Some comments on the α -relaxation dynamics of supercooled CaKNO_3

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The relaxation data for $0.4\text{Ca}(\text{NO}_3)_2 \cdot 0.6\text{KNO}_3$ obtained for temperatures above 100°C by ultrasound measurements and by normal as well as by stimulated Brillouin scattering experiments are reanalyzed in order to show that they all obey the time temperature superposition principle with the same Kohlrausch model as master function. The data follow a similar pattern as the neutron scattering results and the molecular dynamics curves obtained for this system. The relaxation rates characterizing the elastic modulus, the neutron scattering law, the electrical conductivity, and the shear stress follow closely a universal curve. The experimental results are shown to be compatible with the mathematical picture of the α -relaxation process obtained by the mode coupling theory for supercooled liquid dynamics.

1. Introduction

The molten salt mixture $0.4\text{Ca}(\text{NO}_3)_2 \cdot 0.6\text{KNO}_3$, to be referred to as CKN, is one of the simplest glass forming systems. Its dynamics has been studied by several experimental techniques. In the supercooled liquid state there appear structural relaxation processes which manifest themselves as α -resonances in various susceptibility spectra. The relaxation times τ of these processes depend sensitively on the temperature T . The calorimetric glass transition is reached at $T_g = 60^\circ\text{C}$; it occurs when, roughly, τ is of macroscopic size [1,2]. Ultrasonic transmission experiments provided the longitudinal elastic modulus $M(\omega) = M'(\omega) + iM''(\omega)$ for frequencies ω between 1 and 200 MHz and $90 < T < 130^\circ\text{C}$ [3]. The dielectric modulus was measured between 23 and 93°C , where the α -peak position shifts from 1 Hz up to 1 MHz [4]. Brillouin scattering work [5–8] and stimulated Brillouin scattering experiments [9] explored the dynamics on the GHz scale. Inelastic neutron scattering work yielded information on the density fluctuations for frequencies below 200 GHz [10–13]. In the latter case the dynamics is probed on microscopic length scales; the wave vector q of the mea-

sured dynamical structure factor $S_q(\omega)$ is of the order of the inverse interparticle distance. Opposed to that the previously quoted experiments test the dynamics in the hydrodynamic limit $q \rightarrow 0$.

The neutron scattering work has identified a crossover temperature $T_c = 93 \pm 5^\circ\text{C}$ for the dynamics from one characteristic for a simple liquid to one typical for a glass [13]. Molecular dynamics work [14] has provided a variety of information on ionic motion on the same scales as are analyzed by neutron scattering. The quoted results yield a somewhat perplexing picture of the CKN dynamics. For example, the dielectric loss spectra [4] and further dynamic light scattering experiments [15] show asymmetric α -peaks on a $\log \omega$ abscissa. It was possible to describe the found dielectric α -process by the Kohlrausch relaxation model $\Phi(t) = f \exp[-(t/\tau)^\beta]$ with a Kohlrausch exponent $\beta < 1$. This result is similar to what one often observes in simple glass formers [16]. Yet, the acoustic data are fitted well [3] by a $\log \omega$ -normal distribution, where the latter implies a symmetric α -peak on a $\log \omega$ abscissa. The neutron scattering data have been fitted perfectly by a Kohlrausch model [10]. In particular, the parameters f and β were reported to be temperature independent for $T > 130^\circ\text{C}$. The same was found in the corresponding temperature interval for the molecular dynamics studies [14].

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The mentioned result corresponds to a scaling law for the α -relaxation process, which is occasionally referred to as the time temperature superposition principle. Identification of the scaling law is of great relevance since it is a strong hint to the cooperative nature of the α -relaxation process [16]. Yet, the light scattering data have been analyzed by formulas which correspond to temperature dependences of β as well as of f [5–9]. This analysis implies a violation of the time temperature superposition principle. An increase of β towards unity with increasing T was reported as a qualitative difference between $q=0$ and $q \neq 0$ dynamics [8].

In this paper we want to reanalyze the quoted data in order to show that they are indeed mutually consistent for $T > T_c$. As a byproduct it will become evident that the quoted results can be interpreted within a recently developed microscopic theory for the undercooled liquid dynamics. For a review of this so-called mode coupling theory and a reference list to the original papers the reader can consult ref. [17].

2. Analysis of the ultrasonic experiments

Let us start with the acoustic data for $M(\omega)$. The modulus determines the dynamical structure factor in the leading $q \rightarrow 0$ expansion via

$$S_q(\omega) \propto \frac{M''(\omega)/\omega}{[(\omega/q)^2 \rho - M'(\omega)]^2 + [M''(\omega)]^2}. \quad (1)$$

Here ρ is the mass density and the constant of proportionality in eq. (1) is independent of q and ω . Eq. (1) is derived under the assumption that there are no spatial long ranged correlations and that in the relevant ω - q domain couplings of density fluctuations with heat or concentration fluctuations can be neglected [18]. $M(\omega)$ is a special stress correlator.

