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Peter Lunkenheimer, Andrei Pimenov, Martin Dressel, B. Schiener, Ulrich Schneider, Alois Loidl

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Broadband Dielectric Spectroscopy on Glass Forming Liquids

P. LUNKENHEIMER, A. PIMENOV, M. DRESSEL, B. SCHIENER,*
U. SCHNEIDER and A. LOIDL

Experimentalphysik V, Universität Augsburg, D-86135 Augsburg, Germany
**Institut für Festkörperphysik, Technische Hochschule Darmstadt*
D-64289 Darmstadt, Germany

Dielectric spectroscopy covering 17 decades of frequency up to 380 GHz has been performed on the glass formers $[Ca(NO_3)_2]_{0.4}[KNO_3]_{0.6}$, $[Ca(NO_3)_2]_{0.4}[RbNO_3]_{0.6}$, and propylene-carbonate. Special attention is given to the dielectric loss ε'' in the crossover regime from the α-relaxation to the far infrared response. Our data cannot be described by a simple crossover from the α-process to the far infrared bands, instead we obtain clear evidence for additional processes prevailing in this frequency range. We compare the results for $\varepsilon''(\nu)$ with our previous results on glycerol and with the predictions of the mode coupling theory of the glass transition.

§1. Introduction

Despite an enormous theoretical and experimental progress,[1] the glass transition in viscous liquids is still an unresolved problem. Recent experimental studies of glass forming liquids focused on the investigation of the fast dynamics in the GHz-THz region (see, e.g., Refs. 2)-9)). This was stimulated by theoretical approaches where various scenarios have been proposed to describe or predict the dynamic susceptibility at high frequencies. Among them are the coupling model (CM)[10] and the avoided critical point theory[11] which both predict a fast process at high frequencies. On the basis of the universal scaling of the α-relaxation,[12] Nagel and coworkers proposed a divergence of the static susceptibility[13] which essentially implies a constant loss behavior at high frequencies and low temperatures as has earlier been predicted by Wong and Angell.[14] Maybe the most controversially discussed theoretical approach of the glass transition is the mode coupling theory (MCT)[15] which explains the glass transition in terms of a dynamic phase transition at a critical temperature T_c significantly above the glass transition temperature.

So far the high-frequency behavior (10^{10} Hz - 10^{13} Hz) of glass forming liquids has been investigated mainly by neutron and light scattering techniques (see, e.g., Refs. 2)-7)). Only recently, we were able to extend the frequency range of dielectric experiments on glass forming liquids up to some 100 GHz[8] using backward wave oscillators as coherent sources of electromagnetic radiation.[16),17] These experiments which have been performed on glycerol, for the first time revealed the existence of a relatively broad minimum in the frequency dependence of the dielectric loss $\varepsilon''(\nu)$ at frequencies above 100 GHz. Its functional form and temperature dependence cannot be explained by a simple crossover from the structural (α-) relaxation to the far infrared (FIR) response but is indicative of additional fast processes prevailing in this glass former.[8]

In the relatively strong,[18] hydrogen-bonded glass former glycerol (fragility parameter $m \approx 53$[19]), the dielectric spectra seem to be much less influenced by vibrational contributions than neutron and light scattering results. It can be assumed that in more fragile[18] glass formers the additional vibrational excitations, which give rise to the so-called Boson peak are less pronounced.[20] If these considerations are correct, for fragile glass formers the susceptibilities obtained by the scattering methods and by dielectric spectroscopy should agree. In dipolar systems as glycerol, the dielectric susceptibility couples mainly to the reorientational motions of the molecules and its coupling to the density fluctuations, considered by most theoretical approaches, is not well understood. It seems reasonable that for glycerol this coupling is achieved by the tear and repair of hydrogen bonds during the reorientational motion of the molecules. In contrast, in glass forming van der Waals liquids a weaker coupling of the dielectric response and the density fluctuations can be expected and it seems possible that for these materials the $\varepsilon''(\nu)$-minimum is much less pronounced. Another interesting case are molten salts which are characterized by mobile ions. Here a good coupling of the ionic motion, tested by dielectric spectroscopy, and the density fluctuations can be expected intuitively.

