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## Structural relaxation in supercooled glass-forming solutions: a neutron spin-echo study of LiCl, 6D<sub>2</sub>O

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**Abstract.** We have performed neutron spin-echo measurements on the supercooled glass-forming system <sup>7</sup>LiCl, 6D<sub>2</sub>O above its glass transition temperature ( $T_g = 135$  K). This investigation has permitted us to determine the time dependence of the density correlation function  $\phi(Q, t)$  between 2 ps and 2 ns at the maximum of the structure factor ( $Q = 1.9 \text{ \AA}^{-1}$ ). We have shown for the viscosity, the existence of two temperature domains limited by two critical temperatures (fixed points). This crossover from the stable liquid to the metastable liquid might be related to a change in the multiplicity of the microscopic interactions. In this study we show that the dynamics of the structural relaxation is consistent with the two scaling laws of the viscosity. Both the average relaxation time and the stretched exponential behaviour indicate a crossover regime around 210 K. However, the scaling of the density correlation function differs, in the lower-temperature regime, from the scaling of the shear viscosity.

For the supercooled liquid dynamics, the results are more or less correlated to the mode-coupling theory.

### 1. Introduction

Structural relaxation can be analysed with precision in some glass-forming aqueous solutions. Indeed these systems exhibit on supercooling a large metastable temperature range related to the existence of a multiplicity of microscopic configurations which leads to some topological frustration.

This situation is achieved in the well-defined LiCl, R<sub>H</sub>2O system for  $R = 6$ , a concentration at which the bifurcation from a supercooled metastable to a stable state is perfectly avoidable as displayed in the non-equilibrium phase diagram of figure 1 [1]. The glass transition range is around 135 K (calorimetric temperature), and the melting point, near 207 K is determined from the equilibrium phase diagram. Thus an extended metastability domain permits a critical analysis of the transition from an ergodic to a non-ergodic state, and of the mode-coupling approach to the glass transition [2].

In addition, close to this concentration a stable crystallized state exists for  $R = 5$ , from a limit of formation temperature (171 K) to a limit of stability temperature given by a peritectic line at 207 K. Consequently, the proximity of this peritexy with the melting point of LiCl, 6H<sub>2</sub>O suggests that a change in the multiplicity of configurations could take place between the stable and the supercooled liquid phases for  $R = 6$ .

In a recent Brillouin-scattering study of these solutions, the structural relaxation has been investigated through its coupling with the high-frequency acoustic modes [3]. Here we report a more direct investigation of the structural relaxation in LiCl, 6D<sub>2</sub>O using neutron

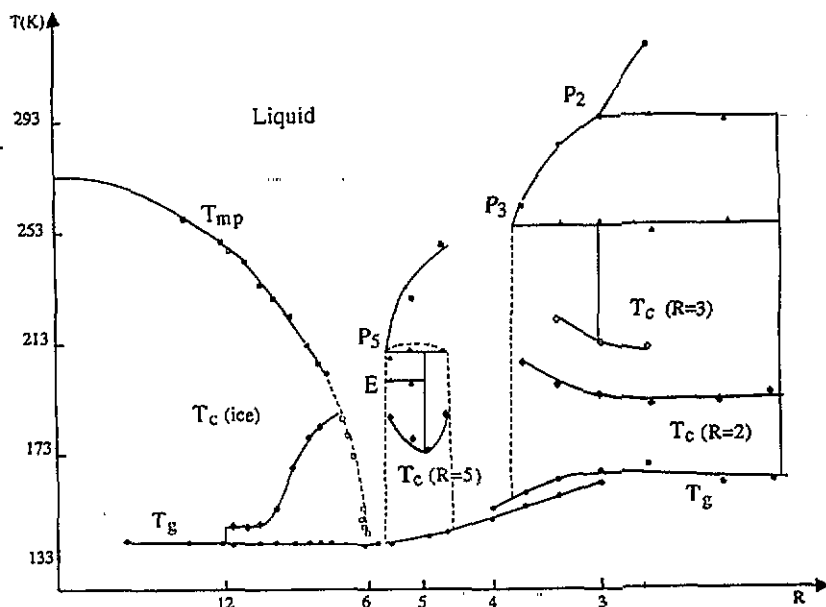


Figure 1. Metastable domains in the phase diagram of LiCl,  $RH_2O$  determined on warming the quenched glassy samples with a heating rate  $V = 3 \times 10^{-2} \text{ K s}^{-1}$ .  $T_g$  is the glass transition temperature,  $T_c$  corresponds to the crystallization (of ice and  $R = 2, 3, 5$  hydrates),  $T_{mp}$  corresponds to the melting point and the horizontal continuous lines  $P_2$ ,  $P_3$  and  $P_5$  are the peritectic lines for the different compounds and  $E$  corresponds to the eutectic point. The broken curves are calculated or postulated metastable extensions of the different compound branches of the liquidus line. The vertical continuous lines are the limits of the hydrates' stability domains.