The experiments demonstrate two important features of α -relaxation. First, there is stretching. The upper half of the detected resonances extends over about two decades frequency variation, i.e. the spectrum extends over a considerably larger frequency interval than expected for a stochastic relaxation process. Second, the spectra depend sensitively on temperature; a 10°C change of T shifts the resonance position by about one decade. Obviously, the available dynamical range of two decades is not sufficient

to compellingly determine details of the resonance shape, leave aside possible changes of the shape due to temperature variations. Data analysis for peaks, where only the upper half can be mapped out, is plagued by model assumptions. The seriousness of this reservation shall be exemplified by showing alternatives to previous data analysis.

Two convenient numbers for the characterization of the resonance are $M_0(T)$ and $M_\infty(T)$ [19]. The low frequency modulus $M_0 = M(\omega \rightarrow 0) = M'(\omega \rightarrow 0)$ quantifies the stiffness of the system with respect to compressions which vary with a frequency ω smaller than the α -peak frequency. One gets $M_0 = \rho c_0^2$, where c_0^2 is the derivative of the pressure with respect to ρ for fixed entropy. In the following we use the values ρ (g cm^{-3}) = $2.23 - 0.793 \times 10^{-3} T(^{\circ}\text{C})$ and c_0 (cm s^{-1}) = $2.01 \times 10^5 - 83.33 T(^{\circ}\text{C})$ [3]. The high frequency modulus M_∞ is the modulus for frequencies above the position of the α -peak. Its introduction depends on the assumption, that the α -process is well separated from high frequency excitations like, e.g., phonons. There should be a frequency interval, where M'' is zero and where M' exhibits a plateau. In glassy systems there are occasionally relaxation processes causing β -peaks [1,2]. They are located between the α -resonances and the frequency band of microscopic excitations. Without an established theoretical understanding it is impossible to clearly define the number M_∞ , a reservation which holds for all of the following considerations. Instead of M_∞ one can also introduce the dimensionless number

$$f_0 = 1 - M_0/M_\infty. \quad (2)$$

If the system were a solid, the dynamical structure factor would exhibit a strictly elastic peak on top of a continuum. Its relative area is the Debye–Waller factor $f_q: S_q(\omega)/S_q = \pi f_q \delta(\omega) + \text{continuum}$. Let us view the α -peak as a smearing of the elastic line to a narrow quasi elastic one and denote its area also as Debye–Waller factor. This factor has been measured for CKN by neutron spin echo experiments for some q as function of T [13]. Now one checks easily from eq. (1) that f_0 is the zero wave vector limit of the Debye–Waller factor: $f_0 = f_{q=0}$.

The normalized modulus $\hat{M}(\omega) = [M(\omega) - M_0]/(M_\infty - M_0)$ can be represented as Fourier transform of some relaxation function, normalized by $\Phi(t=0) = 1$:

$$\begin{aligned}\hat{M}''(\omega) &= \omega \int_0^{\infty} \cos(\omega t) \Phi(t) dt, \\ \hat{M}'(\omega) &= \omega \int_0^{\infty} \sin(\omega t) \Phi(t) dt.\end{aligned}\quad (3)$$

The dynamics, corresponding to the high frequency wing of the α -peak, can often be described by the von Schweidler relaxation law: $\Phi(t) = 1 - Bt^b$; $B > 0$, and $b < 1$ is some non-universal exponent [20]. This law implies for the spectrum

$$\log M''(\omega) = C - b \log(\omega \tau_L).$$

A double logarithmic plot of the data of ref. [3] exhibits this law reasonably with

$$b = 0.34 \pm 0.04. \quad (4)$$

One can shift the found straight lines parallel to the abscissa by choosing the relaxation time τ_L properly. The obtained results are shown by the crosses in fig. 5. The Kramers–Kronig relation then requires that

$$\log[M_{\infty} - \hat{M}'(\omega)] = \tilde{C} - b \log(\omega \tau_L).$$

So a double logarithmic plot should give straight lines of slope b , so that data for various T coincide. Optimizing this result by varying M_{∞} gives a means to determine M_{∞} . The result, converted to f_0 , is shown in fig. 3. The outcome of this analysis is shown as fig. 1 for the normalized modulus.

For $T > 111^\circ\text{C}$ the $\omega\tau > 1$ region cannot be reached and thus the validity of the von Schweidler model cannot be judged for these temperatures. One can, however, continue the analysis for $T < 111^\circ\text{C}$ in the specified frame as follows. One fixes τ_L as before by parallel shift of the data, with results shown in fig. 5.