In the present paper we will give an overview of the results we obtained on the two fragile, molten salt glass formers $[Ca(NO_3)_2]_{0.4}[KNO_3]_{0.6}$ (CKN, $m \approx 94$) and $[Ca(NO_3)_2]_{0.4}[RbNO_3]_{0.6}$ (CRN, $m \approx 80$), and on the van der Waals liquid propylene-carbonate (PC, $m = 104$).

§2. Experimental details

Broadband dielectric measurements involve the use of various techniques. At frequencies 10 μHz $\leq \nu \leq$ 1 kHz measurements were performed in the time domain using a spectrometer that is based on a design described by Mopsik.[21] The autobalance bridge HP4284 was used in the range 20 Hz $\leq \nu \leq$ 1 MHz. For the radio-frequency and microwave range (1 MHz $\leq \nu \leq$ 10 GHz) a reflectometric technique was employed[22] using the HP4191 impedance analyzer and the HP8510 network analyzer. In addition, at frequencies 100 MHz $\leq \nu \leq$ 40 GHz data were taken in transmission with the HP8510 network analyzer using waveguides and coaxial lines filled with the sample material. Various ovens, closed-cycle refrigerators, and He-cryostats have been utilized to cover the various temperature ranges.

In the most relevant frequency range around some 100 GHz, quasi-optical measurements were performed by utilizing the submillimeter spectrometer "Epsilon".[16),17] Following the Mach-Zehnder setup the interferometer allows the determination of both components, the transmission coefficient and the change in phase upon passing of the electromagnetic wave through the sample. Three different backward wave oscillators were employed to continuously cover the frequency range from 60 GHz up to 380 GHz; the signal was detected by a Golay cell and amplified using lock-in technique. The liquids were put in specially designed cuvettes made of polished stainless steel with thin plane-parallel glass windows with a typical diameter of 15 mm; depending on the range of frequency and temperature the thickness of the sample cell was between 1 mm and 30 mm. The cell was placed at the end of

a cold finger of a continuous flow He^4-cryostat allowing to perform the experiments down to 10 K. High temperature measurements were carried out in a custom-made oven up to 500 K. The data were analysed by using optical formulas for multilayer interference[23] with the known thickness and optical parameters of the windows in order to get the real and imaginary part of the dielectric constant of the sample as a function of frequency at various temperatures.

To cover the complete frequency range, a single $\varepsilon''(\nu)$ curve at a given temperature combines results from different experimental setups. For the measurements at $\nu < 40$ GHz there are some uncertainties of the absolute values originating from an ill-defined geometry of the samples or parasitic elements. Therefore it often was necessary to shift the $\log \varepsilon''$ values of the measurements at the lower frequencies with respect to the high-frequency results in order to construct a smooth $\varepsilon''(\nu)$ curve. It is important to note, that $\varepsilon''(\nu, T)$ from each experimental setup is shifted by one gauge factor only, which depends neither on frequency nor on temperature. In addition, the high-frequency results provide a good estimate of the absolute values of ε' and ε''.

§3. Results and discussion

3.1. *CKN and CRN*

We have investigated the high-frequency dielectric response of the ionic conductors CKN ($T_g = 333$ K) and CRN ($T_g = 333$ K). Binary mixtures of potassium nitrate KNO_3 and calcium nitrate $Ca(NO_3)_2$ are well studied ion-conducting glass formers.[24),9)] The ionic mixture $[Ca(NO_3)_2]_{0.4}[KNO_3]_{0.6}$ ($T_g \approx 333$ K) was one of the first glass formers on which the high-frequency behavior has been examined using neutron[3)] and light scattering techniques.[4)] In addition, we investigated another nitrate mixture, that also can easily be vitrified: $[Ca(NO_3)_2]_{0.4}[RbNO_3]_{0.6}$ ($T_g \approx 333$ K). In a recent study up to 300 MHz[25)] in this compound dielectric properties similar to that of CKN have been found. Results from our group on ε'' of CKN up to 40 GHz have already been published elsewhere.[26)] Here we present data in an extended frequency range up to 380 GHz.