spin echo spectroscopy (NSE). Mezei *et al* [4] have demonstrated that this neutron scattering technique permits an analysis of the density correlation function

$$\phi(Q, t) = \langle \delta\rho(Q, t), \delta\rho(-Q, 0) \rangle$$

where  $\delta\rho$  is the Fourier transform of the density fluctuations around the mean value  $\rho$ ,  $Q$  is the momentum transfer and  $t$  the time. NSE spectroscopy permits this analysis to be made in a very broad time interval (between  $t = 1.5 \times 10^{-12} \text{ s}$  using a wavelength  $\lambda = 4 \text{ \AA}$  and  $t = 1.5 \times 10^{-8} \text{ s}$  using  $\lambda = 8 \text{ \AA}$ ).

## 2. Structural relaxation time and viscosity

The viscosity of the LiCl,  $5.75H_2O$  solution has been carefully measured by Moynihan *et al* [5]. An analysis of their results shows that this glass forming system can be classified as 'fragile' [6] and neither exhibits an Arrhenius behaviour nor a Tamari-Vogel-Fulcher law. We have also shown [7] that Taborek's approach [8], including two temperature regimes (one scaled with a  $T^{-1/2}$  law and another with an Arrhenius behaviour) breaking at 210 K, was not adequate to describe the viscosity data.

From the scaling law approach, the viscous behaviour of a system which forms a glass belongs to a class of universality. The relaxation time  $\tau$  is proportional to the viscosity

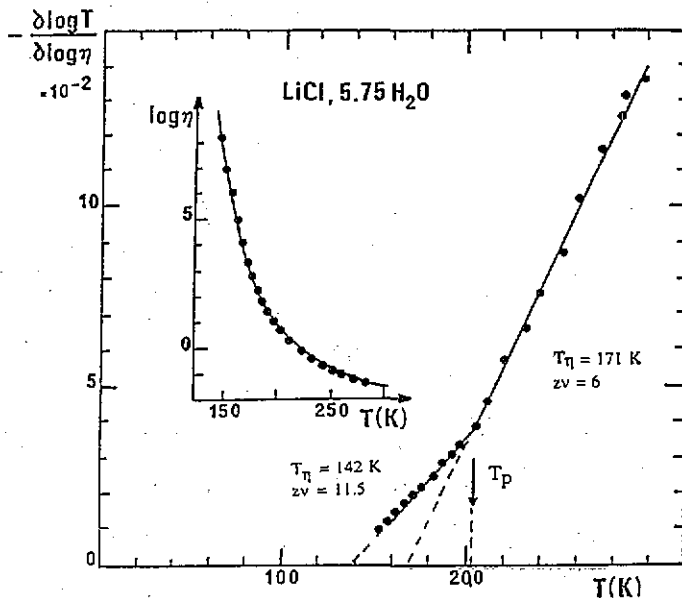


Figure 2. Plots of  $-\partial \log T / \partial \log \eta$  versus temperature and of  $\log \eta$  versus temperature (insert). The viscosity data are from reference [5]. The characteristics of two scaling behaviours are given.

according to  $\eta = G_\infty \tau$ , where  $G_\infty$  is the high-frequency shear modulus. According to Souletie [9], we use a dynamical scaling hypothesis relating  $\tau$  to the coherence length  $\xi$

$$\tau / \tau_0 = (\xi / \xi_0)^z \tag{1}$$

and a static scaling hypothesis which states that

$$\xi / \xi_0 = (1 - T_c / T)^{-\nu} \tag{2}$$

where  $\xi_0$  is the Debye coherence length of the system and  $\nu$  a critical exponent. This law introduces a fixed point  $T_c$  related to the divergence of the coherence length  $\xi$  and to the divergence of the viscosity  $\eta$ .

