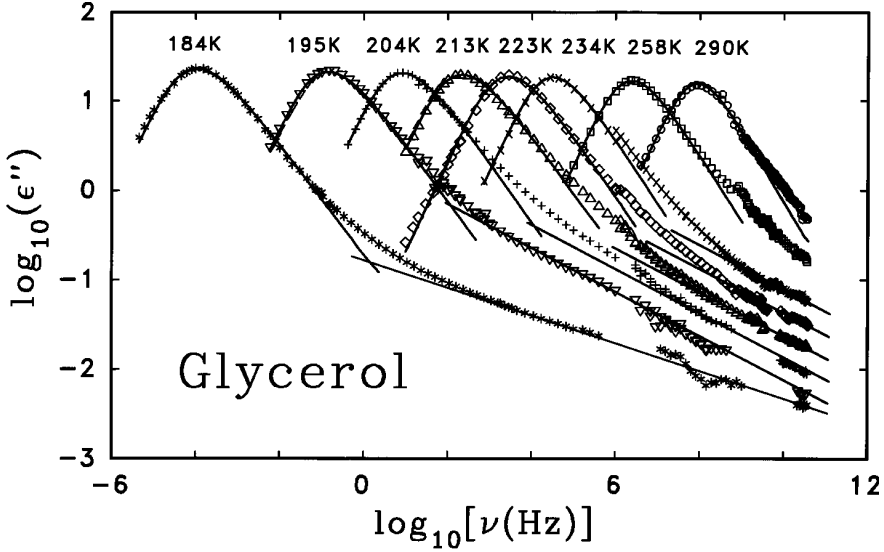
Fig. 1. – Frequency dependence of the dielectric loss in glycerol in a double-logarithmic representation. The solid lines represent a KWW fit for the peak maxima and a power law behaviour of the dielectric loss at the high-frequency tail.

Neutron and light scattering techniques yield susceptibilities that directly couple to density fluctuations and it has been shown by Wuttke *et al.* [8] that both methods, indeed, probe the same dynamics. At high frequencies the density fluctuations are dominated by local vibrational excitations giving rise to the so-called Boson peak [8]. Dielectric experiments measure dipolar reorientations and, *a priori*, it is unclear how strong these relaxations are coupled to density fluctuations [11]. Following a naive intuition it seems clear that the vibrational density of states is strongly decoupled from dipolar reorientation. On the other hand, reorientations in glycerol involve the tear and repair of hydrogen bonds. If structural relaxation occurs while the bond is ruptured, this process may also involve a mass transport. If the coupling of the dipolar active reorientational motions to the translational motions (density correlations) is weak, it seems obvious that the dielectric response not necessarily maps the dynamical susceptibility as determined from the density fluctuations. Depending on the strength of the rotation-translation coupling, this can be very sample specific and similar conclusions have been drawn by Cummins and Li [12] in the case of salol, in a reply to a comment of Dixon *et al.* [13].

The measurements on glycerol have been performed using time domain, frequency domain and microwave techniques. The microwave experiments were taken in reflection and, in the vicinity of 30 GHz, in transmission. To cover the complete frequency range, a single $\epsilon''(\nu)$ curve at a given temperature is superimposed using at least five different experimental set-ups. Due to small uncertainties in the geometrical capacitances it was necessary to shift the ϵ'' values of the different measurements with respect to each other to obtain an $\epsilon''(\nu)$ curve. This is particulary crucial if no overlap in the frequency range exists between the different data sets. It is important to note that $\epsilon''(\nu, T)$ obtained with one experimental set-up is shifted by one gauge factor only, which depends neither on frequency nor on temperature.

