# Experimental report

13/05/2019

**Proposal:** LTP-6-7 **Council:** 10/2014

**Title:** High Pressure Cell for Simultaneous Dielectric and QENS/INS going up to 500 MPa

**Research area:**

**This proposal is a new proposal**


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**Samples:** Glycerol
Polyisobutylene
Dipropylene glycol (C6H14O3)
Cumene
5-phenyl-4-ether
1,2,6-hexanetriol
C8H12
1-Butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide
C11H20N2F6S2O4

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| IN6 | 0 | 4 | 25/08/2016 | 29/08/2016 |
| IN16B | 23 | 14 | 27/06/2016 | 04/07/2016 |
| | | | 04/11/2016 | 11/11/2016 |
| IN5 | 13 | 11 | 28/11/2016 | 01/12/2016 |
| | | | 19/01/2017 | 23/01/2017 |
| | | | 04/06/2018 | 08/06/2018 |
| IN13 | 6 | 6 | 13/10/2015 | 16/10/2015 |
| | | | 08/06/2016 | 13/06/2016 |


**Abstract:**

The main technical aim of this LTP is to design, manufacture and test a high pressure (500~MPa) cell for simultaneous dielectric and neutron spectroscopy in collaborations with the SANE group of the ILL.

This proposed cell will be a new and unique tool for studying a variety systems with dynamics on a large range of time scales. In order to study the broad range of dynamics coming all the way from the ps range to the ks it is necessary to combine complementary techniques; dielectric spectroscopy and neutron spectroscopy being two of the most important tools. Pressure has proven to be a strong tool in separating different processes as well as in understanding how they are controlled by temperature vs. volume effects.

The aim of this proposal is to be able to perform the dielectric and neutron spectroscopy simultaneously while controlling both T and p. The cell will be a strong tool particularly for physically and chemically unstable systems, e.g. biological samples, samples that undergo chemical reactions such as polymerization or systems undergoing a phase transition. We will use the cell for glassy systems while they undergo physical aging.

# Final report LTP-6-7, September 2018

This report summarises results and accomplishments and concludes the three-year long term project, LTP-6-7. The project was initiated in January 2015 and is first and foremost a collaboration between Roskilde University (RU) and the SANE group at the ILL with collaborators at ILL, University of Silesia, LLB, IBS Grenoble and University of Pisa. The main technical aim of this LTP was to "design, manufacture and test a high pressure (500 MPa) cell for simultaneous dielectric and neutron spectroscopy in collaborations with the SANE group of the ILL". The combined cell for doing simultaneous dielectric and neutron spectroscopy under high-pressure was successfully used for the first time during beamtime in July 2016 on IN16B, and has been used frequently since for beamtimes and for beamtime preparation.

The neutron and dielectric community both have strong traditions in studying the dynamics of glass-forming liquids; dielectrics is a fast probe with relatively easily comprehensible data with a basic setup that can readily be set up in a lab at a quite low cost, and neutron spectroscopy is a unique probe for directly measuring the dynamic structure factor, $S(Q, \omega)$, either the self-motion or the collective dynamics. Although, it is different types of dynamics that are probed with the two techniques, they supplement each other well. With neutron spectroscopy as an excellent technique for studying the fast dynamics from for example self-correlations on pico- to nanosecond timescales, dielectrics provides fast (within minutes) and precise measurements in the range from microseconds to hundred of seconds via dipole-dipole correlations. Even if they do not overlap completely in timescales, there is easily an overlap between the techniques in the signal from the alpha relaxation in glass-forming liquids. The two techniques also compliment each other from an experimental and design-wise point of view as the optimal geometry for both techniques are the same: for dielectric spectroscopy, the dielectric signal is directly proportional to the area divided by the sample thickness, likewise for neutron scattering, a large sample area will give a strong signal and a small sample thickness is required to avoid multiple scattering.

## Technical accomplishments

In Fig. 1, we show a drawing of the combined high-pressure cell and its different components. In this design, a cylindrical capacitor is placed inside a hollow cylinder, the high-pressure neutron cell. A plug is placed in the end pointing away from the sample stick that allows to connect the capacitor to wires outside that can measure the capacitance of the liquid sample in the orange cryostat, i.e. inside the neutron beam. This plug is pressure tight up to a maximum pressure of 500 MPa, where the limiting factor is the aluminium (Al-7049-T6) of the sample cell, which was chosen because it had the lowest background of the tested materials.

The largest challenge of this design has been to find a solution for the plug that is pressure-tight up to 5 kbar and electrically isolating, ensuring that the capacitance is just measured across the sample liquid. The fine mechanic work of the plug is done at RU and is shown in cross-sectional view in Fig. 1, and photographs of the casting process is shown in Fig. 2. The wires are fed through a cylinder of brass, and the empty space is filled with STYCAST® 2850 FT, which is a dense paste that is cured into a hard and electrically resistant material. More recently, we have tried out a solution with dental cement, which also works really well.