The Kramers–Kronig relation also requires $\hat{M}''/(1 - \hat{M}') = \tan(\pi b/2)$. For the data $T < 111^\circ\text{C}$ this formula is an independent means to determine b experimentally. The value of b determined in this manner is $b = 0.31 \pm 0.02$. Fig. 2 shows all the data from ref. [3], normalized and shifted with f_0 and τ_L determined above. The results for the normalized modulus follow reasonably a master curve. The wing $\omega\tau_L \geq 10$ is described well by the specified von Schweidler law, which, naturally, fails for $\omega\tau_L \leq 1$. Fitting the data for $\omega\tau_L \leq 1$ by a Kohlrausch law,

Fig. 1. Absorptive part $\hat{M}''$ (a) and reactive part $1 - \hat{M}'$ (b) of the normalized longitudinal elastic modulus versus frequency ω in double logarithmic presentation. The data are from acoustic experiments of ref. [3] and refer respectively to: 93°C ($\square$), 96°C ($\diamond$), 99°C ($\triangle$), 102°C ($\circ$), 105°C ($+$), 108°C ($\times$), 111°C ($\diamond$). The straight lines have slope 0.34. The τ_L are shown in fig. 5 as crosses.

$\hat{M}(t) = \exp[-(t/\tau_L)^\beta]$, one gets $\beta = 0.44$ as exponent. The roughly temperature independent value of 0.57 is also found for f_0 for $T > 111^\circ\text{C}$. The fit deviates systematically a bit from the data for $\hat{M}'$ for $\omega\tau_L \geq 2$, because $\beta > b$.

If one wants to achieve an overall optimal fit one can stick to the mentioned Kohlrausch law but one has to optimize f_0 and τ_L differently below 111°C . Fig. 4 shows a corresponding result. The used f_0 differ from the ones mentioned by less than 2%; the scaling times τ'_L are larger than τ_L but $\log_{10}(\tau'_L/\tau_L) < 0.15$. Fig. 4 demonstrates that a fit of the normalized data in agreement with the time temperature principle is possible. The master curve can be chosen as Kohl-

Fig. 2. Absorptive part $\hat{M}''$ (a,c) and reactive part $\hat{M}'$ (b,d) of the longitudinal elastic modulus obtained from the data of ref. [3]. The symbols ($\square$), ($\diamond$), ($\triangle$), ($\circ$), (+), ($\times$), ($\diamond$) refer to the temperatures 90, 96, 102, 108, 114, 120, 126°C in (a, b) and to 93, 99, 105, 111, 117, 123, 129°C in (c, d). Parameters for the normalization and shifts f_0 , τ_L are shown in figs. 3, 5. The curves (b) result from the von Schweidler law with $b=0.34$. The other curves correspond to the Kohlrausch law $\hat{M}(\hat{t}) = \exp(-\hat{t}^\beta)$, $\hat{t} = t/\tau_L$, $\beta=0.44$.

rausch function. This corresponds to an asymmetric distribution of relaxation rates given by a temperature independent shape function. In ref. [3] a data fit was presented with a distribution of rates whose width decreased with increasing T . In the present notation this would correspond to the introduction of a T -dependent β . The fit in ref. [3] was done by anticipating a T decrease of M_∞ which is considerably larger than that one underlying fig. 4. At present there is no independent experimental information to rule out one or the other assumption on M_∞ .

3. Analysis of Brillouin scattering experiments

Brillouin scattering experiments determine two numbers: the position ω_p of the phonon peak and its half width at half height Δ . The determination of Δ requires assumptions on the background which are difficult to control [5]. Therefore some reservation concerning the reported Δ are necessary. Standard approximations relate the cross section to the dynamical structure factor and thus via eq. (1) to the longitudinal modulus. The resonance position fixes, essentially, $M'(\omega_p)$ and the width determines

Fig. 3. Debye-Waller factor f_q versus temperature. The upper values refer to the neutron scattering data for $q=1.7 \text{ \AA}^{-1}$. The values ($\square$) are reproduced from ref. [13]. The triangles with error bars are estimations from the data of ref. [10] analyzed with a Kohlrausch model for $\beta=0.58$. The upper dashed line corresponds to $f_q=0.84$, the value used for the scaling fit shown in ref. [10]. The lower values refer to $q=0$. The symbols ($\circ$) with error bars are obtained via the von Schweidler- and Kohlrausch-law analysis of the data of ref. [3] as explained in the text. The values ($\diamond$) are obtained from M_∞ of Brillouin scattering results [6] via eq. (2). The lower dashed line is the value $f_0=0.57$ used in the Kohlrausch fit for $T>105^\circ\text{C}$.