Figure 1 shows the imaginary part of the dielectric constant ϵ'' *vs.* frequency on a double-logarithmic plot. The data reveal the dramatic slowing-down of the mean relaxation rate of
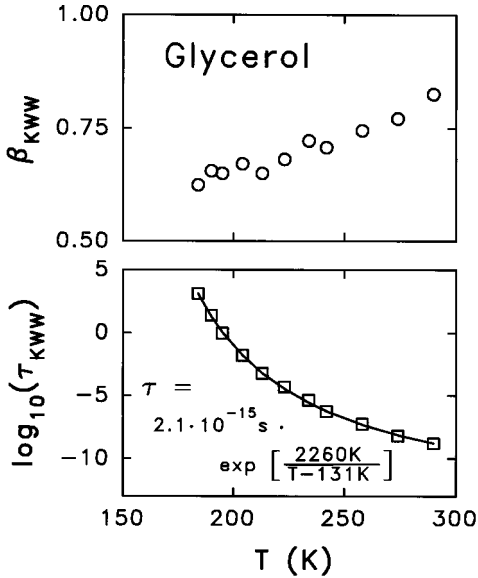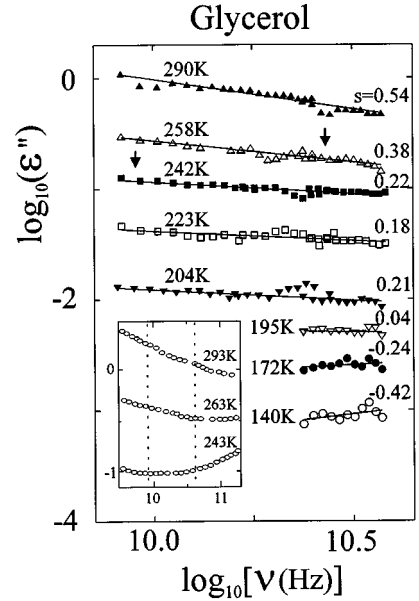
Fig. 2.

Fig. 3.

Fig. 2. – Temperature dependence of the KWW fit parameters: stretching exponent β_{KWW} and mean relaxation time τ_{KWW}. The solid line in the lower frame was calculated using the Vogel-Fulcher law, as indicated.

Fig. 3. – Frequency dependence of the dielectric loss in glycerol between 10 and 40 GHz on a double-logarithmic plot. The solid lines indicate a power law behaviour ν^{-s}, taking only the high-frequency data into account. The exponent s is indicated. The arrows at 258 K and 242 K data hint at the frequencies at which minima in the susceptibilities have been observed by neutron and light scattering investigations. The inset shows the neutron and optical results in the same frequency regime and at comparable temperatures (taken from ref. [8]).

the α process and, more importantly, that the shape of the loss peaks consists of two regimes: The regime close to the maximum that can be described by the Fourier transform of the Kohlrausch-Williams-Watts (KWW) function, $\phi_0 \exp[-(t/\tau)^{\beta}]$, with the stretching exponent β and a relaxation time τ. The KWW-type of spectrum is followed by a power law behaviour in the high-frequency wing of the loss peak, with an exponent s. It is possible to describe both the peak and the wing data above T_g (but not those below T_g) using a common expression within a model of dynamically correlated domains, see [14]. The absolute value of s is significantly smaller than the exponent β which describes the high-frequency side of the KWW function. The KWW function (transformed into the frequency domain) and the high-frequency power law are indicated as solid lines. The data provide some evidence that s is almost constant ($s \approx 0.23$) for $T > T_g$ (cf. straight lines for 195 K $\leq T \leq$ 234 K in fig. 1), but changes significantly for lower temperatures. In contrast, Hofmann *et al.* [6] by analysing their data for frequencies up to some 100 MHz below 230 K found a gradual increase of s with temperature, with $s = 0.23$ at 193 K and $s = 0.39$ at 263 K. By restricting the analysis of the data obtained in the present work to the same frequency range, we also find an increase of s with temperature, thus explaining the apparent discrepancy.

The temperature dependence of the most relevant parameters of the KWW fits, namely the stretching exponent β_{KWW} and the mean relaxation time τ_{KWW}, are given in fig. 2. In
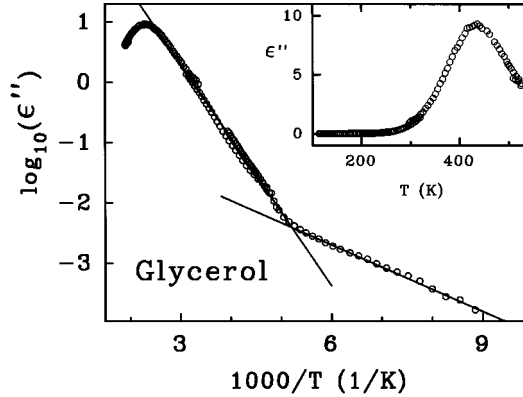
Fig. 4. – Temperature dependence of the dielectric loss ϵ'', measured at 30 GHz, in an Arrhenius-type representation. The solid lines are calculated using a thermally activated behaviour with energy barriers $E_B = 0.25$ eV ($T > T_g$) and $E_B = 0.07$ eV ($T < T_g$). The inset shows the raw data, $\epsilon''(T)$.

