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Loidl, Alois, Ulrich Schneider, Peter Lunkenheimer, and Robert Brand. 1998. “Dielectric and far infrared spectroscopy of glycerol.” *Journal of Non-Crystalline Solids* 235-237: 173–79. https://doi.org/10.1016/S0022-3093(98)00561-4.

Dielectric and far-infrared spectroscopy of glycerol

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1. Introduction

In recent years the high frequency dynamics of glass forming materials (in the GHz to THz frequency regime) has found increasing attention. This development was stimulated by the mode coupling theory (MCT) of the glass transition [1] which makes detailed predictions about the susceptibility, χ, in the frequency range between the α response and the high frequency microscopic bands. Previous experimental results which were obtained using neutron and light scattering techniques provided evidence for additional processes contributing in this regime and often showed good agreement with the theoretical predictions [2]. In addition, there exist a number of competing theoretical approaches as, e.g., the coupling model (CM) of Ngai et al. [3] the avoided critical point theory of Kivelson et al. [4] or the suggestion of Sokolov and Novikov [5] who proposed a coupling of vibrational and relaxational contributions for an explanation of the processes observed.

From the above considerations it becomes obvious that additional experimental data has to be collected to enable critical tests of the different theories. This requirement is especially true for dielectric measurements where there is a lack of data in the relevant frequency range, which is experimentally difficult to access. Only recently was it possible to obtain dielectric data covering a frequency range of more than 17 decades, to 950 GHz in glycerol [6–9] and to 380 GHz in propylene carbonate [8–10], $[Ca(NO_3)_2]_{0.4}[KNO_3]_{0.6}$ [8,10–12], and $[Ca(NO_3)_2]_{0.4}$ $[RbNO_3]_{0.6}$ [12]. However, the data, in comparison with the neutron and light scattering results, were still not complete: data at low temperatures, near T_g, were missing or incomplete and the frequency range was not sufficient to

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investigate the region of the microscopic or boson peak known from the scattering experiments. Now we are able to present dielectric data on glycerol in a considerably enlarged temperature range and extending well into the THz region. Dielectric experiments testing the orientational dynamics are especially important in the light of new theoretical developments extending MCT to molecules with orientational degrees of freedom [13,14].

In the present paper we will restrict ourselves to the presentation of the experimental results. An analysis of the data at $T > T_c$ within the idealized form of MCT has already been reported [7]. The aim of this paper is to provide a data set as complete as possible for future theoretical analyses.

2. Experimental procedures

Concerning the experimental details for the measurements up to 950 GHz we refer the reader to our previous publications [7–10].

In addition, recently we started to perform Fourier transform infrared spectroscopy using a modified spectrometer (Bruker IFS 113v). The apparatus extends the previously available range of frequencies to over 20 decades (3×10^{-6} – 3.6×10^{14} Hz).

We used a mercury lamp as a radiation source and a bolometer operating at liquid-He temperature as a detector. The temperature of the sample was set by a stream of N_2 gas. We used quartz-crystal plates as cell windows, which limit the frequency range to the far infrared (down to about 6 THz).

3. Results

Figs. 1 and 2 show $\varepsilon'(\nu)$ and $\varepsilon''(\nu)$ for various temperatures in the whole frequency range investigated. $\varepsilon''(\nu)$ (Fig. 2) shows the well known α relaxation peaks [6,15–17] which shift to higher frequencies with increasing temperature. They are

