

## Fast Dynamics of Glass-Forming Glycerol Studied by Dielectric Spectroscopy

P. Lunkenheimer, A. Pimenov, M. Dressel, Yu. G. Goncharov,\* R. Böhmer,† and A. Loidl

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

(Received 12 March 1996)

Dielectric spectroscopy up to 370 GHz has been performed on supercooled glycerol for temperatures between 250 and 330 K. The high-frequency dielectric loss,  $\epsilon''$ , has been investigated by coherent-source submillimeter-wave spectroscopy. Special attention is given to the dielectric loss in the crossover regime from the structural relaxation to the far-infrared response. A minimum is observed in  $\epsilon''(\nu)$  which is compared to theoretical concepts that predict fast relaxational processes. [S0031-9007(96)00624-2]

PACS numbers: 64.70.Pf, 77.22.Gm

At present, the relaxation dynamics of glass-forming liquids is a matter of stimulating controversy [1]. The relaxation patterns are nonexponential in time and depend much more heavily on temperature than thermally activated. These experimental facts have been collected applying numerous techniques and have been described within the framework of microscopic theories, phenomenological models, and scaling approaches [1].

Stimulated by predictions of the mode-coupling theory (MCT) [2] neutron and light scattering studies have recently focused on the dynamical susceptibility in the GHz-THz region (see, e.g., [3–8]). In this regime, MCT predicts the existence of a fast process which exhibits criticality close to a dynamic phase-transition temperature  $T_c$  which is located well above  $T_g$ . The critical behavior can be tested by measuring the frequency and temperature dependences of the generalized susceptibility in the region between the structural relaxation peak and the microscopic peak. Many of the results from neutron and light scattering experiments seem qualitatively to be in accord with the predictions of MCT. However, especially in strong glass-forming liquids [9], systematic deviations from the constraints set by the MCT have been detected, in particular, concerning the low-frequency tail of the far-infrared (FIR) response which exhibits a slope often significantly larger than predicted [6–8,10]. A fast process is also postulated by the coupling model (CM) of Ngai *et al.* [11]. At short times, the CM predicts relaxing entities that behave independently from each other and can be described using a Debye correlation function. On time scales longer than a crossover time,  $t_c$ , due to the onset of cooperativity, the dynamics slows down and changes to a stretched exponential [Kohlrausch-Williams-Watts (KWW)] behavior.

The fast process shows up in the crossover region between the structural relaxation and the far-infrared resonances and it is unclear to what extent vibrational excitations contribute to the experimentally observed susceptibility as obtained from neutron and light scattering techniques. In dielectric experiments this crossover region should show up as a minimum in the dielectric loss  $\epsilon''$ , but has never been observed and until now it was rather unclear if there is a minimum in  $\epsilon''(\nu)$  at

all. For example, the relaxation dynamics in glycerol has been studied over almost 16 decades in frequency, up to 40 GHz [12–15]. A minimum could not be detected at the temperatures and frequencies where light and neutron scattering results indicate a well developed minimum in the susceptibility [15]. However, it has been pointed out very early by Wong and Angell [16] that a minimum dielectric loss must exist in this crossover region and they predicted that at low temperatures a plateau should develop due to a constant (i.e., frequency independent) loss.

For the first time we present dielectric loss data on glycerol ranging up to 370 GHz. We have chosen glycerol since it has been studied in detail utilizing neutron [7,8] and light-scattering techniques [6,7], as well as by dielectric spectroscopy [12–15]. In addition, in glycerol ( $T_g \approx 190$  K) the structural and the dipolar relaxation are strongly coupled [17] and hence  $\epsilon''$  can be regarded as closely related to the generalized susceptibility. The radio-frequency experiments have been performed using reflectometric techniques. The microwave data were taken in reflection and transmission [15]. Above 60 GHz a quasioptical method is used [18] with a set of tunable backward-wave oscillators. The arrangement is a Mach-Zehnder interferometer and allows for measuring both the transmission coefficient and phase shift of the electromagnetic wave passing through the sample of a few millimeter thickness. From these two quantities the optical parameters such as  $\epsilon'(\nu)$  and  $\epsilon''(\nu)$  can be estimated [19]. We want to emphasize that the results presented in this work are shown in absolute values. No additional shifts were applied to obtain the almost perfect agreement of the individual data sets.