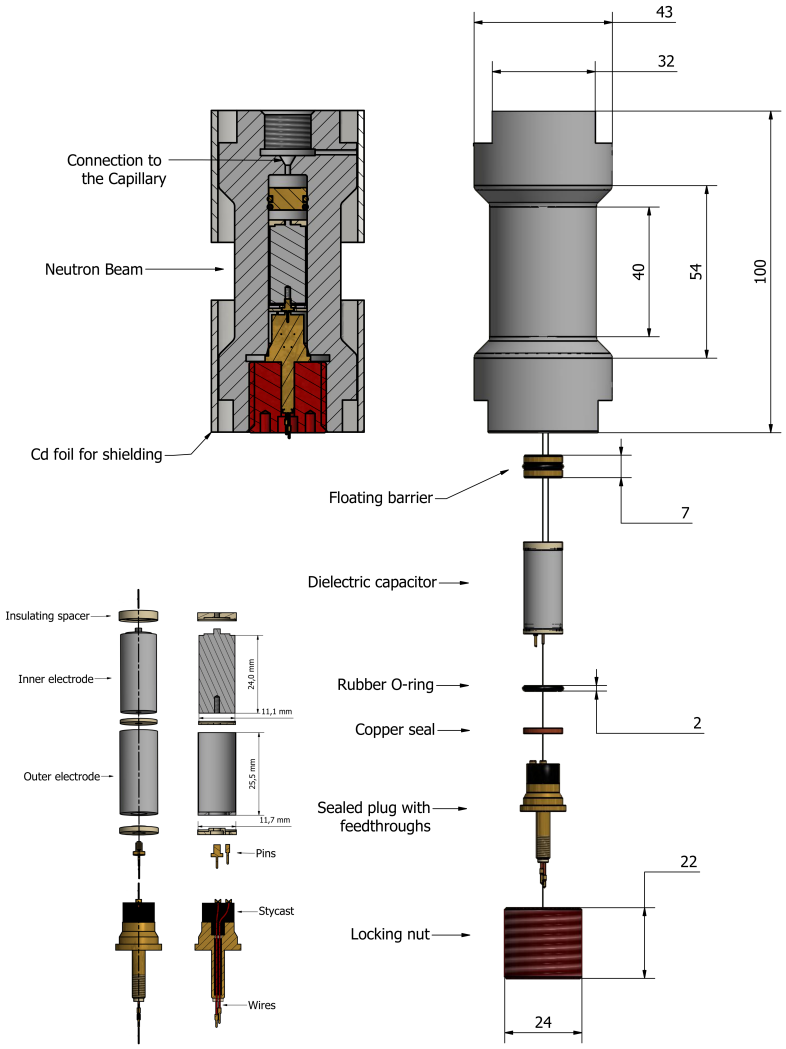


Figure 1: Drawing of the high-pressure cell for doing simultaneous dielectric and neutron spectroscopy in exploded and assembled view.

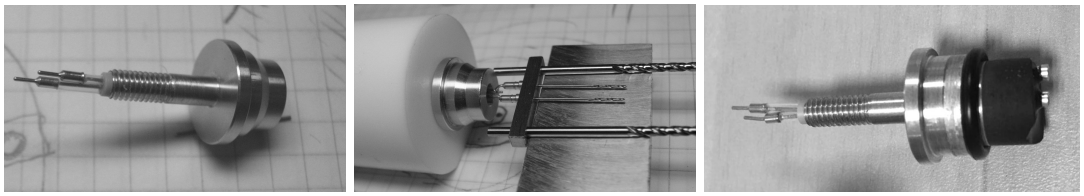

Figure 2: Electrically isolating and pressure-tight plug before and after casting with stycast with wires to connect outside the assembled cell to measure the capacitance of the sample liquid.

The design of the cylindrical capacitor is also shown in Fig. 1, where the inner and outer electrode of the capacitor is in aluminium with peak separators to ensure electric insulation and that the components are held in position, also under high-pressure. Two small brass screws are connected to the plug for measuring the capacitance of the liquid sample between the inner and outer electrode.

The design of the neutron cell is inspired by previous high-pressure work at the ILL, and the design of the sample stick is also from the SANE group at the ILL, but with additional wires going through the sample stick next to the heated capillary for the pressure liquid and BNC-cables in the top to connect to the dielectric equipment outside the cryostat.

In the first design of the sample stick, there were an increase in the capacitance at high frequencies in the last few decades due to induction. The SANE group then produced a second sample stick with four wires to minimise noise through the stick. The problem is not solved, as there is still noise in the last decade, but greatly reduced.

## Main scientific results

As reported in the scientific highlights section of the annual report of the ILL in 2017, we found that for simple van der Waals glass formers, the dynamics over 14 orders of magnitude in timescale can be expressed as a function of a single parameter, effectively reducing the usual temperature-pressure phase diagram into one of just one dimension in accordance with isomorph theory.