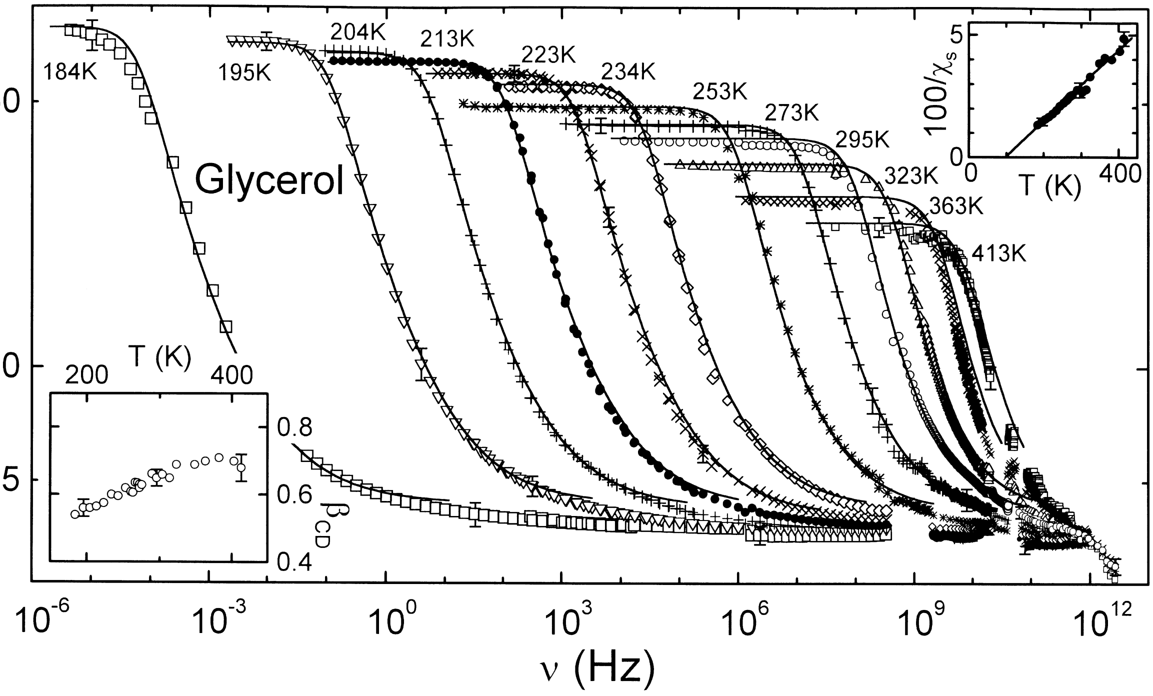

Fig. 1. Frequency dependence of the dielectric constant in glycerol at various temperatures. The lines are fits with the CD function performed simultaneously on ε''. The left inset shows the shape parameter $\beta_{CD}(T)$. The right inset shows the temperature dependence of the inverse static susceptibility. The line indicates a parameterization of the data with Curie–Weiß behavior.

accompanied by relaxation steps in $\varepsilon'(\nu)$ as seen in Fig. 1. The regime close to the maximum can be described by the Fourier transform of the Kohlrausch–Williams–Watts (KWW) function or by the Cole–Davidson (CD) function [15] as shown before [6,9]. The latter leads to better fits (compare the solid and dashed lines for 204 K in Fig. 2) which are shown as solid lines in Figs. 1 and 2. To obtain a model-independent measure of the α-relaxation time, τ, we plot the peak frequency, $\nu_p \approx 1/(2\pi\tau)$, in the inset of Fig. 2. It agrees well with previously published data [6,15–17] extending to somewhat higher temperatures. With decreasing temperature, ν_p decreases at a rate greater than thermally activated and can be parameterized using a Vogel–Fulcher–Tamman (VFT) law with a VFT temperature of 131 K. At temperatures, $T > 330$ K, deviations from VFT behavior occur which amount to a factor of 2 in frequency at 413 K. Similar results were reported in an earlier work [17]. The shape parameter, β_{CD}, resulting from the fits is shown in the left inset of Fig. 1. β_{CD} increases slightly with temperature and tends to become constant variance at $\beta \approx 0.7$ for $T > 300$ K. The temperature dependence of the static susceptibility obtained from these fits (right inset of Fig. 1) agrees with the results of Davidson and Cole [15]. It can be parameterized by a Curie–Weiß law with a Curie–Weiß temperature near 100 K but also other descriptions may be possible.