$M''(\omega_p)/M'(\omega_p)$. More precisely, one should use the formulae

$$M_L(\omega_p) = \frac{\rho\omega_p^2}{q^2} (1 + 2\delta'),$$

$$\frac{M''(\omega_p)}{M'(\omega_p)} = \frac{2\Delta}{\omega_p} (1 + \delta''), \quad (5)$$

where δ' and δ'' are correction factors determined by the modulus off the resonance position [18]. In the data analysis to be quoted δ' and δ'' are neglected. The possible error due to this neglect was pessimistically estimated to be up to 10% in M'' [18]. We have

Fig. 4. Normalized imaginary part (a) and real part (b) of the acoustic modulus calculated from the data of ref. [3] obtained in the interval $90 \leq T \leq 129^\circ\text{C}$. For normalization constant f_0 and scaling time τ_L' see text. The full curve corresponds to $\tilde{M}(t) = \exp[-(t/\tau_L')^\beta]$, $\beta=0.44$.

used Kohlrausch formulae for the modulus in order to convince ourselves that the error due to the neglect of δ' is smaller than 1% for $M'(\omega_p)$ and due to the neglect of δ'' is smaller than 5% for $M''(\omega_p)$ for CKN.

Brillouin scattering work is of particular interest since its dynamical range extends up to 10 GHz. It explores the range just below the band of the microscopic excitations typical for condensed matter. This range is obviously of importance if one wants to understand the gradual appearance of the α -peaks upon cooling the system towards the glass transition. A drawback of this technique is the dynamical range of only one decade. It is too small to map out the stretched resonances which are typical for glassy dy-

Fig. 5. α -relaxation times for temperature above $T_c = 93^\circ\text{C}$. (+) and ($\square$) are for the longitudinal elastic modulus obtained by ultrasonic transmission experiments [3] and by stimulated Brillouin scattering data [9]. ($\diamond$) refer to the data τ_n used for the scaling analysis of neutron scattering data in ref. [10]. (Δ) is given by the shear relaxation time $\tau_s = \eta/G_\infty$ with η from ref. [22] and G_∞ from ref. [6]. ($\circ$) refers to the relaxation time τ_σ obtained from the electrical conductivity in ref. [23]. The full curve is the power law $\tau_L = C_L [T_c / (T - T_c)]^\gamma$ with $T_c = 93^\circ\text{C}$, $\gamma = 4.06$.

namics. The problem of the unknown line shape is even more serious at the high frequencies used by Brillouin scattering methods, since there the problem of the separation of α - and β -relaxation is more relevant. Furthermore there is an unresolved problem, which causes reservations on using eq. (5) for the study of glassy systems. In ordinary condensed matter one can assume dipole moments of the ions to fluctuate on a frequency scale larger than the resonance value ω_p studied by Brillouin scattering [21]. Therefore the coupling of light to matter can be treated by the introduction of elasto-optic constants. But in glassy systems deviations from isotropy, deviations of pair distributions from the averaged value and the like will fluctuate partly on the same frequency scale $1/\tau_L$, which is to be analyzed. These fluctuations require the introduction of frequency

dependent generalizations $A(\omega) = A'(\omega) + iA''(\omega)$ of the elasto-optic constants. The usual approximation $A(\omega) \approx A(\omega=0)$ will not be valid for $\omega\tau_L \approx 1$ and therefore frequency dependent prefactors occur in the connection of $S_q(\omega)$ with the measured cross sections. The ω -dependence of $A(\omega)$ will mix with that of $M(\omega)$ and it is unclear how to disentangle these effects.

For $T < 90^\circ\text{C}$ the scattering work is done at such high frequencies relative to $1/\tau_L$ that the experiment determines M_∞ [6], and only this, with high accuracy. The corresponding results for f_0 , obtained from eq. (2), are shown in fig. 3 to extend smoothly the values discussed above. The Brillouin scattering data for $90 < T < 130^\circ\text{C}$ [5] shall not be considered here. For $T \approx 100^\circ\text{C}$ the neutron scattering work has identified a minimum in the susceptibility spectrum located at about 2.5 GHz [11,12]. The finding has been confirmed by molecular dynamics work on CKN [14]. The identified frequency and temperature variation of this spectral part is quite different from the one identified for the α -relaxation process. Hence it is clear now that in this range of temperatures and frequencies Brillouin scattering does not detect a clean α -process. The scattering data for $130 < T < 187^\circ\text{C}$ are not available for us in a form allowing a detailed analysis.