Writing equations (1) and (2) for  $\eta$  in a differential logarithmic form  $-\partial \log T / \partial \log \eta$ , one can easily extract  $T_c$  and  $z\nu$  from viscosity data [7]. In the case of  $\text{LiCl}, 5.75\text{H}_2\text{O}$  the viscosity shows clearly the existence of two regimes (see figure 2) with the following characteristics

$$\eta / \eta_0 = (1 - 171 / T)^{-6} \quad T > T_p \tag{3}$$

$$\eta / \eta_0 = (1 - 142 / T)^{-11.5} \quad T < T_p \tag{4}$$

with  $T_p = 207$  K. Interestingly the three temperatures derived from this analysis can be related to already known characteristic temperatures of the system. The fixed temperature  $T_c = 142$  K corresponds to the lowest limit of metastability of the system  $T_0$  as detected in the neutron scattering structure factor measurements [7]. It is also detected in measurements of the specific heat  $C_p(T)$  and of the molar volume  $V_m(T)$  [10, 11]. The other two temperatures are related to characteristic temperatures of the pentahydrate:  $T_p$  is the temperature of the peritexy (i.e. the higher limit of its stability) and  $T = 171$  K the lowest limit of crystallization.

The high-temperature scaling law of the viscosity exhibits a divergence towards the crystallization temperature of the pentahydrate. The crossover occurs around the peritectic temperature of the pentahydrate. As mentioned above, these results suggest the existence of a change in the multiplicity of the microscopic interactions in  $\text{LiCl} \cdot 6\text{H}_2\text{O}$ .

### 3. NSE experiments

#### 3.1. Sample

The  ${}^7\text{LiCl} \cdot 6\text{D}_2\text{O}$  sample was prepared from dehydrated  ${}^7\text{LiCl}$  with  ${}^7\text{Li}$  enrichment of 99.94% ( ${}^6\text{Li}$  has a strong absorption cross section for neutrons) and  $\text{D}_2\text{O}$  of 99.7% purity (deuterated water was chosen because its scattering is almost coherent). The sample concentration was determined to an accuracy of 1%. A flat niobium cell of inner dimensions  $30 \text{ mm} \times 40 \text{ mm}$  with wall thickness of 1 mm and sample thickness of 4 mm, was used in reflection geometry in order to minimize the flight-path difference.

#### 3.2. Measurements

The NSE measurements were performed with the IN11 spectrometer at the Institut Laue-Langevin (ILL), Grenoble. The incoming neutron beam had an average wavelength of  $4.7 \text{ \AA}$  with 18% FWHM. We probed the intermediate scattering function  $S(Q, t)$  at  $Q_0 = (1.9 \pm 0.2) \text{ \AA}^{-1}$ , i.e. near the first maximum ( $2.0 \text{ \AA}^{-1}$ ) of the structure factor  $S(Q)$  [12].

Two precession field geometries were used in order to obtain a broad range of relaxation times [4]. Thus the characteristic times probed are in the range  $2 \cdot 10^{-12}$  to  $2 \cdot 10^{-9}$  s corresponding to a neutron energy transfer between  $300 \text{ \mu eV}$  and  $0.3 \text{ \mu eV}$ . The sample thermal history was carefully monitored in order to prevent bifurcation to the crystallized pentahydrate.

In a preliminary investigation  $S(Q_0, t = 0)$  was measured with and without spin-flip (respectively  $S_{\text{FL}}$  and  $S_{\text{NFL}}$ ) over a broad temperature range (from 40 K to 260 K). Such a measurement allows us to separate the amount of coherent and incoherent scattering using the following relations

$$S_{\text{NFL}} = S_{\text{coh}} + \frac{1}{3} S_{\text{inc}} \quad (5)$$

$$S_{\text{FL}} = \frac{2}{3} S_{\text{inc}} \quad (6)$$

It is also used to normalize the spin-echo signal which is proportional to  $(S_{\text{NFL}} - S_{\text{FL}})$ .

The evolutions of  $S_{\text{NFL}}$  and  $S_{\text{FL}}$  versus temperature are displayed in figure 3. From  $S_{\text{FL}}$  we observe that the incoherent scattering  $S_{\text{inc}}(Q_0, t = 0)$  is constant with temperature while the coherent scattering  $S_{\text{coh}}(Q_0, t = 0)$  dominant in  $S_{\text{NFL}}$  displays two distinct anomalies occurring at characteristic temperatures of the system. The continuous drop in intensity starting at  $T_0$  can be attributed to the development of high-frequency excitations or changes in the local structure escaping the  $Q$  and  $\omega$  detection windows of the instrument (namely  $1.7 \text{ \AA}^{-1} < Q < 2.1 \text{ \AA}^{-1}$  and  $\omega < 5 \text{ meV}$ ). The small anomaly at  $T_p$ , the temperature of the peritexy of the pentahydrate, has already been detected in structure factor and calorimetric measurements [13]. In addition the small fraction of incoherent scattering produces a spin-echo signal of opposite phase. In the observed temperature range, this incoherent scattering is almost elastic and thus its contribution is only to decrease  $S(Q_0, 0)$  by a few percent.