At frequencies, $\nu > \nu_p$, $\varepsilon''(\nu)$ follows a power law, $\varepsilon'' \sim \nu^{-\beta}$ (Fig. 2). At higher frequencies deviations from this power law occur: At temperatures $T > 253$ K, ε'' shows a smooth transition into a minimum while at lower temperatures a second power law ν^{-b} develops with $b < \beta$ before the minimum region is reached. The new high-precision measurements at $\nu > 40$ GHz presented here

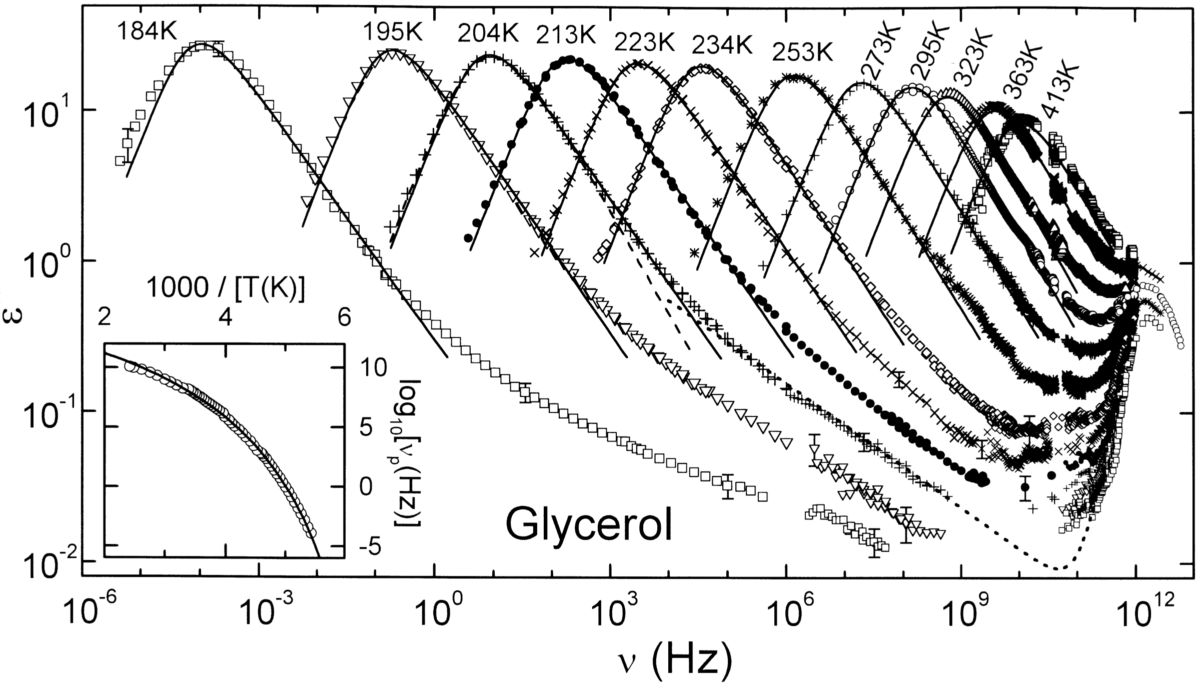

Fig. 2. Frequency dependence of the dielectric loss in glycerol at various temperatures. The solid lines are fits with the CD function, the dashed line is a fit with the Fourier transform of the KWW law. The dotted line has been calculated using the sum of two power laws. The inset shows the α relaxation peak frequency in an Arrhenius representation. It has been determined from the derivative of the loss curves. The experimental errors are $\Delta T = \pm 1$ K and $\Delta\nu_p = \pm 8\%$. The line is a fit using the VFT expression, $\nu_p = 5.6 \times 10^{13} \exp(-2160\ \text{K}/[T - 131\ \text{K}])$.

indicate that for $T < 234$ K this power law does not extend to as high frequencies as suggested by the measurements reported in Ref. [6]. This high frequency wing is accompanied by an additional decrease in $\varepsilon'(\nu)$ (Fig. 1). The wing is a commonly observed feature and often can be described by Nagel's universal scaling ansatz [18]. Its slope, b, was recently shown to decrease with decreasing temperature for various materials [19] as is also observed here.