So we are left with the scattering data for $187 < T < 382^\circ\text{C}$. Fig. 6 shows a scaling analysis of the data from ref. [5]. The data at frequencies $\omega\tau_L > 10^2$, which correspond to temperatures below 130°C , are allowed to deviate from the Kohlrausch curve due to β -processes. Reduction of the modulus was done with a M_∞ which is obtained from eq. (2) with a temperature independent $f_0 = 0.57$, the dashed lower line in fig. 3. The relaxation times τ_L used are not treated as independent fit parameters. Rather they are extrapolations of other relaxation data according to eqs. (6) and (7) to be explained below. The data used for the extrapolation and the extrapolation curve are shown in fig. 5. The master curves shown in fig. 6 as full lines are Kohlrausch functions with the same $\beta = 0.44$ as used in figs. 2 and 4. The reactive part of the modulus is shown in fig. 6b to follow the time temperature superposition principle well. The absorptive part, which contains larger experimental uncertainties, shows some systematic deviations from the curve required by the experimental data for M' via a Kramers-

Fig. 6. Reduced elastic modulus as function of the logarithm of the rescaled frequency calculated from the Brillouin scattering data of ref. [5]. Reduction was done with M_∞ obtained in eq. (2) with $f_0 = 0.57$. The scaling times follow the full line in fig. 5, showing eq. (7). The full lines are Kohlrausch functions with $\beta = 0.44$.

Kronig relation. We anticipate that these deviations are still compatible with the experimental error bars and argue that the shown fit is not worse than the one proposed in ref. [7].

The conclusion on the violation of the time temperature superposition principle, implied in ref. [8], results from the assumption, that f_0 decreases appreciably below the lower line in fig. 3 used in our fit. There is no independent experimental evidence to argue against one or the other model for f_0 at present. Naturally, the fit in ref. [7], using the equivalent of T -dependent f_0 and β , involves more fit parameters than the two numbers underlying fig. 6. So one should

reasonably expect the fits of ref. [7] to be somewhat better than the ones shown here.

For $T < 90^\circ\text{C}$ Brillouin scattering detects also transversal excitations. The measured velocity of these shear waves provided the transversal high frequency shear modulus $G_\infty = 3.15 \times 10^{10}$ dyne/cm² [6]. Taking this value as temperature independent for $T > 110^\circ\text{C}$ one can use the known data for the viscosity η [21] in order to calculate via Maxwell's formula $\eta = \tau_s G_\infty$ a characteristic shear relaxation time τ_s . The results are shown in fig. 5.

4. Analysis of stimulated light scattering experiments

By stimulated Brillouin scattering one determines a non-linear response of the system which is approximately related to the Fourier backtransform $\chi_q(t)$ of $\omega S_q(\omega)$. Identifying a decaying wave contribution one determines two parameters: an oscillation period and a decay constant. As pointed out in ref. [9], the latter has an error in CKN as large as 10%. This is possibly caused by the problem of background subtraction due to further slowly relaxing contributions to $\chi_q(t)$. The two parameters can be related to the modulus as explained above. The dynamics of CKN was explored for $71 < T < 308^\circ\text{C}$ for a frequency range between 0.05 and 3.9 GHz [9].

In ref. [9] the data were analyzed with two assumptions. First, $1/M_\infty = (2.41 + 2.86 \times 10^{-2} T/^\circ\text{C}) \times 10^{-12}$ cm²/dyne was used from ref. [5] in order to determine the normalized modulus $\hat{M}$. Second, the α -resonance was modelled by the Cole-Cole susceptibility expression: $\hat{M}_{CC} = 1/[1 + (-i\omega\tau_0)^\alpha]$. Here $\alpha \leq 1$ is a non-trivial exponent characterizing stretching. It was found that α increases with temperature, a result which was declared [9] as confirmation of the earlier finding by normal Brillouin scattering experiments [7]. The Cole-Cole model yields a spectral peak M''_{CC} which is symmetric on a log ω abscissa. So the model used in ref. [9] agrees in this respect with the one used in ref. [3] but it disagrees with the picture underlying the analysis in ref. [7]. The same three reasons for reservations, explained in detail above, apply for the results of stimulated Brillouin scattering: the used relation between signal and modulus is not well established; there is no experimental evidence for the assumed $M_\infty(T)$; the data

for $T \approx 100^\circ\text{C}$ presumably do not refer to α -relaxation.

So far there is no experimental or theoretical reason to doubt that glassy systems at high temperatures exhibit normal hydrodynamic behaviour. With $[M(\omega) - M_0]/\omega = F(\omega)$ the existence of a hydrodynamic limit is equivalent to the existence of the low frequency limit $F(\omega \rightarrow 0) = i\eta_L$, where η_L denotes the longitudinal viscosity. The limit exists, if a Kohlrausch law is used for $\hat{M}$, no matter what is the value of exponent β , as can be inferred from (3). The low frequency limit of the Cole–Cole expression reads $M_{CC}(\omega\tau_0 \ll 1) = 1 - (-i\omega\tau_0)^\alpha$. Therefore $F(\omega) \propto 1/\omega^{1-\alpha}$, and the limit does not exist unless $\alpha = 1$. Notice that the specified qualitative discrepancy between Kohlrausch law and Cole–Cole law in the very low frequency limit is unrelated to the problem of validity of the time temperature superposition principle. The reported finding $\alpha \rightarrow 1$ [9] for large T , i.e. for small τ_0 , merely confirms, that the system approaches normal hydrodynamic behaviour. It is a misinterpretation [9] to relate this finding to the stretching phenomenon.