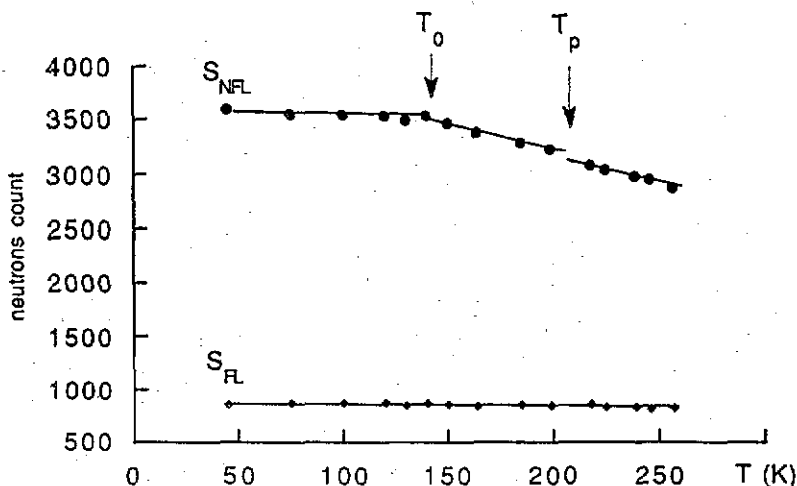


Figure 3. Spin flip  $S_{FL}$  and non-spin flip  $S_{NFL}$  signals versus temperature. The  $S_{FL}$  represents the incoherent part of the scattering, whereas  $S_{NFL}$  is a combination of the coherent and incoherent scattering. Two characteristic temperatures are marked with arrows.  $T_p$  is the peritaxy temperature of the pentahydrate and  $T_0$  is the lower limit of metastability of the  $\text{LiCl} \cdot 6\text{H}_2\text{O}$  compound.

#### 4. Results and analysis

We have measured the NSE spectra at seven temperatures from 167 K to 257 K. At each temperature, the intensity corrected for the low level of static scattering from the empty cell is normalized, using a static reference signal from the sample at 40 K. Thus the spectra represent directly  $S(Q_0, t)/S(Q_0, 0)$  versus time. These curves show a slowing down of the relaxation of the dynamical structure factor when the temperature decreases.

According to Stokes–Einstein theory, the viscosity is related to a local relaxation time following the relation  $\tau_\eta \propto \eta/T$ . Thus in a first attempt of data analysis, all the results obtained at various temperatures are displayed in figure 4(a) as a function of  $tT/\eta$ . According to [14] and contrary to what has been obtained in many other glass-forming systems [15, 16], this renormalization of the time scale does not show evidence of a master curve, mainly in the intermediate ( $tT/\eta$ ) domain. Only the short-time (or high-frequency) limit of the scattering function appears to be renormalized by viscosity.

Taking into consideration the aspect of the curves, we can try to obtain a time–temperature superposition process for different temperature domains. The relaxation times are the inflexion points (or extrapolation of inflexion points for the lower temperatures) of the data. We have reproduced the results obtained in each temperature domain by stretched exponentials (the so-called Kohlrausch behaviour)

