

Proposal: 6-05-921 **Council:** 10/2012
Title: The connection between fast and slow dynamics in glass-forming liquids: a test of the "isomorph theory" of simple liquids.
This proposal is a new proposal
Research Area: Soft condensed matter

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Samples: dibutylene phthalate and dipropylene glycol

Instrument	Req. Days	All. Days	From	To
IN16	7	7	13/03/2013	20/03/2013

Abstract:
 The molecules in a liquid close to the glass transition move on a range of timescales. Vibrations take place on the picosecond timescale while relaxations can be as slow as minutes or hours. It has several times been suggested that there is a close connection between the fast and slow dynamics, even though they differ in time scales by ten or more orders of magnitude. The recently developed isomorph theory rationalizes this connection. The aim of this experiment is to measure fast dynamics (~ nanosecond) along lines in the phase diagram where the slow alpha relaxation is constant (so called isochrones), because the isomorph theory predicts that the fast relaxation should be invariant along these lines. The experiment requires measurements at elevated pressure, which is in itself interesting because relatively little INS/QENS high pressure data is available on glass-forming liquids.

Experimental Report, exp.# 6-05-921, IN16 13th-20th March 2013

Main Proposer: Kristine Niss, RUC, Denmark

1 Summary

The aim of this experiment was to study dynamics of the glass-forming liquid 5PPE as a function of pressure. The scientific aim was to examine the fast (nanoseconds) dynamics along isochrones of the slow dynamics e.i. lines of constant relaxation time found by dielectric spectroscopy in the miliherzt-megahertz range (= microsecond to hours). The experiment was however not successful because of problems with the pressure cell supplied by ILL, which made it impossible to get reproducible results.

Detection of the problems and debugging was extremely tricky because we saw no leaks and no (significant) pressure decrease was detected at the pressure gauge situated at the top of the sample stick. We spend 5 days on debugging (including some experiments which we thought were good, but later had to discard, because they could not be reproduced). The pressure transmitting liquid was fluorinert FC77 (fluorinated alkane): it shows a glass transition at room temperature and at high pressure around 0.8 GPa (see Feng Chen et al., Rev. Sci. Instrum., Vol. 75, No. 11, 4578 (2004)). It is probable that, being the cold point around liquid nitrogen temperature, at some pressure between ambient and 0.8 we may fall outside the hydrodynamic regime. It is also possible that there was a problem with freezing of the pressure liquid, but data on the melting line are not available. We conclude that the stick needs to be heated, something which was also prepared, but not installed when we performed the experiment. Moreover the ILL high pressure technicians continued debugging after our experiment had ended and they found a leak between the sample liquid and the pressure liquid.

Finally we spend 2 days on measurements with a normal ambient pressure cell - half of this time was used for empty cell and vanadium measurements.

We will ask for a new beamtime to replace this experiment, when the reactor is running again.

2 Experimental problems and debugging

The pressure cell used was and 5kbar Aluminium P-cell with an outer diameter of 18 mm and usable height of 30-40 mm. The pressure is applied with a flourinated liquid (FC77) which is separated from the sample by a small piston. The pressure is applied from the outside of the cryostat via a capillary.

The high pressure experiments resulted in 5 days of fruitless tests and experiments. We applied pressure, saw no leaks, and no (or very little) pressure decrease was detected at the pressure gauge situated at the top of the sample stick. Yet our measurements were not reproducible. Thus the problems were located in the stick, the pressure liquid or inside the cell. The sample is one of our standard samples and we use it for reference in all our in house experiments at Roskilde University, because it is chemically and physically stable. We could therefore conclude that the lack of reproducibility is not due to lack of sample stability.

The rest of this section gives an account of how we spend our days of experiment.

Day 1

Our tests were primarily performed by monitoring the elastic intensity after applying pressure. We saw an increase in intensity as expected. However, this increase had different degrees even if we applied the same pressure. During the first night we performed elastic scans at atmospheric pressure.

Day 2

On the second day of experiment we realized that the pressure liquid could be crystallized by the cold point which was above the sample stick on the cryostat. The cold point is around nitrogen temperature and the pressure liquid

is outside the hydrodynamic regime (i.e. very high viscosity, that implies no prompt response to pressure change along the line) and possibly even frozen, especially as pressure is increased. This was a known problem by the ILL sample environment staff and a connection heating wires had been mounted on the stick, however the actual wires were missing. We concluded that even though the pressure was high at the top of the stick, it was not transmitted to the sample, because solidified pressure liquid blocked the capillary.

Based on this conclusion we changed the experimental procedure. Instead of leaving the stick in the cryostat when applying pressure, we now took out the stick each time the pressure had to be changed. The stick was carefully heated to ensure full melting of the pressure liquid and the pressure was then either raised or decreased. The stick was subsequently remounted in the cryostat. This procedure gave a much greater effect of pressure than we had seen before, which supported the conclusion that solidification of the pressure transmitting liquid had been the problem.

Day 3

During the third day we ran a number of experiments, which by the first inspection looked good. We collected both spectra and elastic scans at 200 MPa.

Day 4

However, when looking at the data on the fourth day we realized that the effect of pressure had gradually disappeared (the scans approach the values we had obtained earlier at P_{atm}). Yet the monitored pressure at the top of the stick was still stable. We decreased the pressure and this had no further effect, supporting the hypothesis that the sample was no longer under pressure.

