

A NEW HIGH PRESSURE APPARATUS FOR NEUTRON DIFFRACTION IN LIQUIDS AND GLASSES AT 0.7 GPa

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We describe a safe, simple, all-hydraulic pressure system for neutron scattering from glass or liquid samples at 0.7 GPa (100,000 psi). The central feature of the design is a novel floating barrier. The barrier isolates the hydraulic working fluid from the glass or liquid sample in the neutron beam. The effectiveness of the system is demonstrated by neutron diffraction spectra of fully-deuterated methanol at 0.62 GPa.

KEY WORDS: Neutron diffraction, glasses, liquids, high pressure, methanol

INTRODUCTION

Thermal neutron diffraction is a powerful method used for creating structural models of glasses and liquids. Controlled variation of pressure is a highly-selective probe for testing these models.¹ However, bringing the two techniques together to carry out neutron diffraction measurements at high pressure presents formidable difficulties.

X-ray diffraction measurements are now possible in the megabar range using diamond anvil cells. However, the sample volumes demanded for an acceptable signal/noise ratio in neutron spectroscopy are orders of magnitude greater than the 3×10^{-6} cm³ volume associated with a typical anvil cell. The requirement of a large sample volume restricts the maximum pressure of a neutron diffraction experiment to *ca.* 4.5 GPa. Nonetheless, the effort that must be put forth to carry out neutron diffraction experiments at these modest pressures is warranted for the study of glasses and liquids. A pulsed neutron source has an epithermal neutron flux that leads to momentum transfers of 35 \AA^{-1} and more with a concomitant enhancement of the real space resolution function.² And, the intermediate-range order of many glasses and liquids responds to pressure variations even below 0.5 GPa.

Note that isothermal variation of pressure at constant composition is a more selective probe of structure than variation of temperature. For most normal condensed phases, a change in temperature at constant composition changes the density of the system along with the amplitude of vibration of the component atoms. [Vitreous silica is a well-known exception.] Separating the two effects is not straightforward.³

The optimum pressure transmitting fluid (PTF) for a high-pressure neutron scattering experiment is helium gas. However, large-volume, gas-pressurized cells are inherently dangerous and their support systems are difficult to maintain. There is also the complication of gas solubility in liquid samples.⁴ Alternatively, hydraulic systems have negligible stored energy and are easily and safely operated by inexperienced personnel. However, total hydraulic systems have not been readily exploited for neutron scattering measurements at high pressures. An isostatic fluid environment requires a hermetic capsule or a tied-off balloon to contain a liquid sample and to prevent diffusion or mixing with the PTF. Invariably, the PTF migrates around the capsule or the balloon and into the neutron beam. For glass samples, a separate sample container is neither necessary nor desirable. Here, an isostatic pressure is obtained by letting the PTF come into intimate contact with the glass sample powder. The fluid is chosen for maximum neutron transmission consistent with no chemical reaction with the sample. Usually the PTF turns out to be a deuterated, low molecular weight, low viscosity compound. Such compounds are often too costly to be used to fill up the large volumes associated with the second stage of a hydraulic pressure intensifier. Typically, they are corrosive to the seal components and too low in viscosity to be easily contained in a moving piston seal. With regard to separating the sample signal from the background, the selection of a PTF for a glass sample is more critical than for a crystalline sample for well known reasons.

In this manuscript, we describe a hydraulic apparatus for neutron scattering at pressures up to 0.7 GPa. It is safe, simple to operate, and meets all the needs for working with glass or liquid specimens as discussed above. The key to creating a completely hydraulic environment lies in a novel floating barrier which effectively isolates the hydraulic working fluid from any fluids in the neutron beam.

DESCRIPTION OF THE APPARATUS

1. *The Pressure Generator*

Figure 1 is a schematic drawing of the 0.7 GPa, all-hydraulic system for neutron scattering experiments with glass and liquid specimens. Functionally, the apparatus is viewed as a three-component system consisting of a high-pressure source [a], a sample cell [b], and an impermeable barrier [c] that transmits pressure from the source to the cell while separating the two dynamically (see Figure 1). The pressure source is a commercially-available, high-pressure generator⁵ with a 25:1 intensification ratio. Primary pressures up to 0.055 GPa (8000 psi) are generated by an electrically-driven, 1/2 HP, submerged pump⁶ using ordinary hydraulic fluid [d]. Pressures up to 1.4 GPa (200,000 psi) can be generated in the 140-cm³ volume of the second stage of the intensifier. We find that Octoil-S (dioctyl sebacate) is a non-corrosive, hydrostatic, second-stage working fluid for pressures up to 0.7 GPa. It has a low-enough viscosity/pressure relationship to permit pressure gradients to dissipate in long lengths of capillary tubing in 5–10 minutes. And its viscosity is