the temperature range investigated and with decreasing temperature, β_{KWW} decreases almost linearly from 0.8 to approximately 0.55 at T_g, while τ_{KWW} increases significantly stronger than thermally activated. It can be parameterized according to a Vogel-Fulcher law with a Vogel-Fulcher temperature $T_0 = 131$ K. β_{KWW} and τ_{KWW} are in close agreement with published data [3]-[6]. The static susceptibility, which can be determined by the area under the KWW peak, is steadily increasing with decreasing temperatures and can parameterized according to $\chi = 8875$ K/$(T - 52$ K), but, clearly, also other descriptions are possible.

The main result of the present investigation is shown in fig. 3. Here we plotted the high-frequency results, only. $\epsilon''(T)$ has been fitted using a simple power law behaviour, $\epsilon'' \approx \nu^{-s}$. It is clear that near room temperature the frequency dependence is strongly affected by the α relaxation (see fig. 1). The mean relaxation rate at 290 K is close to 100 MHz. Between 242 K and 200 K, the slope coincides with the slope as determined at lower frequencies. Approximately at T_g, $\epsilon''(\nu)$ becomes constant and a positive slope develops for $T < T_g$. The results of fig. 3 can be directly compared to the results as observed from neutron and light scattering experiments carried out at comparable frequencies (inset in fig. 3 [8]). The arrows, at the 258 K and 242 K data sets, indicate the minima observed with the latter techniques. The scaling behaviour of these minima and the exponents of the high- and low-frequency wings constitute fundamental results of the mode-coupling theory [7]. The dielectric results in glycerol exhibit no minimum in $\epsilon''(\nu)$ at $T > T_g$. Obviously $\epsilon''(\nu)$ probes a different quantity than $\chi''(\nu)$ as observed in neutron and light scattering experiments. Due to the fact that $\epsilon^*(\nu) = 1 + \chi^*(\nu)$, the imaginary parts of these two quantities should be equal if dielectric and neutron scattering techniques couple with equal strength to the same relaxation process. Hence, we conclude that at high frequencies ($\nu > 10$ GHz) dipolar reorientations in glycerol are not strongly coupled to the density fluctuations which determine $\chi''(\nu)$ as obtained from neutron and light scattering experiments. The most plausible explanation is that in those experiments the strong increase of the dynamical susceptibility for frequencies $\nu > 100$ GHz is due to local vibrational excitations. This is also clear by comparing the relative temperature dependence of ϵ'' (30 GHz) and χ'' (30 GHz) [8]. Between room temperature and T_g, ϵ'' decreases by almost three orders of magnitude, χ'' only by one. It is important to note that i) the slope b as determined dielectrically is in rough agreement with the slope s as determined from the neutron and light scattering results and ii) the slope $-s$ changes significantly for $T < T_g$. It approaches zero close

to T_{g}, and becomes even positive for further decreasing temperatures. A zero slope would meet the predictions of Menon and Nagel [10] concerning a divergence of the static susceptibility. However, a naive interpretation can be given alternatively: When the α process has slowed down to extremely long times, at low enough temperatures and at high frequencies $\epsilon''(\nu)$ must increase again towards the microscopic (infrared) peaks of the electrical absorption spectrum.