The data of  $\epsilon''(\nu)$  shown in Fig. 1 reveal a well developed  $\alpha$  peak which, close to the maximum, can be described by the Fourier transform of the KWW function,  $\phi_0 \exp[-(t/\tau)^\beta]$ , with the stretching exponent  $\beta$  and the relaxation time  $\tau$  (dashed lines) [13,15]. The exponent  $\beta$  increases with temperature varying between 0.65 at 180 K and 0.85 at 330 K. The relaxation time  $\tau$  increases significantly stronger than thermally activated and can be parametrized according to a Vogel-Fulcher (VF) law with a VF temperature close to 130 K [13,15].

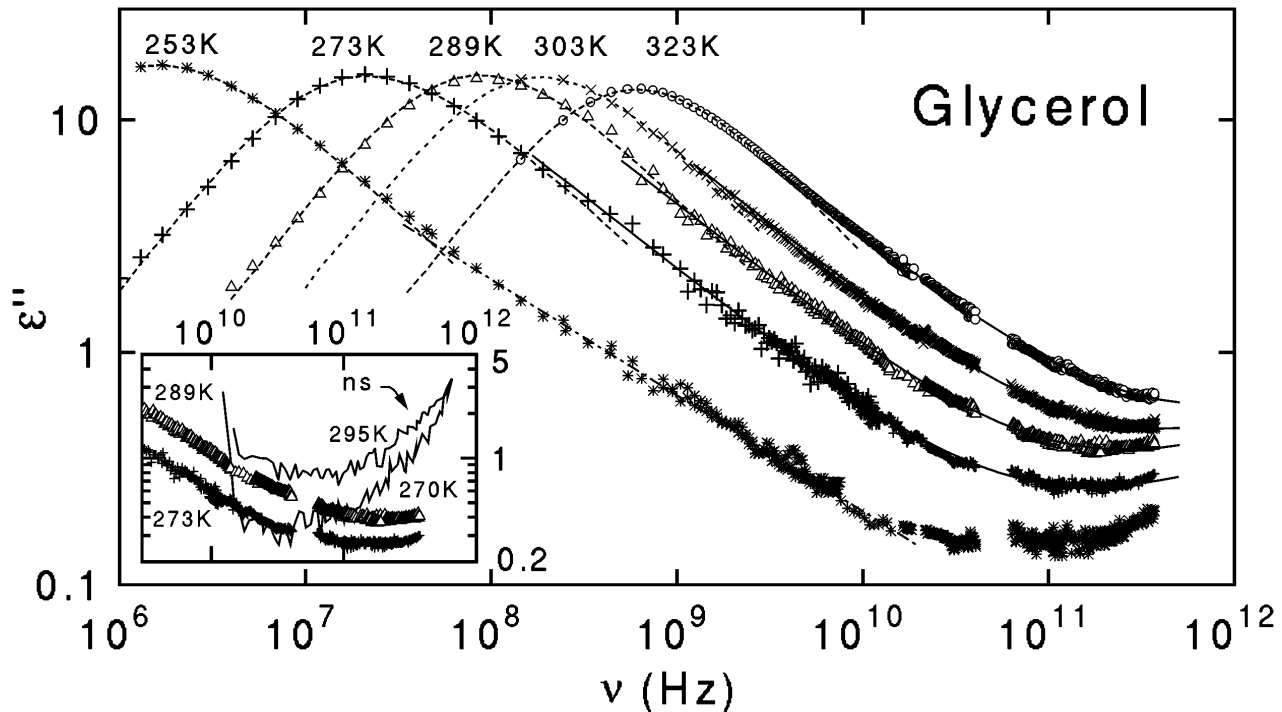


FIG. 1. Frequency dependence of the dielectric loss in glycerol at various temperatures in a double-logarithmic representation. The dashed lines are the results of fits using the Fourier transform of the KWW function. The solid lines are calculated from Eq. (1) with  $\lambda = 0.705$ . The dash-dotted line indicates the high-frequency "wing," observed at  $T < 260$  K. In the inset, the data are compared to the neutron scattering data (ns) as observed by Wuttke *et al.* [8] (solid lines) which have been calculated from the scattering cross section  $S$  using  $\epsilon'' \sim S\nu$ . For the scattering data, arbitrary units have been used.