Figure 1 shows ε'' for CKN as a function of frequency ν in a double-logarithmic plot. $\varepsilon''(\nu)$ reveals a minimum similar to that observed with neutron[3)] and light scattering techniques.[4)] Indeed, when scaled appropriately, χ'' obtained from the scattering experiments[3),4)] agrees well with our results for ε'' as is shown in Fig. 2. Our data also agree reasonably well with the most recent data by the group of Funke[9)] which, however, are too incomplete to enable an unambiguous evaluation of the susceptibility minimum. The $\varepsilon''(\nu)$-minimum (Fig. 1) is relatively broad and, most important, exhibits a high-frequency wing which increases significantly less than $\varepsilon'' \sim \nu$ (indicated by the dotted line). At 342 K, $\varepsilon''(\nu)$ seems to become constant for $\nu < 1$ GHz. This may be due to the appearance of a constant loss region as predicted by Wong and Angell.[14)] However, at these low values of ε'' the uncertainty of the data is rather high and further measurements with better resolution have to be performed at low temperatures. The data for CRN resemble

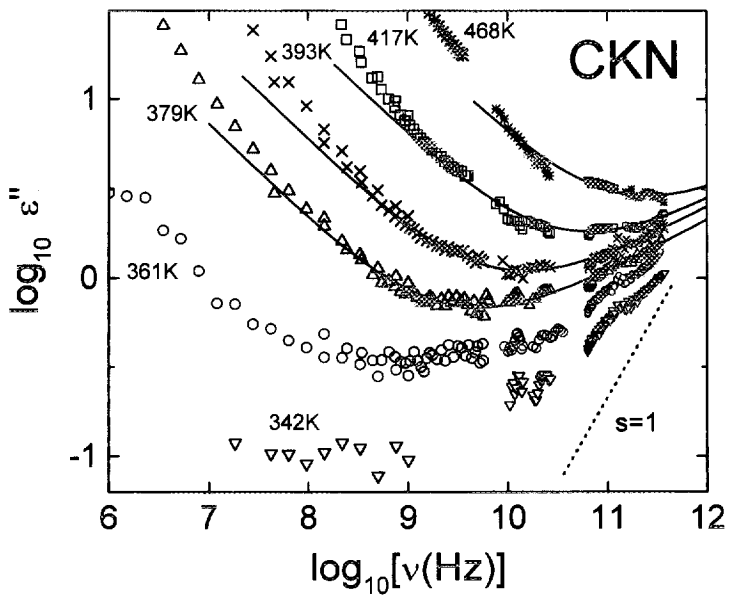

Fig. 1. Frequency dependence of the dielectric loss of CKN for various temperatures (double logarithmic representation). The solid lines are fits using Eq. (3·1). The dotted line indicates a linear behavior.

the results obtained for CKN with a relatively broad minimum, and a power law exponent at its high-frequency wing which clearly is smaller than unity.[27]

We want to emphazise that the observed $\varepsilon''(\nu)$-minimum cannot be described by a simple crossover from the α-relaxation response to the FIR absorption bands. In this case the increase of $\varepsilon''(\nu)$ towards the FIR bands follows a power law with an exponent equal or larger than unity, a behavior that is common to a variety of glasses.[28] Similar to our results in glycerol,[8] the $\varepsilon''(\nu)$-minima observed in CKN and CRN are too broad to be decribed by the simple ansatz $\varepsilon'' = c_1\nu^{-b} + c_2\nu^a$ with $a \geq 1$ and $b \leq 1$. In glycerol it was possible to describe the data by assuming an additional (temperature dependent) constant loss.[8] In CKN (Fig. 1) and CRN,[27] the minimum is located at significantly lower frequencies compared to glycerol[8] and the high-frequency slope of the $\varepsilon''(\nu)$-minimum cannot be described in this way. The difference between the experimental results and the dotted line with $s = 1$ (Fig. 1) gives an estimate of the additional high frequency processes in CKN and CRN in the GHz range. This behavior puts serious constraints to any theory describing the high-frequency response of viscous liquids. To our knowledge, the MCT is presently the only theory which predicts such a sublinear power law increase of $\varepsilon''(\nu)$ at frequencies above the minimum.[15]

