

Structural relaxation in supercooled $(\text{Na}_2\text{O}-\text{Li}_2\text{O})-2\text{P}_2\text{O}_5$: a neutron spin-echo study

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Abstract

The structural relaxation of viscous $(\text{Na}_2\text{O}-\text{Li}_2\text{O})-2\text{P}_2\text{O}_5$ is investigated by neutron spin-echo experiments. The spectra show stretching and time–temperature scaling as known from α -relaxation in supercooled liquids and derived from mode-coupling theory (MCT). The momentum transfer dependence of the correlation times is found to exhibit a maximum value at the first maximum of the structure factor $S(Q)$ in agreement with predictions of MCT. In contrast, the Q -dependence of the stretching exponent β does not seem to oscillate in phase with $S(Q)$ in this network glass.

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1. Introduction

When a liquid can be supercooled far enough below its melting temperature T_m , structural relaxation becomes critically slow, so that it becomes a glass at the glass transition temperature T_g . Stretching and time–temperature scaling have been identified as generic properties of structural or α -relaxation in supercooled liquids. More recently, additional precise scaling laws have been predicted by a mode-coupling theory (MCT) [1]. An increasing number of experimental and numer-

ical results [2] indicates that the essential features of the dynamics of liquids approaching T_g is correctly contained in the MCT description, at least for fragile glass-forming liquids in the Angell's classification scheme [3]. Such supercooled liquids exhibit the most rapid changes of the viscosity just above T_g due to weak inter-molecule bonding forces.

It is now of considerable interest to explore if the MCT scenario is applicable also to stronger glass-forming systems. In particular, very few studies on oxide glasses have been performed so far. In the present paper, we use neutron spin-echo (NSE) to investigate the structural relaxation dynamics of $(\text{Na}_2\text{O}-\text{Li}_2\text{O})-2\text{P}_2\text{O}_5$ in the supercooled liquid phase.

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2. Experimental details

(Na₂O–Li₂O)–2P₂O₅ is a mixed alkali phosphate glass-forming liquid that can be easily supercooled down to the glass transition temperature T_g without any sign of crystallisation. The melt-quenched glass is a stable colourless amorphous solid with a glass transition temperature $T_g = 515$ K and a melting temperature $T_m = 749$ K. The temperature dependence of the viscosity of (Na₂O–Li₂O)–2P₂O₅ is known to be intermediate between fragile molecular liquids and strong network glasses in the Angell's classification [4]. The sample was prepared from pure ⁷Li isotope starting materials as described previously in Ref. [5]. The obtained glassy sample was then crushed into fine powder in a glove box under argon and transferred to a niobium slab container 4 mm in thickness, to be used during the neutron scattering experiments at high temperature. The niobium cell was sealed with a pure aluminium 1 mm thick wire.

The NSE experiment has been performed at the spectrometer MUSES at the LLB Saclay. A mean incident wavelength of $\bar{\lambda}_i = 5.0$ Å was used with a wavelength spread of $\Delta\lambda_i/\bar{\lambda}_i \approx 15\%$. Data were taken in the Q range 0.6 – 1.8 Å^{−1} at several temperatures in the supercooled liquid phase. The temperature stability was ± 2 K and the spectra were collected in runs of 8–12 h per spectrum depending on the wavevector Q . Each measured spectrum was first normalised by the signal obtained with the spin-echo scan switched-off, $S(Q, t \approx 0)$. The spectra were then corrected for instrumental resolution by normalisation to a reference scan that was measured on a slab of silica at room temperature.