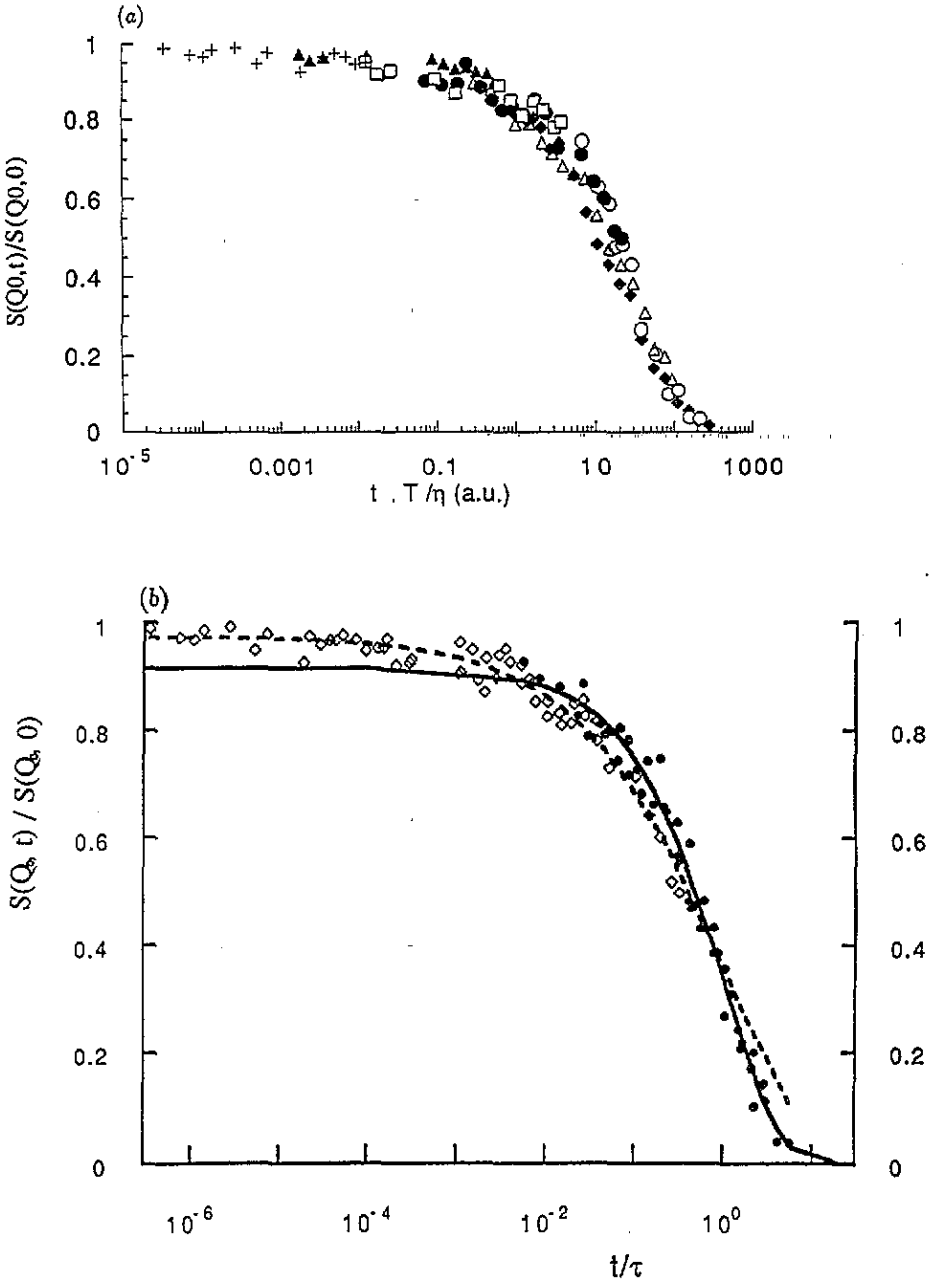
$$f(Q_0, t) = S(Q_0, t)/S(Q_0, 0) = A \exp -(t/\tau)^\beta. \quad (7)$$

We have obtained two laws

$$[S(Q_0, t)]/[S(Q_0, 0)] = 0.914 \exp -(t/\tau)^{0.69} \quad T > T_p \quad (8)$$

$$[S(Q_0, t)]/[S(Q_0, 0)] = 0.970 \exp -(t/\tau)^{0.46} \quad T < T_p. \quad (9)$$

These laws, represented in figure 4(b), show the evidence of two particular regimes of the structural relaxation.



**Figure 4.** (a) Density correlation function  $S(Q_0, t)/S(Q_0, 0)$  measured at different temperatures and plotted on a reduced scale of times:  $tT/\eta$ , where  $\eta$  is the viscosity of the system. + 167 K,  $\blacktriangle$  179 K,  $\square$  188 K,  $\bullet$  199 K,  $\triangle$  210 K,  $\blacklozenge$  225 K,  $\circ$  257 K. (b) The same data plotted versus  $(t/\tau)$  where  $\tau$  is the inflexion point of the data at each temperature (data represented in figure 5), ( $\diamond$ ):  $T < T_p$ , ( $\bullet$ ):  $T > T_p$ . The lines are fits corresponding to the Kohlrausch laws described in equations (8) (full curves) and (9) (broken curves).

In order to obtain a better definition of the parameters  $A$ ,  $\beta$  and of the relaxation time (called here  $\tau_S$ ), we have tried to treat separately the results obtained at each temperature,

a method which implies the adjustment of three parameters  $A$ ,  $\beta$  and  $\tau$ , which is relatively easy when the relaxation time is located in the experimental time window (figure 5). For temperatures lower than 190 K one finds that the parameters  $A$  and  $\beta$  are strongly correlated, hence the value of  $A$  was carefully explored in order to optimize the reliability factor. However at 167 K the signal is too flat to be analysed, except for an estimation of  $A$ . The values obtained for the various parameters are given in table 1 and displayed in figures 6 and 7 in which the error bars are quoted (note that they correspond to usual RMS deviations).