Fig. 7 exhibits a scaling analysis of the data of ref. [9] for $100 < T < 230^\circ\text{C}$. As done before, $f_0 = 0.57$ is used as temperature independent. The scaling times τ_L are not treated as fit parameters. Rather they are taken directly from the frequencies ω_L of the absorption peaks of ref. [9]; $\omega_L\tau_L = 1$. The τ_L are shown in fig. 5. The full curve exhibits the same Kohlrausch law with exponent $\beta = 0.44$ as used above in figs. 2, 4, 6. In view of the anticipated experimental uncertainties for $\hat{M}''$ one concludes that the results are compatible with the time temperature superposition principle. The Kohlrausch law fits the data within the experimental uncertainties.

5. Discussion

Let us consider the various relaxation times compiled in fig. 5. In addition to τ_L , obtained for the elastic modulus in connection with fig. 2 and the stimulated Brillouin scattering in connection with fig. 7, data are shown for the relaxation time τ_n used for the scaling analysis of the neutron scattering data [10], the shear relaxation time τ_s obtained from the viscosity, and the relaxation time τ_σ derived in ref. [23] from electrical conductivity data. One should notice

Fig. 7. Reduced absorptive part $\hat{M}''$ (a) and reactive part $\hat{M}'$ (b) of the longitudinal elastic modulus versus $\log \omega\tau$, as determined for $100 < T < 230^\circ\text{C}$ from the stimulated Brillouin scattering results of ref. [9]. The symbols ($\square$), ($\diamond$), (Δ), ($\circ$), ($\times$), ($\oplus$) stand for data obtained within $\pm 1^\circ\text{C}$ at the temperatures 99, 109, 177, 185, 195, 218°C . (+) denote other temperatures where less than three frequencies belong to a fixed temperature. The reduction was done with a temperature independent $f_0 = 0.57$ and eq. (2). The relaxation time τ_L was directly determined from the absorption peaks ω_L reported in ref. [9] via $\omega_L\tau_L = 1$; the τ_L are shown in fig. 5. The full curves represent Kohlrausch functions with $\beta = 0.44$.

that the relaxation processes described by these four time scales are pairwise quite different.

There is some arbitrariness in the definition of a relaxation time. If a certain α -process is considered and described by the normalized function $\Phi(t)$, one can define τ , e.g., by requiring $\Phi(\tau) = 1/e$. One can also look for the maximum ω_m of the susceptibility spectrum and define $\tau = 1/\omega_m$. Another way would

be to consider the inflection point of the reactivity curve ω_i and use $\tau = 1/\omega_i$. The definition for τ_s used above corresponds to define a time by the low frequency expansion $\omega\Phi(\omega) = 1 - i\omega\tau$, etc. For a Debye process, accidentally, all mentioned four definitions yield the same number for τ . But for a Kohlrausch process with $\beta < 1$ all four numbers are pairwise different. Because of this arbitrariness it makes no sense to compare, for example, the relaxation time τ_L obtained by Brillouin scattering with the value for τ_s obtained from the Maxwell formula for the viscosity. Nevertheless, fig. 5 exhibits a non-trivial result. If one increases the temperature from about 100 to 200°C the relaxation times all increase by about three orders of magnitude. But all four data sets follow the same master curve $f(T)$, if shifted properly parallel to the vertical axis. Thus they obey a law

$$\tau_x = C_x f(T), \quad T > T_c. \quad (6)$$

The strong T -dependence is described by the same function $f(T)$ for all processes. The various properties specifying the relaxation process under consideration and the precise definition of τ merely enter the prefactor C_x . The latter is temperature independent; better it varies so slowly with T that its variation cannot be detected on the used logarithmic scale necessary for the proper data presentation. This experimental fact is another hint on a common cooperative mechanism underlying the different α -relaxation processes. It was pointed out earlier [23] that τ_σ behaves differently than τ_s for T falling below 100°C. Fig. 5 indicates a similar anomaly for τ_L . So the claimed universality is restricted to T above T_c : it breaks down for T near and below T_c . This observation is another manifestation of the crossover temperature T_c . In this paper we are interested in the region $T > T_c$. Therefore the dielectric loss data of ref. [4] have not been incorporated in the detailed analysis. For $T > 230^\circ\text{C}$ there are only the data for τ_L available, to be deduced from refs. [5,9]. So one cannot analyze the universality problem there. But the analysis of the Brillouin scattering data [5] in fig. 6 indicates the possibility that the universality law (7) holds also for $T > 230^\circ\text{C}$. In any case, the fit curve, shown in fig. 5, contains the Brillouin scattering data up to 300°C and thus it describes the presently known dynamics of CKN over a dynamical range of 4.5 decades.