Fig. 3 provides a magnified view of the ε'' data for $\nu > 60$ GHz. The $\varepsilon''(\nu)$-minimum already demonstrated to occur for temperatures above 250 K in our earlier work [7] is now observed down to $T_g \approx 185$ K (Figs. 2 and 3). With decreasing temperature, its amplitude and frequency decreases and its width increases. Near 2 THz a peak is observed. Its frequency is temperature independent within the experimental error and its amplitude increases with temperature. Corresponding to the microscopic peak in $\varepsilon''(\nu)$, $\varepsilon'(\nu)$ exhibits a steplike decrease near 1 THz (see inset of Fig. 3). For 363 K no minimum or no microscopic peak but only a plateau is detected. For lower temperatures the increase of $\varepsilon''(\nu)$ towards the peak becomes increasingly steep and finally reaches a power law ν^3

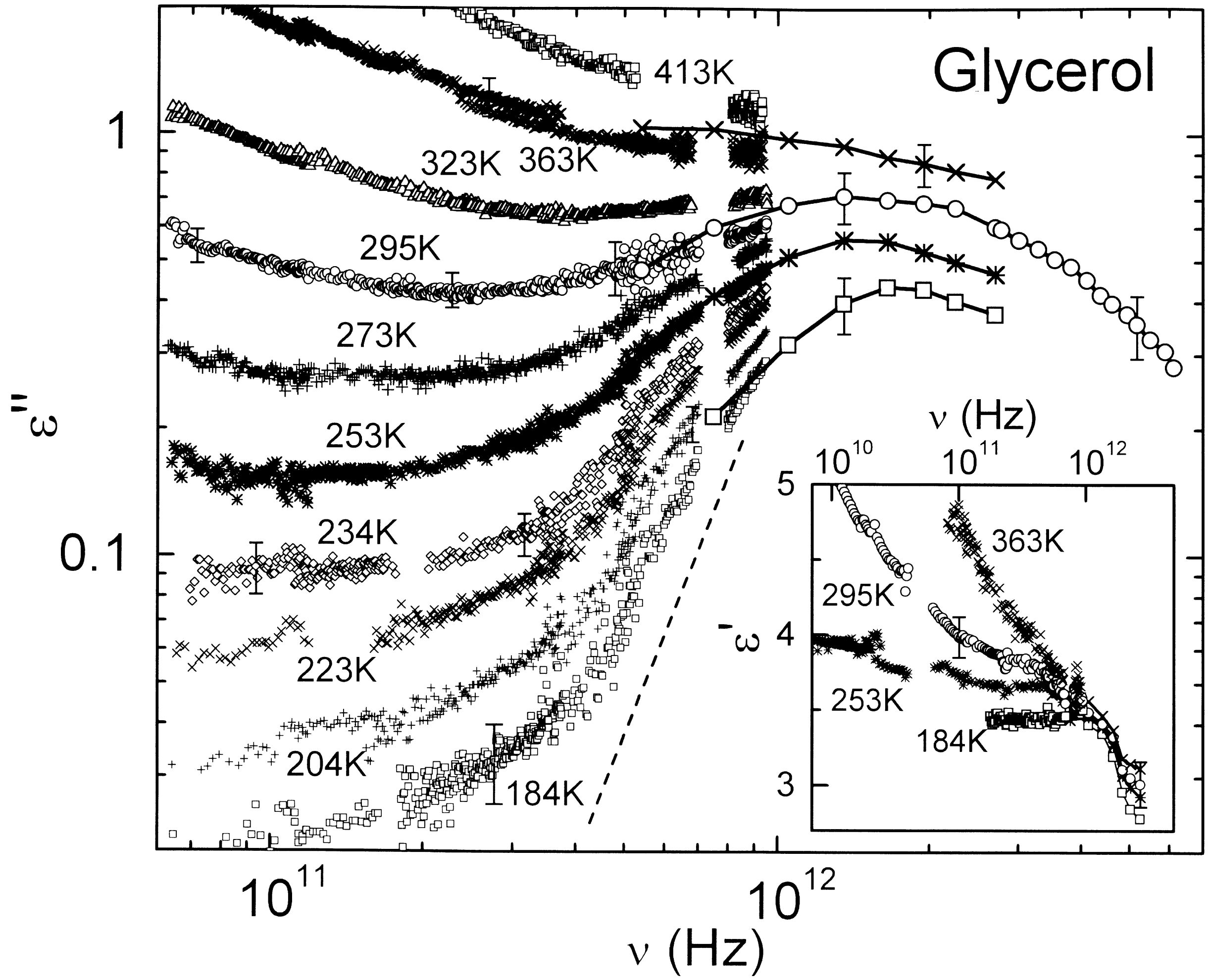

Fig. 3. Magnified view of the data of Fig. 2 at high frequencies. The dashed line indicates a power law ν^3. The solid lines in the infrared region are drawn to guide the eye. The inset shows the high frequency region of $\varepsilon'(\nu)$.