According to these findings, in the following we try to compare our results with the scaling predictions of the simplest version of MCT. Both the minimum and the transition region to the α-process can be described by the MCT using the interpolation:[15]

$$\varepsilon''(\nu) = \varepsilon_{\min}[a(\nu/\nu_{\min})^{-b} + b(\nu/\nu_{\min})^a]/(a+b)\ . \qquad (3\cdot1)$$

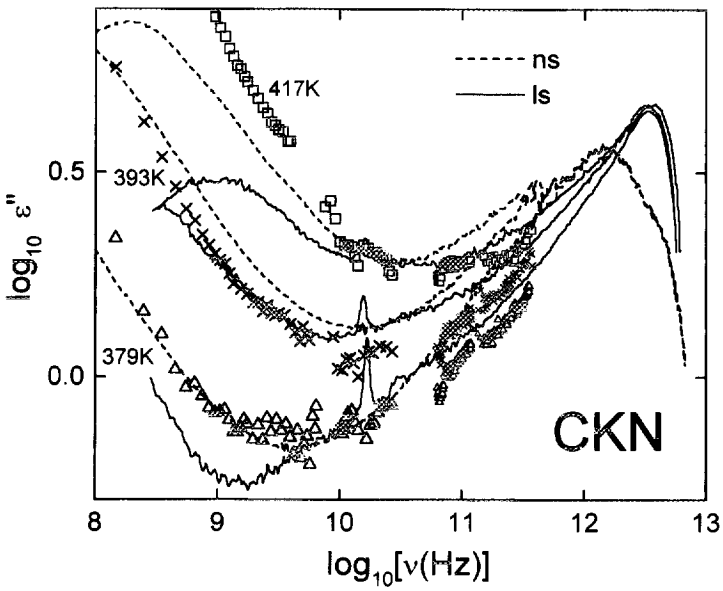

Fig. 2. High-frequency dielectric loss of CKN (symbols) compared with results obtained using neutron scattering[3] (dashed lines) and light scattering[4] (solid lines). The scattering results which have been obtained at 423 K, 403 K, and 383 K (from top to bottom) have been shifted along the ordinate axis to match the dielectric data near 10 GHz.

The exponents a and b describe the high and low frequency wing 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 Γ denotes the Gamma function. This restricts the exponent a to values below 0.4, i.e., a significantly sublinear increase of $\varepsilon''(\nu)$ at frequencies above the minimum is predicted. $\varepsilon_{\min}$ and $\nu_{\min}$ are the height and the position of the minimum, respectively. We fitted $\varepsilon''(\nu)$ using this formula. We obtain a consistent description of the ε''-minima using $\lambda = 0.76$ ($a = 0.3$, $b = 0.54$) for CKN (solid lines in Fig. 1) at $T \geq 379$ K and $\lambda = 0.91$ ($a = 0.2$, $b = 0.35$) for CRN.[27] At low frequencies, the fits underestimate the data. This may be ascribed to additional conductivity contributions which lead to a divergence of ε'' for decreasing frequencies. The parameters for CKN agree reasonably well with those obtained by Li et al.[4] ($a = 0.273$, $b = 0.458$, $\lambda = 0.811$) from fits of Eq. (3·1) to their light scattering results.

The critical temperature T_c should manifest itself in the temperature dependence of the $\varepsilon''(\nu)$-minimum.[15] MCT predicts for $T > T_c$: $\varepsilon_{\min} \sim (T - T_c)^{1/2}$ and $\nu_{\min} \sim (T - T_c)^{1/(2a)}$. The MCT also predicts a critical temperature dependence of the time scale of the α-process: $\nu_{\max} \sim (T - T_c)^{\gamma}$ with an exponent γ which is determined by the slopes of the susceptibility minimum: $\gamma = 1/(2a) + 1/(2b)$. Since the dielectric loss maxima are obscured by the dc-conduction process, we take $\nu_{\max}$ from the fits to the imaginary part of the dielectric modulus, $M'' = \mathrm{Im}(1/\varepsilon^*)$, published elsewhere.[25),26)] We are aware of the ongoing controversy about the use of the electrical modulus formalism;[29)] but we think that at least in CKN this procedure is justified by the fact that the relaxation times evaluated from $M''(\nu)$ at high temper-