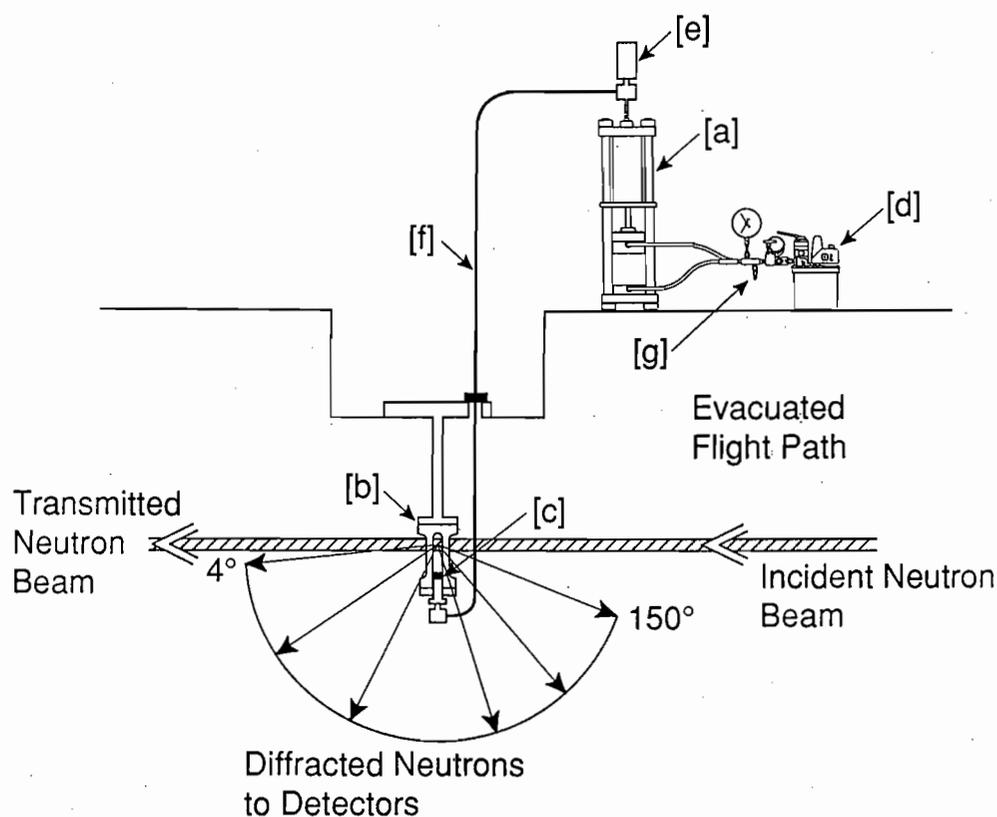


Figure 1 Schematic diagram of a total hydraulic system for neutron scattering (not to scale). See text for explanation of labels.

high-enough at room temperature (0.018 Pa·s) so it does not leak past the Teflon/silver piston seal of the intensifier. Pressures are monitored on the high-pressure side of the intensifier by a transducer strain gauge⁷ [e]. The intensifier, in turn, is connected to the sample cell [b] by 3 meters of 0.64-mm (0.025-in) bore, stainless steel, high pressure tubing [f]. Tubing with this inner diameter is rated to 1.0 GPa (150,000 psi); but it is still flexible, and it can be looped and bent to connect easily to the cell which hangs in the evacuated flight path centered on the neutron beam. An adjustable relief valve in the electric pump is set to 0.025 GPa (3600 psi) to prevent accidental over-pressurization of the cell. An in-line, 0.026 GPa (3750 psi) rupture disk [g] serves as an added safety precaution.

2. The 0.7 GPa Pressure Cell

The pressure cell is similar in design to one in use at Argonne's Intense Pulsed Neutron Source (IPNS) for crystalline powders.⁸ It is a simple single cylinder of 7075-T6 aluminium alloy with a 1.15-cm bore that has been autofrettaged to final size at 0.7 GPa (100,000 psi). In principle, this cell can be operated up to 0.8 GPa—but it has been proof-tested only to 0.7 GPa. The cell design is optimized for time-of-flight

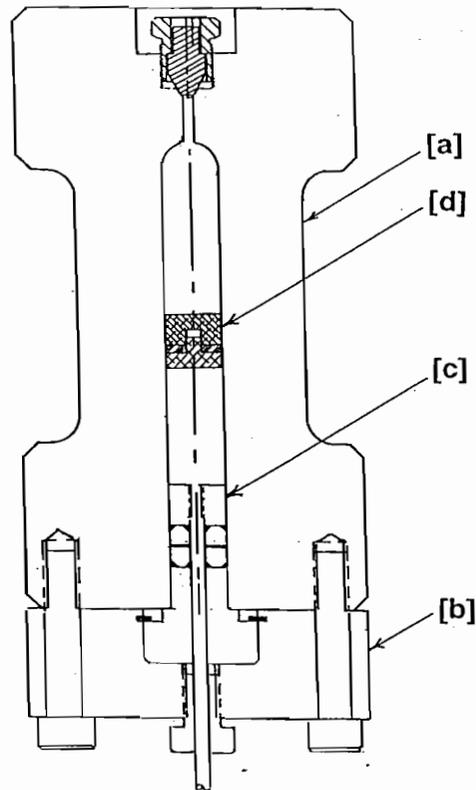


Figure 2 The 0.7 GPa aluminium cell for neutron scattering from glasses and liquids. See text for explanation of labels.