Most of the results of the mode coupling theory, to be referred to as MCT, concern the β -relaxation process, which is not considered in this paper. But there are also some results for the α -process [17], which can be confronted with the experimental findings analyzed above. The MCT has been worked out for simple one component liquids. Its application to the ionic mixture CKN requires therefore a strong reservation. However, in refs. [11–14] it was reported that some predictions of the theory for the β -process correlate reasonably with the experiments for CKN. We take this as a justification to consider this theory also in the present paper. It seems legitimate to ask the question: can the presently known experiments on the CKN α -process be used to show that the quoted theory is inadequate for the description of this system? The MCT deals with a bifurcation singularity called glass transition singularity, which manifests itself in a crossover temperature T_c . For temperatures near and below T_c hopping processes cause the α -relaxation rate. T_c marks the crossover from transport dominated by non-linear fluctuations to thermally activated ones [24]. Ignoring the hopping processes, T_c presents a singularity for the dynamics and one can use $(T - T_c)/T_c$ as a small separation parameter for asymptotic expansions. These asymptotic results shall now be discussed. So one has to be aware that the formulae to be quoted become irrelevant for T too close to T_c , since then hopping processes take over. They become irrelevant also for T too far above T_c , since then the separation parameter is not small enough. In CKN the analysis of the β -process has located T_c near 93°C [13]. So we have to restrict our analysis to $T > 100^\circ\text{C}$, say. It is one issue of the discussion to learn from the experiment, how large $(T - T_c)/T_c$ can be chosen for the application of the theory.

For the α -process the MCT yields the scaling law for the correlator formed with two variables X and Y of even time inversion symmetry: $\Phi_{XY}(t) = F_{XY}(t/\tau)$. Here the master function F_{XY} is independent of temperature. The temperature merely enters the scale τ , which thus appears as a universal function of T : $\tau = f(T)$. So the α -relaxation processes are predicted to obey asymptotically for $T \rightarrow T_c + 0$ the time temperature superposition principle. The neutron scattering work [10], the molecular dynamics simulations [14], and figs. 2, 4 and 6 show, that all presently

known data follow the theoretical pattern. Fig. 5, illustrating eq. (6), demonstrates the predicted scale universality. The reader should acknowledge that it is a truly important experimental finding [10] that the relaxation scale variation for microscopic density fluctuations is the same as the one for hydrodynamic shear. This finding and its extension by fig. 5 is a support of the physical picture underlying the MCT.

According to the MCT there is a regime of power law relaxation as formulated first by von Schweidler: $F_{XY}(t) = f_{XY} - h_{XY}t^b + O_{XY}(1/t^b)$. The exponent $b < 1$, as opposed to all the other details of F_{XY} , is the same for all variables X and Y for the singularity under study. However, the numerical value for b depends on many details of the CKN structure, which have not been analyzed analytically so far. At present it is therefore not possible to quote the prediction for the numerical value of b . The range of validity of the von Schweidler law is rather subtle. It holds only for $t/\tau \ll 1$; it describes the high frequency wing of the α -peaks. But the time must not be too short either: $t > \tau'$, where τ' is the critical scale for the β -process. Testing of the latter result was one issue of the experiments reported in ref. [11]. Figs. 1 and 2 show that the data fit to the prediction. The found value for exponent b is in reasonable agreement with the neutron scattering results [11]. In the neutron scattering work fluctuations have been analyzed on interparticle distance scales. This excludes the possibility to trace back the von Schweidler fractal behaviour to some fractal in configuration space. The experiment supports a result of the MCT: power law dynamics is due to the interplay of non-linearities and retardation effects. The mentioned theory yields a region of validity of the von Schweidler law also for $T < T_c$; but exponent b might exhibit a smooth temperature variation [25]. Fig. 8 exhibits a replot of the dielectric loss data of ref. [4], verifying this result. Extrapolation of $b(T)$ to $T = T_c$ is compatible with eq. (4).