for 184 K (dashed line in Fig. 3). This finding excludes an explanation of the microscopic peak in terms of relaxational processes. Similarly steep increases were commonly found in glass forming systems using neutron and light scattering experiments [20]. In Fig. 4 we compare $\varepsilon''(\nu)$ with $\chi''(\nu)$ calculated from the neutron and light scattering results on glycerol [21]. As the scattering results give no information of the absolute magnitudes of χ'' the data sets have been scaled to the height of the α process for $T = 363$ K. The THz peak as determined from the dielectric experiments is located at the same frequency as that detected by neutron and light scattering and thereby can be identified with the boson peak. However, in comparison to the height of the α relaxation, the amplitude of this peak is much smaller than in the scattering experiments.

4. Discussion

We will restrict our discussion to the minimum region and the THz peak as the α relaxation region of glycerol has already been thoroughly investigated [6,15–17].

We have shown [7–9] that the $\varepsilon''(\nu)$-minimum at $T \geqslant 253$ K cannot be ascribed to a naive superposition of α relaxation and microscopic (or boson) peak. This becomes even more obvious for lower

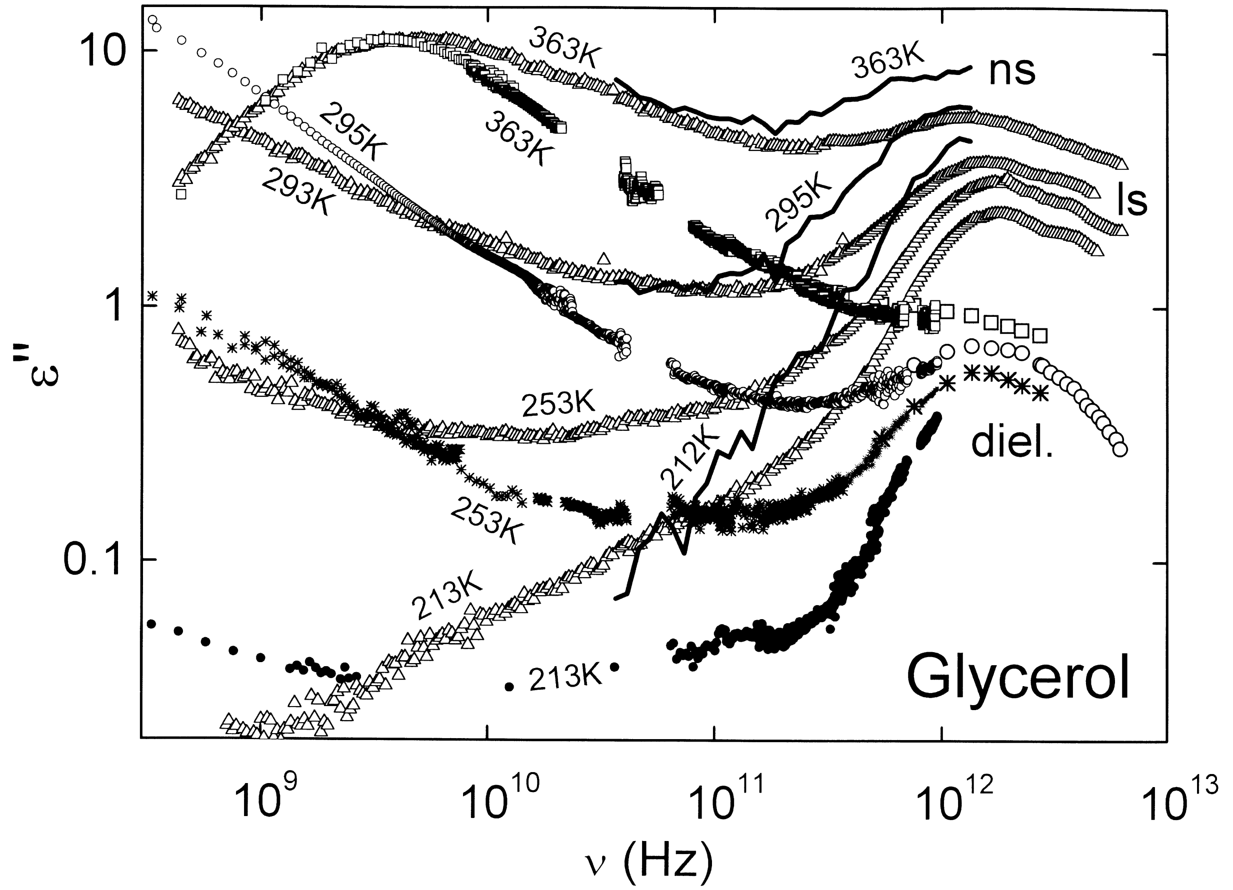

Fig. 4. Frequency dependence of the dielectric loss of glycerol compared to the imaginary part of the susceptibility as calculated from the light (△) and neutron scattering results (lines) of Wuttke et al. [21]. The scattering data sets have been vertically shifted to give a comparable intensity of the α process at 363 K. The error bars of the ε'' data are the same as in Figs. 2 and 3.

temperatures. The dotted line in Fig. 2 is the sum of two power laws describing the high-frequency wing of the α relaxation peak and the increase to the boson peak for 204 K. Clearly the minimum is too flat to be explained by this simple ansatz and additional processes have to be assumed to explain the data. It is interesting to note that at low temperatures $\varepsilon''(\nu)$ has only a small variation over a considerable frequency range which could be an indication of the constant loss behavior proposed by Wong and Angell [22].

The $\varepsilon''(\nu)$ data (Figs. 2 and 3), especially at low temperatures, indicate that the minimum region is composed of two regimes: a relatively wide and flat minimum and a steep increase to the boson peak. The boson peak seems to be an extra contribution superimposed on the minimum at high frequencies. This superposition was already suspected in our earlier publication to be responsible for the deviations from theoretical predictions for the minimum region observed above 300 MHz [7].