On the fourth day we again did a large series of test experiments. We stepped up and down in pressure with different protocols, e.g. also monitoring what happened as function of time after applying pressure. We again saw the effect of pressure decreasing. We speculated that even when we applied pressure with the stick outside and the pressure liquid melted it subsequently crystallized in the capillary by the coldpoint and therefore contracted. This resulted in a pressure decrease at in the cell and sample.

As a last strategy we did decided to heat up the cryostat. This was had to done by cutting of the helium and nitrogen supply and let it run empty. This procedure is time consuming and in the mean time we filled a normal cell and ran a temperature elastic scan during the night.

Day 5

During the night the detector bank totally died. The first message we got was that it would probably take days to get it fixed. However, after lunch it was back. The cryostat was now warm, meaning that there was no longer a cold point and we performed tests with changing pressure at room temperature. However, the measurements were not consistent with anything we had seen before. As mentioned above, it was later found by the technicians that there was a leak between the sample liquid and the pressure liquid.

Day 6-7

Finally we gave up on the pressure cell and used the last two days for measurements with a standard liquid cell. We performed an elastic temperature scan and took spectra at 4 temperatures (including 4 K to be used for resolution). Moreover we measured empty cell and vanadium. These results are reported in the next section.

3 Ambient pressure data

From the elastic scans we calculated the means square displacement (msd) which is displayed in Fig. 1. Here it is clearly seen that there is a kink in the msd close to the glass transition temperature (T_g). This behavior is almost

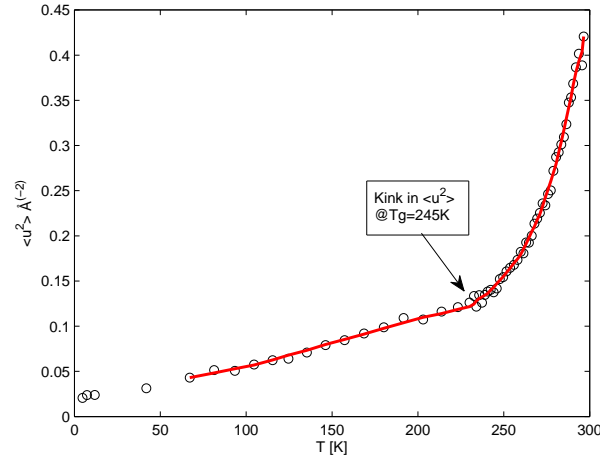


Figure 1: Means square displacement calculated from the elastic scans (assuming a Q^2 -dependence of log intensity). Red curve is smoothed data. It is clearly seen that there is a kink in the temperature dependence at T_g .

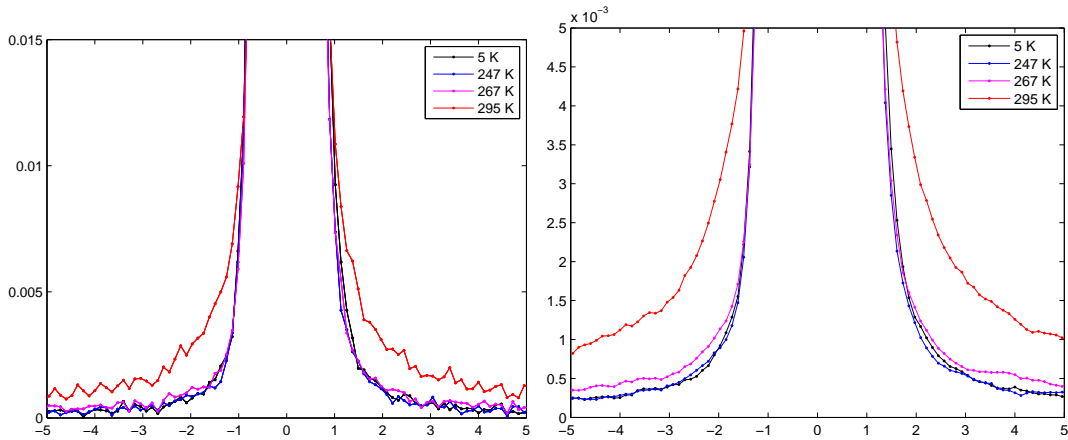


Figure 2: Inelastic spectra at four different temperatures (5 K is considered to represent the resolution function). Left: Cell subtracted. Summed over Q . No normalization. Right: Same data but on a different scale, moreover smoothing has been applied.

always seen in glass forming liquids. One interpretation of this kink would be that the msd has a relaxational contribution above T_g . However, the spectrum obtained at T_g (Fig. 2 and Fig. 3) collapses with the resolution function. The lower elastic intensity must therefore be associated with a larger amplitude of the vibrational part of the msd (or alternatively relaxations that are faster than the nanosecond scale).

At $T=267\text{ K}$, it appears at first sight that there is still no relaxation seen in the spectrum (Fig. 2). However, a close inspection by zooming and smoothing the data suggests that in fact there is a small signal at this temperature. The corresponding dielectric relaxation time is around one milli second. That is around 6 decades slower than the relaxation seen by IN16. This suggests that we are seeing something which is probably not the alpha-relaxation itself, but maybe a precursor of it.

At $T=297\text{ K}$ the alpha relaxation time is in the nanosecond range. We therefore believe that the relaxation itself is a signature of the alpha-relaxation itself.

We have extensive data on this sample in terms of dielectrics (including high pressure), broadband mechanical data and dynamic heat capacity data. A detailed analysis of how the msd relates to relaxation, mechanical moduli and heat capacity is therefore possible from these data. But has not yet been performed.