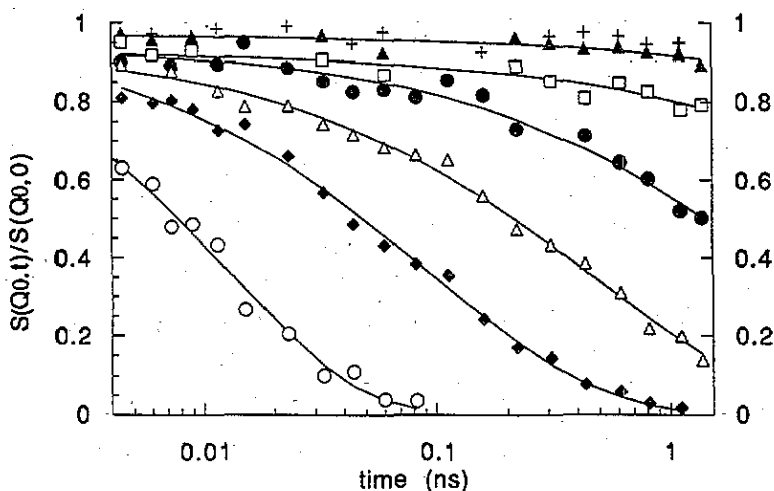


Figure 5. Neutron spin-echo response at  $Q = Q_0 = 1.9 \text{ \AA}^{-1}$  for LiCl,  $6\text{D}_2\text{O}$  at various temperatures. The lines are calculated from equation (7) with coefficients in table 1. + 167 K,  $\Delta$  179 K,  $\square$  188 K,  $\bullet$  199 K,  $\Delta$  210 K,  $\blacklozenge$  225 K,  $\circ$  257 K.

Table 1. Values of the different parameters of the stretched exponential.

$T$ (K)	167	179	188	199	210	225	257
$A$	0.975	0.97	0.93	0.94	0.945	0.98	0.975
$\beta$	—	0.52	0.50	0.58	0.57	0.60	0.78
$\tau_S$ (ns)	—	265	48	3.1	0.478	0.094	0.013

It appears that, as expected, the error bars on the three parameters become significant when the relaxation time is outside the experimental window.

We can now describe the scattering relaxation times  $\tau_S$  (in seconds) using a scaling law approach (see figure 7).

The data for  $T > T_p$  are easily fitted by the power law

$$\tau_S = 1.44 \times 10^{-14} (1 - 172/T)^{-6.1} \quad (10)$$

with a good precision on the fixed point temperature ( $172 \pm 1$  K) and on the power index ( $6.1 \pm 0.1$ ). This power law can be extended to the description of data at temperatures lower than  $T_p$  but the point at 179 K is definitively out of reach.



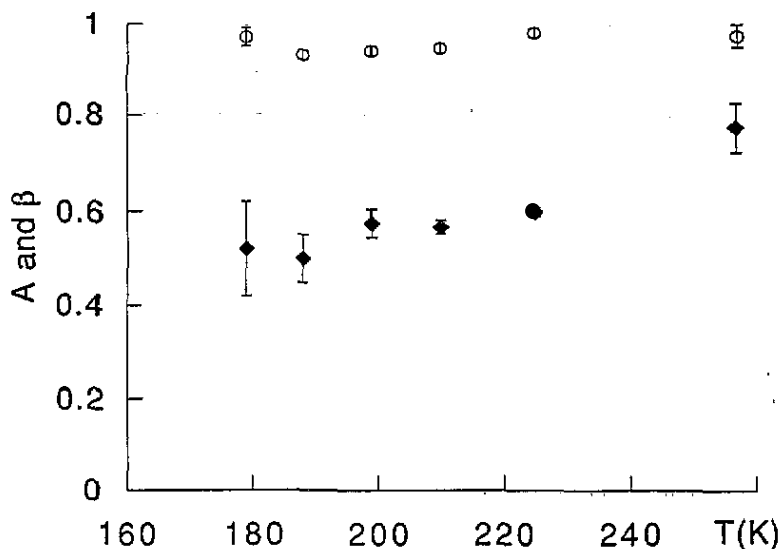


Figure 6. Exponent  $\beta$ ( $\blacklozenge$ ) and coefficient  $A$ ( $\circ$ ) of the stretched exponential, plotted versus temperature.