In Fig. 4, independent of the scaling procedure, it is obvious that the ratio of the amplitudes of the α peak and the boson peak as determined from dielectric measurements is larger if compared to the light scattering results. The same seems to be the case for the somewhat restricted neutron scattering results. In addition, the ε'' minimum obtained in the present work is located at frequencies differing from that of the χ'' minimum in the scattering results. A similar behavior was found in our dielectric experiments on propylene carbonate and Salol [9] and in molecular dynamics simulations of OTP [23] and of a system of rigid diatomic molecules [24,25]. An explanation for the difference of light scattering and dielectric results was given recently by considering the different dependencies of the probes on orientational fluctuations [26].

In a recent theoretical work [14] the MCT was generalized to molecular liquids of molecules with orientational degrees of freedom. The resulting MCT equations were solved for a system of dipolar hard spheres and a larger ratio of α and boson peak intensities for ε'' as found in the present work was obtained. However, the position of the minimum is predicted to be the same, independent of the experimental method [25]. A possible reason for the discrepancy to the experiment is the importance of 180° flips of the non-spherical molecules which cannot be taken into account by a hard sphere model [25].

5. Conclusions

With the present work for the first time we provide dielectric data on glycerol over 18 decades of frequency including the α peak response down to T_g and a peak at some THz which we identify with the boson peak. From a pure model-free examination of the data we conclude that the minimum observed in $\varepsilon''(\nu)$ includes contributions from fast processes in addition to the α process and the boson peak contribution.

Acknowledgements

We gratefully acknowledge stimulating discussions with C.A. Angell, W. Götze, K.L. Ngai, W. Petry, R. Schilling, L. Sjögren, and A.P. Sokolov. We thank J. Wuttke for supplying the light and neutron scattering results. This work was partly supported by the Deutsche Forschungsgemeinschaft, Grant-No. LO264/8-1.

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