At temperatures  $T > 260$  K, the high-frequency wing of the loss peak reveals only one power law which smoothly connects to the low-frequency side of the minimum (Fig. 1). In this regime the structural relaxation can be fitted much better using the Cole-Davidson (CD) ansatz [12] and, rather important, can be described by a constant  $\beta_{CD} = 0.63(\pm 0.02)$ . At lower temperatures, an additional power law develops at high frequencies (dash-dotted line) which significantly differs from the KWW and, to a lesser degree, also from the CD fit. At these temperatures, the  $\alpha$  response can be described perfectly well using Nagel's universal scaling ansatz [13].

In the inset of Fig. 1 the present dielectric results are compared with the neutron scattering data of Wuttke *et al.* [8]. The strong increase of the neutron data towards high frequencies is not reproduced by the dielectric results. Obviously, excitations of vibrational origin contribute to the density fluctuations measured by the neutron techniques but are not (or not so strongly) coupled to the dipolar reorientations which determine the dielectric response. This additional density of states, usually denoted as the boson peak, seems to significantly contribute to density correlations especially in strong liquids, as has been worked out in detail by Sokolov *et al.* [10]. It is an important point of this Letter that the boson peak does not play a significant role in the high-frequency dielectric spectroscopy. In the  $\alpha$ -relaxation regime the reorientation of the glycerol molecules involves the tear and repair of hy-

drogen bonds which leads to the observed strong coupling of structural and dipolar relaxation [17]. This obviously is not the case for the vibrational excitations connected to the boson peak which seem to be only weakly coupled to the rotations of the molecules.

The main goal of the present dielectric investigation is the analysis of the observed minimum in the dielectric loss at high frequencies. At first, we tried to analyze the minimum region in terms of a simple crossover from the structural relaxation to the FIR response. Figure 2(a) shows the dielectric loss vs frequency at 273 K, replotted from Fig. 1. The high frequency wing of the  $\alpha$  response follows a power law with an exponent of  $-0.63$ . The solid line in Fig. 2(a) represents a CD fit with  $\beta_{CD} = 0.63$ . The increase of  $\epsilon''$  towards the FIR bands is assumed to follow a power law with an exponent 1, a behavior that is common to a variety of glasses [20]. In the region of the minimum, the two contributions are assumed to be superimposed. Depending on the strength and the resonance frequency of the FIR peak, two possible scenarios are obtained [Fig. 2(a)]. In scenario 1 (dashed line) the height, but not the frequency of the minimum can be described correctly. In scenario 2 (dash-dotted line) the minimum is too deep and additional processes have to be considered. If one introduces an additional constant loss contribution [16], it is possible to obtain good fits to the data. However, to take account of the whole data set (Fig. 1), a *temperature dependent* constant

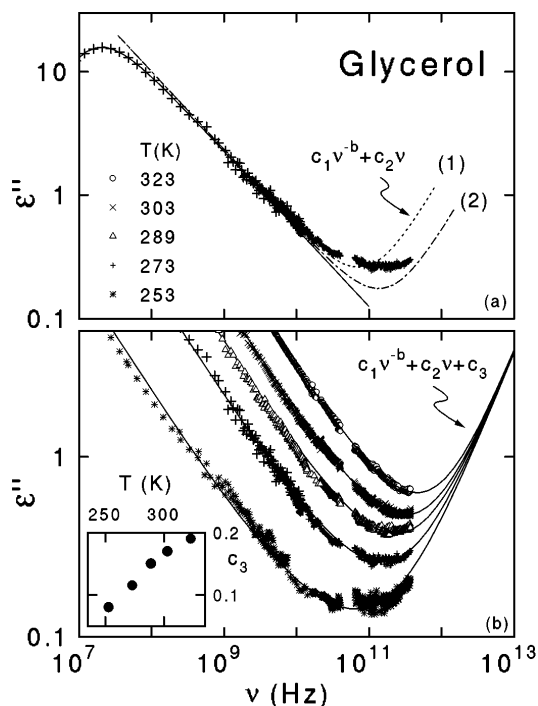


FIG. 2. (a) Frequency dependence of the dielectric loss in glycerol for 273 K. The solid line is a fit using the CD ansatz with  $\beta_{CD} = 0.63$ . The dashed and dash-dotted lines have been calculated using the expression indicated in the figure with  $b = 0.63$ . (b)  $\epsilon''(\nu)$  for various temperatures. The solid lines are fits by the expression indicated in the figure with  $b = 0.63$  and  $c_2 = 3.7 \times 10^{-13}$  for all temperatures. The resulting temperature dependence of  $c_3$  is shown in the inset.