The MCT identifies the von Schweidler behaviour as the essence of the α -relaxation stretching. The α -peaks are obtained as asymmetric resonances on a $\log \omega$ abscissa with the high frequency wing expanded compared to the low frequency one. Experimental verification of stretching for $T \rightarrow T_c$ with a $\log \omega$ -normal distribution, as anticipated in ref. [3] or a Cole-Cole law for the modulus, as assumed in ref. [9] would invalidate this theory. But figs. 2, 4, 6

Fig. 8. Double logarithmic presentation of the loss spectrum of the dielectric modulus as obtained in ref. [4]. From left to right the temperatures in $^{\circ}\text{C}$ are 60.1, 65.3, 71.4 and 80.7. The straight lines have slopes $b = 0.53, 0.49, 0.45, 0.37$.

and 7 as well as the results of refs. [10,14] show, that all known results fit into the theoretical picture. The master function F_{XY} depends on the details on the system's static structure factor and it has not been calculated yet for CKN. The Kohlrausch function, however, is not an exact solution of the non-linear mode coupling equations determining the shape function F_{XY} . But in all cases studied so far in detail [17], the Kohlrausch function was a good fit to the major part of the α -relaxation resonances. Deviations of Kohlrausch fit and true spectrum are expected for the very large frequency α -peak wing because usually $b \neq \beta$. Kohlrausch exponent β , as opposed to the von Schweidler exponent b , is a mere fit parameter without any physical or mathematical meaning. This statement holds with the reservation that not all mathematical implications of the mode coupling equations are fully understood at present. As demonstrated by a number of examples elsewhere [17], the Kohlrausch exponent β , as opposed to b , can be different for different correlation functions.

The temperature variation of parameters like f_q is of particular interest within the MCT. For the idealized transition, quantities like the Debye-Waller factor f_q should vary smoothly with T for $T \geq T_c$ and then they should sharply, but continuously increase for lower T . Hopping processes smear out the ideal cusps, unfortunately. Via eq. (2) this result could provide

an explanation of experimental observation, which is made quite often for glass formers that M_∞ increases faster with decreasing T than does M_0 . The data shown in fig. 3 as well as the results shown for the α -decay in ref. [14] support this result. Obviously, data statistics and error bars in fig. 3 do not allow any further conclusion.

If hopping is neglected, the MCT yields for the universal function in eq. (6) a power law divergence for $T \rightarrow T_c +$:

$$f(T) = [T_c / (T - T_c)]^\gamma. \quad (7)$$

Close to T_c the hopping processes prevent the divergence and yield a crossover to $F(\tau) \sim \exp(E_0/T)$ [24]. The full curve in fig. 5 shows eq. (7) for $\gamma = 4.06$, $T_c = 93^\circ\text{C}$. If one optimises the power law fit for the quoted T_c using γ as fit parameter, one finds for the data for τ_L , τ_n , τ_s , τ_σ respectively the optimal values $\gamma = 4.06, 4.09, 4.04, 3.84$. So we estimate

$$\gamma = 4.0 \pm 0.2. \quad (8)$$

The data support the theoretical picture for the observed strong increase of the relaxation rates in supercooled CKN. Usually, power law fits of relaxation times are not very informative since, e.g., the fit parameters γ and T_c depend sensitively on the temperature interval one chooses for the fit. In the present context such reservation does not apply. The value T_c is not adjusted to the data studied in this paper; but it is taken from the experiments on β -relaxation [13]. The MCT relates exponent γ to the von Schweidler exponent b [17]. The value for this anomalous dimensionality following from eq. (4) is $\gamma = 3.6 \pm 0.5$. So this theoretical prediction is compatible with the data also.

6. Conclusion

The preceding discussion shall be summarized by four conclusions.

(1) The experimental data on α -relaxation of CKN for $230 > T > 100^\circ\text{C}$, achieved by ultrasound measurement, by normal and stimulated Brillouin scattering, and by neutron spin echo spectroscopy can be described quantitatively within one simple phenomenological picture. There holds the time temperature superposition principle. The Kohlrausch law with an

exponent β , implying considerable stretching, is a reasonable overall presentation of the α -process. In particular, the Debye-Waller factor f_q or some equivalent quantity like the ratio of high and low frequency modulus M_∞/M_0 are insensitive to temperature variations and so is the Kohlrausch exponent β . All relaxation rates follow the same universal curve over at least three orders of magnitude. Von Schweidler description of the high frequency α -peak wings and a power law interpolation for the relaxation rates are adequate.

(2) Other data fits, which anticipate, e.g., qualitatively different behaviour of elastic modulus and neutron scattering cross section, are also possible. In particular one can fit data with a temperature dependent stretching exponent provided one also introduces a corresponding temperature dependence for f_0 . Such fits imply the violation of the time temperature superposition principle and require more adjustable parameters for the fits than used in (1).

(3) The data analysis referred to in (1) agrees in all details with the mathematical picture provided by the mode coupling theory for the α -process. In addition the analysis is consistently tight to the previous analysis of the β -relaxation in CKN.

(4) Further progress in our understanding of the CKN dynamics depends on the possibility to eliminate the alternative between (1) and (2). To achieve this goal one would need data for the dynamics over a range of at least three decades. One has to map out more than the upper half of the α -resonance peak. The data should be done for temperatures between 100 and 200°C and thus probe the dynamics in the GHz band. Such data sets would presumably be sufficient to decide on the validity of the mode coupling description of the α -process in CKN.

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