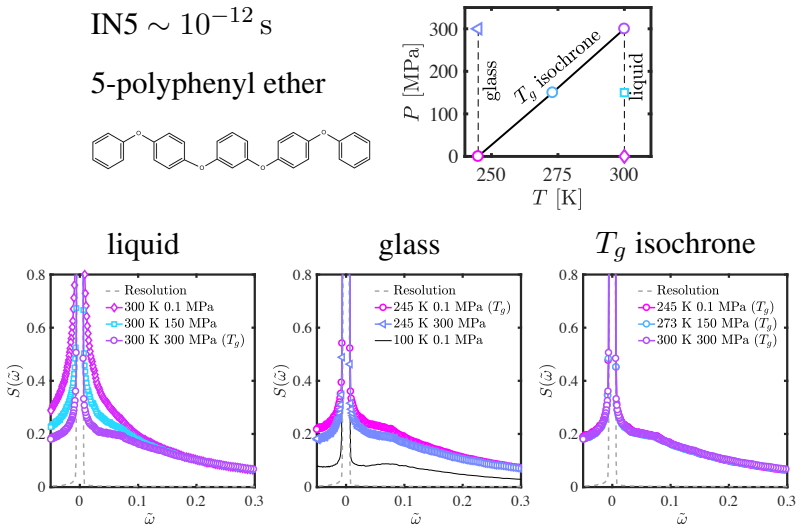


Figure 3: IN5 spectra of a simple glass former (PPE) shown as a function of energy transfer on reduced energy unit scale in accordance with isomorph theory, $\tilde{\omega} = \omega\rho^{-1/3}T^{-1/2}$. All spectra are showed summed over $Q$. The state points of the two isotherms and the $T_g$ isochrone mapped out with dielectrics ($\tau_\alpha = 100\,\mathrm{s}$) are shown in the $(T, P)$ phase diagram. Figure from ILL annual report 2017, adapted from Nat.Comm. **9**, 518 (2018).

For the investigated simple van der Waals systems, this is found to be true even when the vibrational and fast relaxational dynamic contributions on a picosecond time scale are completely separated from the alpha relaxation at the glass transition, which is on a time scale of seconds. This invariance in dynamics is shown in Fig. 3 for the simple van der Waals liquid 5-polyphenyl ether (PPE) with spectra from IN5. The combined

high-pressure cell for simultaneous dielectric and neutron spectroscopy was crucial for this study to ensure the precision of the glass transition of the stuied liquids.

## List of publications

Publications directly related to the LTP:

Hansen, H. W., Frick, B., Capaccioli, S., Sanz, A., and Niss, K.
Isochronal superposition and density scaling of the $\alpha$-relaxation from pico- to millisecond.
*Journal of Chemical Physics* **149**, 230901 (2018).

Sanz, A., Hansen, H. W., Jakobsen, B., Pedersen, I. H., Capaccioli, S., Adrjanowicz, K., Paluch, M., Gonthier, J., Frick, B., Lelièvre-Berna, E., Peters, J., and Niss, K.
High-pressure cell for simultaneous dielectric and neutron spectroscopy.
*Review of Scientific Instruments* **89**, 023904 (2018).

Hansen, H. W., Sanz, A., Adrjanowicz, K., Frick, B., and Niss, K.
Evidence of a one-dimensional thermodynamic phase diagram for simple glass-formers.
*Nature Communication* **9**, 518 (2018).

## Benefit for LTP users and ILL users

The newly developed high-pressure cell is available through the user programme at the ILL. The ensure the continuous transfer of knowledge and use at the ILL, the ILL spectroscopy group has invested in a frequency generator from NovoControl for controlling the dielectrics. A PhD student is starting at the ILL on 1 May 2019 in a collaboration between the ILL and RU. The simultaneous measurements are a key feature of this project on glycerol-water mixtures, and will ensure the continuous development and use of the simultaneous measuring techniques.

## Success of LTP

The new combined cell for doing simultaneous dielectric and neutron spectroscopy have proven to be an effecient tool. The new cell provides the possibility to test experimental protocols offline before a beamtime, for example to locate particular state points in temperature and pressure, which can then be relocated online, or map out areas in temperature and pressure where the sample is prone to crystallisation.

The fast and precise dielectric frequency-dependent measurements serve not only as an extension of the dynamic timescales we can access, but also as an extra probe located directly in the neutron beam for checking the sample conditions, in large part due to the sensitivity of the dynamics of glass-forming liquids to relatively small changes in temperature and pressure. But also includes the monitoring of pressure transmission of the sample, the coming into and reaching thermal equilibrium, checking that the pressure liquid has not reached and mixed with the sample environment, that there is no leak, and so on.

The combined measurements provides certainty on state points and allow for repetition

of measurements offline either beforehand for preparation of beamtime or afterwards for checking reproducibility. In conclusion, the new combined high-pressure sample cell has meant that we have been able to do more accurate measurements in temperature and pressure, but the success is also to a large extent because of its role as sample environment monitor, which means that we can optimise how we spend the valuable beamtime.