To elucidate the temperature dependence of $\epsilon''(\nu)$ at high frequencies in more detail, fig. 4 shows $\epsilon''(T)$ as measured, using a precision transmission technique, at 30 GHz in an Arrhenius-type representation. The inset of fig. 4 shows the raw data $\epsilon''(T)$ at 30 GHz. The peak maximum indicates the temperature at which the mean relaxation rate roughly equals the measuring frequency. Below the loss peak maximum, $\epsilon''(T)$ as measured at 30 GHz behaves as thermally activated with an energy barrier $E_{\mathrm{B}} \approx 2900$ K. A break of slope appears close to T_{g}. Below the calorimetric glass transition the barrier is reduced to a value $E_{\mathrm{B}} \approx 810$ K. This could indicate that at high temperatures the dielectric absorption is due to dipolar reorientations dominated by cooperative effects. Because of the rapid temperature dependence of the α process, the associated loss dies out and the absorption due to a different, second process can dominate the imaginary part of the dielectric susceptibility. Since this second process reveals a much lower hindering barrier, it may be ascribed to single-particle excitations. But of course one has to keep in mind that below T_{g} the sample is far from thermodynamic equilibrium. It is interesting to compare these findings with measurements of the spin-lattice relaxation times T_1 in several partly deuterated glycerols [15]. T_1 measures the spectral density in the MHz regime, which via the fluctuation dissipation theorem is proportional to the associated absorptive part of the susceptibility χ''. Since in the NMR investigation of ref. [15] a frequency-independent change of slope in the temperature dependence of the relaxation time is found near T_{g}, it is suggested that the dielectric experiment couples to the same degree of freedom (^{1}). This conjecture is supported by the fact that the activation energy of the low-temperature process deduced from fig. 4 is in close agreement with that observed in the NMR investigation. The observation of apparently frequency-independent anomalies in the vicinity of the calorimetric glass transition was recently also recognized in neutron scattering, Mössbauer and molecular-dynamics studies [16]. In those cases the anomaly was of vibrational origin.

(^{1}) Our data in the 50 MHz regime are not sufficiently accurate for $\epsilon'' < 10^{-2}$ in order to allow for a direct comparison with the NMR data.

REFERENCES

[1] See, *e.g.*, NGAI K. L., RIANDE E. and WRIGHT G. B. (Editors), *Relaxations in Complex Systems*, *J. Non-Cryst. Solids*, Vols. **1-2** (1994) 172-174.
[2] DAVIDSON D. W. and COLE R. H., *J. Chem. Phys.*, **18** (1950) 1417; *J. Chem. Phys.*, **19** (1951) 1484.
[3] DIXON P. K., WU L., NAGEL S. R., WILLIAMS B. D. and CARINI J. P., *Phys. Rev. Lett.*, **65** (1990) 1108.
[4] MENON N., O'BRIEN K. P., DIXON P. K., WU L., NAGEL S. R., WILLIAMS B. D. and CARINI J. P., *J. Non-Cryst. Solids*, **141** (1992) 61.
[5] SCHÖNHALS A., KREMER F., HOFMANN A., FISCHER E. W. and SCHLOSSER E., *Phys. Rev. Lett.*, **70** (1993) 3459.
[6] HOFMANN A., KREMER F., FISCHER E. W. and SCHÖNHALS A., in *Disorder Effects on Relaxational Processes*, edited by R. RICHERT and A. BLUMEN (Springer Verlag, Berlin) 1994, p. 309.

[7] GÖTZE W. and SJÖGREN L., *Rep. Prog. Phys.*, **55** (1992) 241 and references therein.

[8] WUTTKE J., HERNANDEZ J., LI G., CODDENS G., CUMMINS H. Z., FUJARA F., PETRY W. and SILLESCU H., *Phys. Rev. Lett.*, **72** (1994) 3052; WUTTKE J., PETRY W., CODDENS G. and FUJARA F., *Phys. Rev. B*, **52** (1995) 4026.

[9] RÖSSLER E., SOKOLOV A. P., KISLINK A. and QUITMANN D., *Phys. Rev. B*, **49** (1994) 14967.

[10] MENON N. and NAGEL S. R., *Phys. Rev. Lett.*, **74** (1995) 1230.

[11] BUCHALLA G., DESCH U., GÖTZE W. and SJÖGREN L., *J. Phys. C*, **21** (1988) 4239.

[12] CUMMINS H. Z. and LI G., *Phys. Rev. E*, **50** (1994) 1720.

[13] DIXON P. K., MENON N. and NAGEL S. R., *Phys. Rev. E*, **50** (1994) 1717.

[14] CHAMBERLIN R. V., *Phys. Rev. B*, **48** (1993) 15638.

[15] SCHNAUSS W., FUJARA F. and SILLESCU H., *J. Chem. Phys.*, **97** (1992) 1378.

[16] ANGELL C. A., POOLE P. H. and SHAO J., preprint.