loss is necessary, as demonstrated in Fig. 2(b). Here the experimental results were fitted using  $\epsilon'' = c_1\nu^{-b} + c_2\nu + c_3$ , with  $c_2 = 3.7 \times 10^{-13}$  and  $b = 0.63$ . The temperature dependence of the constant loss,  $c_3$ , is shown in the inset. It has to be stated clearly that there is no theoretical foundation of such an assumption. But from these considerations it becomes obvious that an additional process at high frequencies has to be taken into account. Fast processes are considered by the CM and the MCT.

Following the predictions of the CM, for large  $\beta$  values the fast process becomes less prominent and a minimum cannot be expected as a consequence of the fast process alone. In order to describe the minimum observed in the neutron and light-scattering experiments on glycerol [7,8], and also in the results of a molecular dynamics simulation of *ortho*-terphenyl [21]. Roland and co-workers [21,22] took into account additional vibrational contributions. But then again the problem of the temperature dependent constant loss is encountered.

In the following we try to describe our data using the MCT. Figure 3 gives an enlarged view of the minimum region. With decreasing temperature,  $\nu_{min}$  successively shifts into the frequency window. Both the minimum and the transition region to the  $\alpha$  process can be described by the MCT using the interpolation [2]

$$\epsilon''(\nu) = \epsilon''_{min} [a(\nu/\nu_{min})^{-b} + b(\nu/\nu_{min})^a] / (a + b). \quad (1)$$

The exponents  $a$  and  $b$  describe the high- and low-frequency wings of the minimum, respectively, which are identical for all temperatures and constrained by the exponent factor  $\lambda = \Gamma^2(1-a)/\Gamma(1-2a) = \Gamma^2(1+b)/\Gamma(1+2b)$  where  $\Gamma$  denotes the gamma function.  $\epsilon''_{min}$  and  $\nu_{min}$  are the height and the position of the minimum, respectively. The solid lines in Figs. 1 and 3 are obtained by Eq. (1) with  $\lambda = 0.705$  ( $a = 0.325$ ,  $b = 0.63$ ).

In Fig. 3 some discrepancies between data and fit become obvious at the highest frequencies investigated. This may well be due to the remainders of the excess vibrational contribution observed in the neutron- and light-scattering experiments. However, in contrast to the scattering results [6–8], this contribution is small enough to have only a negligible influence on the data for  $\nu \leq \nu_{min}$  and an unequivocal determination of  $\epsilon''_{min}$  and  $\nu_{min}$  should be possible. However, the deviations at high frequencies could also be interpreted as systematic deviations from MCT predictions. This has been documented by Sokolov *et al.* [10] for many glass-forming systems and ascribed to a coupling of vibrational and fast relaxational excitations [23].

The critical temperature  $T_c$  can be deduced from the temperature dependence of the  $\epsilon''$  minimum. From the scaling relations of MCT, it follows for  $T > T_c$  [2]:  $\epsilon''_{min} \sim (T - T_c)^{1/2}$  and  $\nu_{min} \sim (T - T_c)^{1/(2a)}$ . The MCT also predicts a critical temperature dependence of

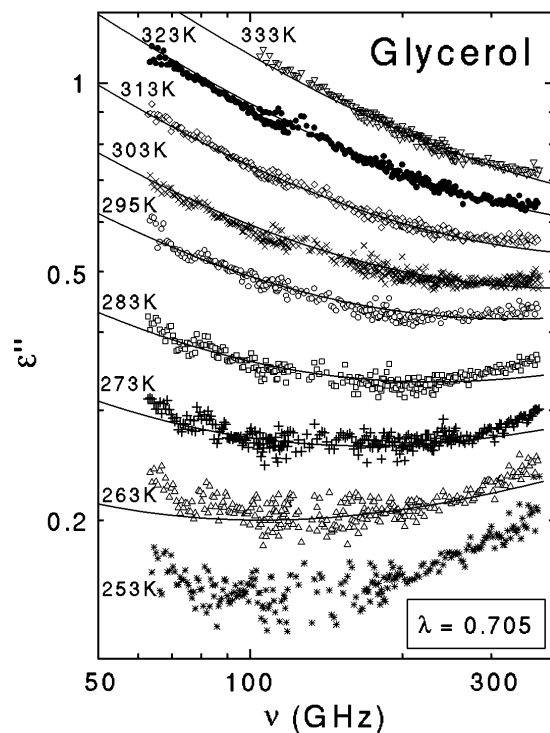


FIG. 3. Magnified view of  $\epsilon''(\nu)$  in glycerol at  $\nu > 50$  GHz. The lines are calculated from Eq. (1) with  $\lambda = 0.705$ .