atures closely follow those obtained from mechanical experiments.[26] Figure 3 shows the results for ε_{min}, ν_{min}, and ν_{max} for CKN (closed symbols) and CRN[27] (open symbols). Here representations have been chosen that lead to straight lines that extrapolate to T_c if the above critical temperature dependences are obeyed. Indeed for CKN all three data sets can consistently be described with a critical temperature $T_c \approx 375$ K as indicated by the solid lines. This compares well to the $T_c = 378$ K obtained by Li et al. from light scattering experiments.[4] For temperatures near T_c the data deviate from the predicted behavior, possibly due to hopping processes which are considered in extended versions of MCT.[15] For CRN the three quantities lead to values for T_c around 365 K which, however, differ by approximately 15 K (dashed lines in Fig. 3). In this context it is interesting that for λ close to unity the simple scaling relations mentioned above are expected to fail.[30]

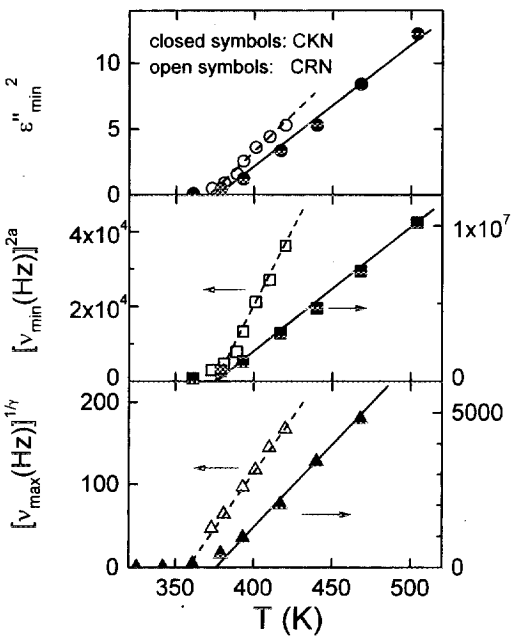

Fig. 3. Temperature dependence of the height and position of the dielectric loss minimum and of the α-peak position of CKN (closed symbols) and CRN (open symbols). Representations have been chosen that result in straight lines according to the predictions of the MCT. For CKN the solid lines extrapolate to a T_c of 375 K for all three quantities. For CRN T_c varies between 360 and 375 K.

The MCT predicts a significant change in the behavior of $\varepsilon''(\nu)$ at T_c: For $T < T_c$, $\varepsilon''(\nu)$ should exhibit a so-called "knee" at a frequency ν_k, i.e., a change of power law from $\varepsilon'' \sim \nu^a$ at $\nu > \nu_k$ to $\varepsilon'' \sim \nu$ at $\nu < \nu_k$. Indeed in CKN (Fig. 1) and CRN,[27] for $T < T_c$, the slope of $\varepsilon''(\nu)$ becomes larger than a, determined at $T > T_c$. But there is no clear indication of the "knee" and we have to stress that these data are at the edge of the resolution of the experimental setup.

3.2. *Propylene-carbonate*

Finally, we show first results on PC. Figure 4 shows the dielectric loss of PC over more than 17 decades of frequency. The data up to 1 GHz have already been published previously.[31] At low frequencies a well developed α-peak is observed which agrees well with the results from other groups.[32] At high frequencies a minimum shows up. The solid lines are fits using the MCT interpolation formula, Eq. (1) with $\lambda = 0.78$ ($a = 0.29$ and $b = 0.5$). The obtained λ is identical to that obtained from light scattering results[33] and also consistent with a recent analysis of solvation dynamics experiments.[34] The inset gives a magnified view of the high-frequency range. A good agreement of data and fits is