3. Results and discussion

Fig. 1 shows a set of normalised intermediate scattering function $\phi(Q, t) = S(Q, t)/S(Q, t = 0)$ measured on (Na₂O–Li₂O)–2P₂O₅ at $Q = 1.8$ Å^{−1} for six temperatures ranging from 637 to 773 K. The spectra show a typical slowing down of the relaxation dynamics when the temperature is decreased. The data were analysed following a

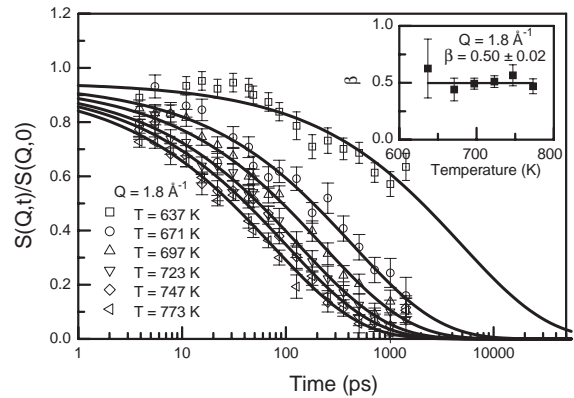


Fig. 1. Intermediate scattering function $\phi(Q, t) = S(Q, t)/S(Q, t = 0)$ measured on (Na₂O–Li₂O)–2P₂O₅ at $Q = 1.8$ Å^{−1} for six temperatures ranging from 637 to 773 K. Lines are the resulting KWW fit curves (Eq. (1)) described in the text. The inset shows the temperature dependence of the Kohlrausch stretching exponent.

three-step procedure. First, all the spectra taken at the same Q value were fitted individually to a stretched exponential function or Kohlrausch–Williams–Watt (KWW) law:

$$\phi(Q, T, t) = A_Q(T) \exp \left\{ - \left[\frac{t}{\tau_Q(T)} \right]^{\beta_Q(T)} \right\}, \quad (1)$$

where $A_Q(T)$ is the amplitude of the α -relaxation, $\beta_Q(T)$ is the stretching parameter (specifying the deviation from exponential relaxation) and $\tau_Q(T)$ is the α -relaxation time, all of them being the fitting parameters.

As presented in the inset of Fig. 1, a first result of such an analysis is to show that in (Na₂O–Li₂O)–2P₂O₅, the stretching parameter β seems to be temperature independent at least in the temperature range investigated. However, scattering of data does not exclude a small temperature variation of β .

In a second step, the spectra were fitted simultaneously with a common stretching exponent β_Q whereas $A_Q(T)$ and $\tau_Q(T)$ were again let free. It was possible to conclude from this analysis that the amplitude parameters $A_Q(T)$ vary slowly with temperature as a Debye–Waller factor. In

order to get improved values of β_Q and $\tau_Q(T)$, we then repeat a third time the KWW fits with a linear temperature dependence of $\ln A_Q(T)$ leading to the resulting KWW fit curves plotted in Fig. 1.

Assuming a temperature independent stretching parameter is in fact a reformulation of the time–temperature superposition principle, a central prediction of the MCT. In Fig. 2, master curves $\phi(Q, t/\tau_Q(T))/A_Q(T)$ for α -relaxation are shown for two different wavevectors, obtained by rescaling the time axis by the α -relaxation time $\tau_Q(T)$ and the amplitude axis by the $A_Q(T)$. The scaling prediction of MCT is confirmed within experimental accuracy in this network glass.

Turning to the Q -dependence of the α -relaxation parameters, it clearly appears from Fig. 2 that the stretching exponent β_Q is not Q independent in $(\text{Na}_2\text{O}-\text{Li}_2\text{O})-2\text{P}_2\text{O}_5$. The master curve shown at $Q = 1.2 \text{ \AA}^{-1}$ is much more stretched than the one found at $Q = 1.8 \text{ \AA}^{-1}$. Following the same analysis for all the wavevectors measured in this