the time scale of the  $\alpha$  process:  $\nu_{\max} \sim (T - T_c)^\gamma$  with  $\gamma = 1/(2a) + 1/(2b)$ . Figure 4 shows the experimental results for  $\epsilon_{\min}^2$ ,  $\nu_{\min}^{2a}$ , and  $\nu_{\max}^{1/\gamma}$  as a function of temperature. All three quantities can consistently be described assuming  $T_c = 262$  K (solid lines in Fig. 4). But clearly, only the plot  $\epsilon_{\min}^2(T)$  is really convincing. Near  $T_c$ , deviations from the MCT predictions are observed and may be ascribed to hopping processes, which can only be treated within advanced versions of the MCT [2].

Within MCT a temperature independent behavior of shape and relaxation strength,  $\Delta\epsilon$ , of the  $\alpha$ -relaxation process is expected for  $T > T_c$ . The published temperature dependences of  $\epsilon$  and  $\Delta\epsilon$  [14,15] are at variance to this prediction. However, in the relevant temperature range both quantities vary only weakly, and using a CD ansatz a reasonable description of the data (Fig. 1) is possible with a temperature independent  $\beta \approx 0.63$ .

In conclusion, for the first time we have presented high-frequency dielectric loss spectra of glycerol which reveal a susceptibility minimum. The spectra seem to be much less influenced by vibrational contributions than neutron and light-scattering results. The observed minimum in  $\epsilon''(\nu)$  cannot be described by a pure crossover from the  $\alpha$ -relaxational process to the far-infrared response but an additional temperature dependent constant loss contribution has to be assumed. The frequency and temperature dependences of the measured dielectric response are in rather good accord with the predictions of the MCT. However, we have to state clearly that, while the presented results give a clear hint to the origin of the pronounced deviations from MCT predictions as observed in the scattering exper-

iments, they do not constitute a final proof of the validity of MCT predictions in glycerol. Therefore further investigations of the dynamic susceptibility to higher frequencies and lower temperatures are highly desirable.

We acknowledge stimulating discussions with C.A. Angell, W. Götze, K. Ngai, W. Petry, and A.P. Sokolov. This research was partly supported by the SFB 262.

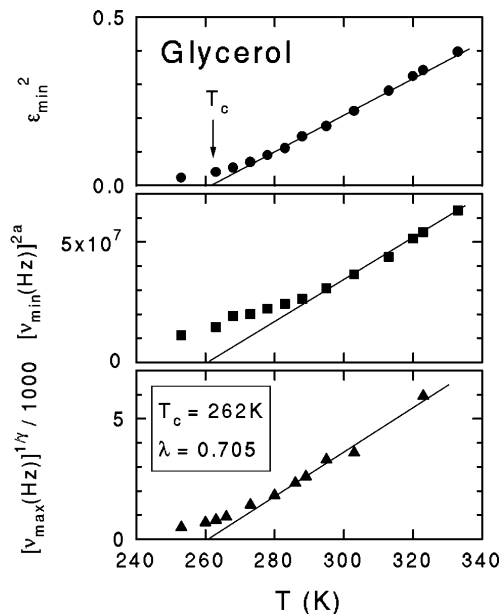


FIG. 4. Temperature dependence of the height,  $\epsilon_{\min}$ , and position,  $\nu_{\min}$ , of the dielectric loss minimum and of the peak position,  $\nu_{\max}$ , of the  $\alpha$  relaxation. The solid lines are consistent with a critical temperature of  $T_c = 262$  K.

\*Permanent address: Institute of General Physics, Russian Academy of Sciences, Moscow, Russia.

†Present address: Institut für Physikalische Chemie, Johannes Gutenberg-Universität, Mainz, Germany.

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