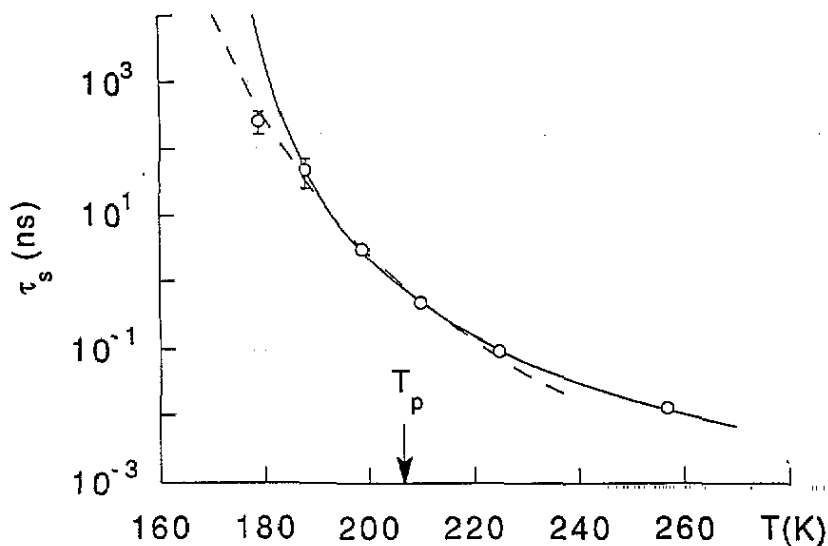


Figure 7. Relaxational times  $\tau_s$  for LiCl,  $6D_2O$  plotted versus temperature. The lines are fits corresponding to the power laws described in equations (10) (full lines) and (11) (dotted lines).

In order to better describe the low-temperature data, the same kind of law is calculated for  $T < T_p$ , one finds

$$\tau_s = 2.6 \times 10^{-17} (1 - 142/T)^{-15}. \quad (11)$$

However the poor accuracy of the data in that range affects the precision of the fixed point temperature ( $142 \pm 5$  K) and of the power index ( $15 \pm 3$ ).

The two power laws are represented in figure 7 and give a good representation of the temperature dependence of the experimental  $\tau_S$ .

We note that the values of  $A$  are nearly temperature independent in the  $T > T_p$  domain, where their average is close to the value obtained at the lowest temperature. We therefore chose  $A = 0.97$  to process all the data and extract the  $\beta$  values from equation (7). The results are given in table 2.

Table 2. Values of the  $\beta$  exponent of the stretched exponential when  $A = 0.97$ .

$T$ (K)	179	188	199	210	225	257
$\beta$	0.48	0.44	0.505	0.52	0.605	0.84

We see in figure 8 that in the  $T > T_p$  range the  $\beta$  values increase almost linearly with temperature, reaching the value  $\beta = 1$  near 280 K, while below  $T_p$  we can conclude that this linear dependence is not maintained,  $\beta$  being more or less temperature independent (about 0.5).

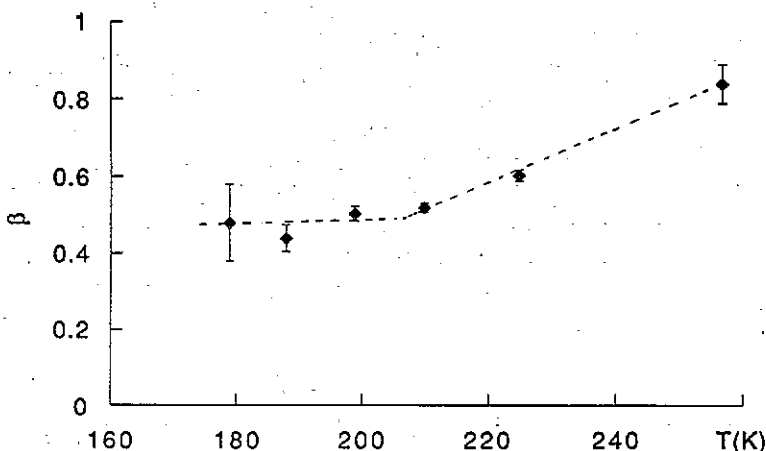


Figure 8. Variation of the  $\beta$  exponent of the Kohlrausch exponential versus temperature when  $A$  is fixed to the value 0.97 (the broken curve is only to guide the eyes).

## 5. Discussion

We compare now our results with the predictions of mode-coupling theory (MCT) [17]. Using different correlations like shear viscosity and density fluctuations we have verified a time-temperature superposition process in the supercooled liquid regime. In this regime, below a phase transition temperature related to the existence of a peritaxy of the nearest stable compound ( $R = 5$ ), the sensitive temperature dependence of the dynamics is reduced to the scaling of the relaxation times  $\tau_S$ . The master function is temperature independent,  $\beta$  being nearly constant ( $\approx 0.5$ ). This domain can be related to a so-called  $\alpha$  relaxation. The scaling of the measured density fluctuations and the one of the shear viscosity are

characterized by the same critical temperature,  $T_0 = 142$  K which was identified as the end of the metastability.