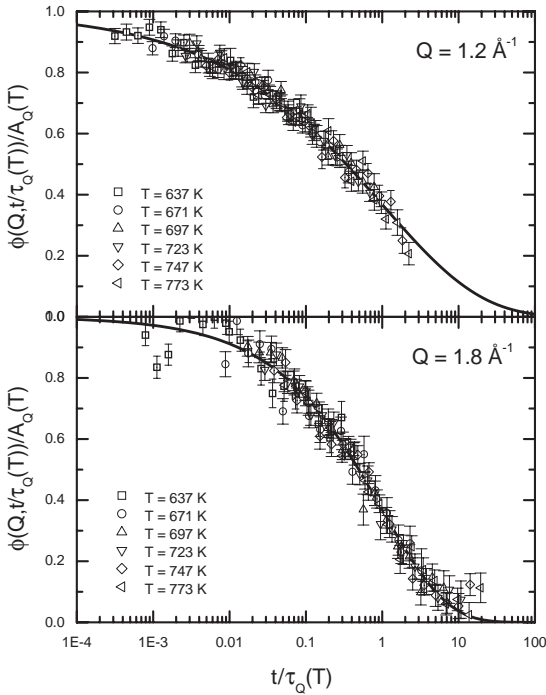


Fig. 2. Scaling analysis of the α relaxation in $(\text{Na}_2\text{O}-\text{Li}_2\text{O})-2\text{P}_2\text{O}_5$: master curves $\phi(Q, t/\tau_Q(T))/A_Q(T)$, where $A_Q(T)$ and $\tau_Q(T)$ are obtained from iterative fits with Eq. (1).

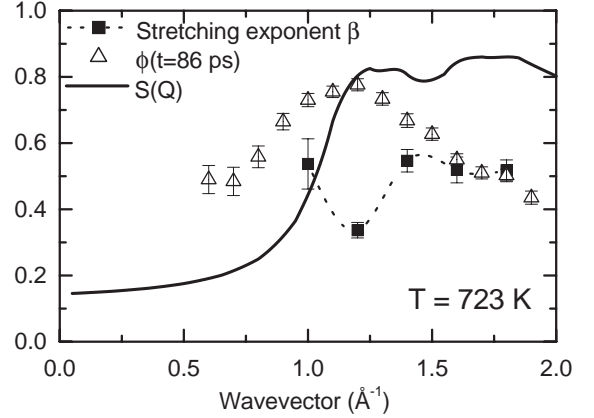


Fig. 3. Dependence on scattering vector Q : (■) stretching exponent β_Q obtained by the three-step procedure described in the text; (Δ) intermediate scattering function at a fixed time $\phi(t = 86 \text{ ps})$ revealing a maximum of the structural relaxation time around $Q = 1.2 \text{ \AA}^{-1}$, the position of the pre-peak; (solid line) static structure factor $S(Q)$ of $(\text{Na}_2\text{O}-\text{Li}_2\text{O})-2\text{P}_2\text{O}_5$ at $T = 723 \text{ K}$.

experiment we found a variation of β with Q as shown in Fig. 3 (■). A striking feature is the minimum of β at $Q = 1.2 \text{ \AA}^{-1}$, the location of the first peak in the static structure factor $S(Q)$. Since for a hard-sphere system this quantity is predicted by MCT to oscillate in phase with $S(Q)$ [6], a more detailed MCT analysis of the relaxational dynamics of this network glass is needed. In contrast to the Q dependence of β , the timescale of the structural relaxation seems to oscillate in phase with $S(Q)$ as shown in Fig. 3 where the value of the intermediate scattering function measured at $T = 723 \text{ K}$ for a fixed time $\phi(t = 86 \text{ ps})$ is plotted against Q (Δ).

The results obtained on the temperature dependence of the structural relaxation of the oxide glass $(\text{Na}_2\text{O}-\text{Li}_2\text{O})-2\text{P}_2\text{O}_5$ with NSE on the ns timescale are compatible with the predictions of the mode-coupling theory and also consistent with the behaviour of the relaxational dynamics in the ps time range analysed in previous work [7]. However, the Q dependence is much less understood and a more detailed MCT analysis combining both sets of experiments to enlarge the time window is needed.

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