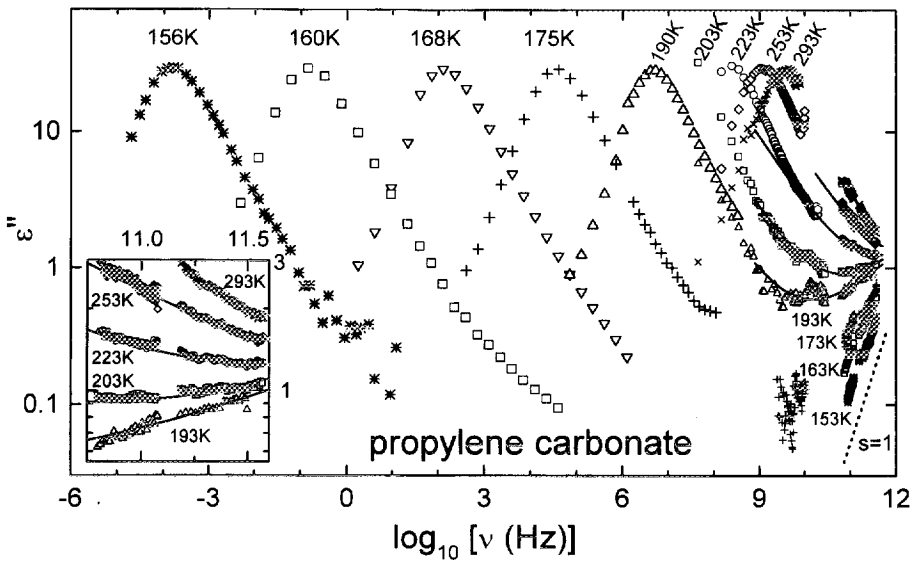

Fig. 4. Frequency dependence of the dielectric loss of PC for various temperatures (double logarithmic representation). The solid lines are fits using Eq. (3·1). The dotted line indicates a linear behavior. The inset gives a magnified view of the high-frequency behavior.

obtained. At temperatures $T \leq 193$ K the slope of $\varepsilon''(\nu)$ increases significantly and approaches a linear behavior (dotted line). This behavior could be indicative of the "knee" predicted by the MCT with ν_k located above the accessible frequency range. However, again we have to emphasize that the data are taken at the edge of the resolution of the instruments and further experiments have to be conducted to corroborate these preliminary low-temperature results. In Fig. 5 the critical behavior at T_c is examined. $\varepsilon_{\min}$, $\nu_{\min}$ and $\nu_{\max}$ are plotted according to MCT, the resulting straight lines extrapolate to T_c (cf. §3.1). Indeed the three quantities follow this prediction (solid lines) and a T_c of 187 K is obtained. This lies in the same range as the T_c obtained from light scattering[33] (179 K), neutron scattering[35] (180-200K), and solvation dynamics experiments[34] (176 K).

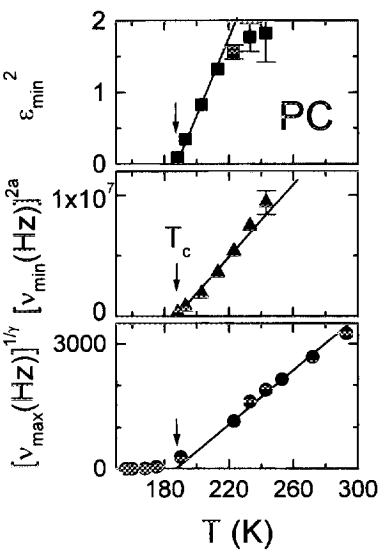

Fig. 5. Temperature dependence of the height and position of the dielectric loss minimum and of the α-peak position of PC. Representations have been chosen that result in straight lines according to the predictions of the MCT. The solid lines extrapolate to a T_c of 187 K for all three quantities.

§4. Conclusions

Together with our previously published data on glycerol,[8] we have now investigated the high-frequency dielectric loss spectra of four materials which belong to three very different classes of glass formers. The measured $\varepsilon''(\nu)$ of all materials investigated reveals a minimum at high frequencies. While in the relatively strong, hydrogen-bonded glass former glycerol, the dielectric spectra seem to be much less influenced by vibrational contributions than neutron and light scattering results, in the two ionically conducting glass formers CKN and CRN we find good agreement of the dielectric response with the susceptibilities as determined from the scattering experiments. In all materials investigated, the observed minimum in the frequency dependence of the dielectric loss cannot be described by a pure crossover from the α-relaxational process to the far-infrared response. The frequency and temperature dependences of the measured dielectric response including the α-process and the transition region to the microscopic peak are in rather good accord with the predictions of the MCT. The data show unambiguously that there are non-trivial additional processes contributing to the susceptibility at high frequencies which should be taken into account by any theoretical approach of the glass transition.

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