The scalings obtained, point out that the relaxation times  $\tau_S$  calculated from NSE and  $\tau_\eta$  calculated from viscosity given in table 3 exhibit differences in the lower-temperature domain (outside of the error bars). These results imply that the behaviour of the measured density fluctuations for  $Q = Q_0$  is not the same as the one of the shear viscosity (which corresponds to the hydrodynamics limit).

**Table 3.** Values of  $\tau_\eta$  (from viscosity) and  $\tau_S$  (from NSE) at each temperature.

$T$ (K)	167	179	188	199	210	225	257
$\tau_\eta$ (ns)	3146	90.8	12.27	2.28	0.54	0.151	0.0147
$\tau_S$ (ns)	—	265	48	3.1	0.478	0.094	0.013

This last result does not agree with one of the general characteristics of the mode coupling theory applied to a liquid–glass transition. In addition,  $T_0 = 142$  K does not appear equivalent to the critical temperature  $T_c$ ; as a matter of fact, we know that below  $T_0$  the structural evolution of the system becomes time dependent whereas the density fluctuations are frozen in [7].

Moreover, the quasi-elastic fraction  $A$  is nearly constant and has a large value (0.97). Its increasing at lower temperatures predicted by MCT would be hardly detectable. In addition, if one considers the temperature dependence of  $S_{\text{coh}}(Q_0, t = 0)$  displayed in figure 3, we see that above  $T_0 = 142$  K a fraction of the signal escapes the observation window. Therefore, if in this system it exists a high-frequency mode which couples with the structural relaxation, it should be at an energy greater than 5 meV, this means in a time range ( $t < 0.1$  ps) at least three orders of magnitude lower than the structural relaxation, i.e. too far for an efficient coupling.

The crossover temperature  $T_p$  cannot be considered as the MCT critical temperature, as proposed by Taborek [8], because it is related to a phase transition. This transition temperature has been observed by calorimetric and density measurements [10, 11]. It has also been correlated in a recent structural analysis, to a modification of the mean- and long-range order [18].

However, due to the less accurate data in the low-temperature regime, if the high-temperature law was extended to describe the data for  $T < T_p$ , the divergence of  $\tau_S$  at  $T = 171$  K would correspond to a freezing of the system at a temperature where no anomaly is observed (neither in the structure nor in the macroscopic properties). In addition, the time–temperature superposition principle verified for shear viscosity would not be hold back on the scaling of the measured density fluctuations.

Thus a crossover towards the actual temperature range where the system freezes in ( $T_0 = 142$  K) is the most likely.

## 6. Conclusion

This investigation of the time dependence of the density correlation function does not allow us to completely unravel the mechanism of the relaxation process in the fragile glass-forming system LiCl, 6H<sub>2</sub>O. Several descriptions of the data can be proposed, but none of them are fully satisfactory. At high temperature, i.e. in the stable liquid phase, the structural relaxation

time appears to obey a scaling law comparable to that of the viscosity with a fixed point  $T_p = 171$  K corresponding to the limit of formation of the crystallized pentahydrate. In the temperature range of the peritexy of the pentahydrate, the relaxation behaviour appears consistent with the crossover regime observed in the viscosity although the time window accessible by NSE does not permit us to determine precisely the low-temperature behaviour of the average relaxation time  $\tau_s$  and of its distribution represented by the exponent  $\beta$  of the stretched exponential. The crossover between two scaling laws suggests a change in the dimensionality of the interactions leading to the freezing-in of the system. A description within the framework of mode coupling theory also raises difficulties. Firstly, the data rescaled by the viscosity are not adequately described by a master curve. Secondly, detection of a critical dynamical temperature is uneasy since most of our investigations seem to be above its expected value. Thirdly the quasi-elastic (non-ergodic) fraction  $A$  is very high and any increase of its value at low temperature is hardly detectable.

Certainly the low-temperature response needs to be investigated by complementary techniques such as dielectric spectroscopy and dynamic light scattering in order to explore longer relaxation times. Indeed, photon correlation spectroscopy and spontaneous Brillouin spectroscopy on the archetype  $x(\text{KNO}_3)$ ,  $(1-x)(\text{CaNO}_3)_2$ , exhibit the same type of evolution [19], particularly, for the width parameter  $\beta$ . Although this fragile system presents a rapid crystallization in the intermediate temperature range, between the liquid-like and the glass-like regime (which is not favourable to such an analysis), it appears some similarity with the investigated fragile system  $\text{LiCl} \cdot 6\text{H}_2\text{O}$ .

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