data collection over a scattering angle of $2\theta = 4^\circ\text{--}150^\circ$ on GLAD—the *Glass, Liquids and Amorphous Materials Diffractometer*⁹ (see Figure 1). Consequently, there is no inner or outer shielding. Therefore, the cell can be used with arbitrary detector arrays on elastic or inelastic spectrometers. However, corrections are required for the backgrounds created by multiple scattering processes in the thick aluminium walls.

Figure 2 is a schematic diagram of the 0.7 GPa cell. The body of the cell [a] through which the neutrons pass is 5.08-cm OD \times 5.08-cm high. The bottom end cap [b] is 2.54-cm high and carries the seal that is used for pressurizing the cell with Octoil-S. The seal [c] is a mechanically-preloaded, Bridgman, unsupported-area seal with gaskets of lead, indium, and Teflon. Access through the top of the cell is via a 1.59-mm diam. hole that is sealed with a standard cone closure plug. A floating barrier [d] transmits high pressure while isolating the working fluid (Octoil-S) from the neutron beam.

3. The Floating Barrier

An isostatic sample environment is created by transmitting the hydraulic pressure into the sample volume through a novel floating barrier. An exploded view of the barrier is shown in Figure 3. The barrier is a modification of a Bridgman unsupported

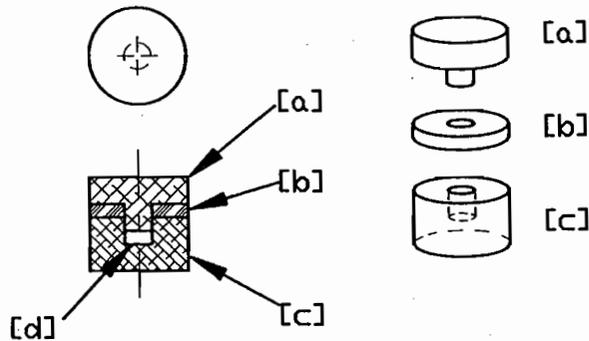


Figure 3 Details of the floating barrier. See text for explanation of labels.

area seal. A neoprene gasket [b] is cemented with a cyanoacrylate ester glue between an aluminium mushroom [a] and an aluminium plug body [c] in a helium-filled glove bag. The captured gas volume [d] has a much lower compressibility than the liquids on either side of the barrier and acts as a soft spring. Even slight pressurization of the Octoil-S moves the mushroom cap into the plug body and forces the neoprene gasket to seal against the side walls. An impermeable barrier to fluid flow is created at any pressure up to 0.7 GPa even though there is essentially no pressure differential across the barrier. The floating barrier moves smoothly into and out of the sample volume as the cell is cycled in pressure. With care, the barriers are reusable. However, they are easy and cheap to fabricate and we view them as consumables for the lengthy neutron diffraction experiments.

EXPERIMENTAL PROCEDURE AND RESULTS

The procedure for loading the pressure cell is different for glass and liquid samples. Glass samples are powdered and mixed with a minimum amount of pressure transmitting fluid into a thick paste. (Bulk glass specimens should not be used if the internal pressure is to be kept isostatic). The paste is charged into the completely open cell, filling it completely, while taking care to avoid trapping gas bubbles. The barrier is inserted and then forced up into the cell with a wooden dowel rod to a depth of 2.86 cm—just the length that the Bridgman unsupported seal will protrude into the cell. Excess sample paste exudes through the cone opening in the top. The cone seat is wiped clean and the cone plug is seated. A small amount of Octoil-S is introduced into the volume above the barrier, and the end cap with the Bridgman seal is pushed into place forcing oil out of the coupling elbow. The Bridgman seal is mechanically preloaded and the coupling connected to the prefilled high pressure line. If the sample is thick, subsequent pressurizing to 0.6 GPa advances the floating barrier <7 mm since the sample is largely incompressible glass. The cell can be physically centered with respect to the neutron beam.

Loading a liquid sample is quick and easy with one caveat. The floating barrier and the end cap carrying the Bridgman seal are already in place. The cell is filled with the liquid sample through the top opening using a hypodermic syringe. Approximately 8.3 cm^3 of liquid sample fill the cell. The cone plug is seated and the cell is connected to the pressure line. Note, however, that at high pressure, the final position of the floating barrier is a function of the compressibility of the sample itself. With a liquid sample such as methanol, the barrier will move up into the cell *ca.* 25 mm at 0.7 GPa. This means that the cell must be aligned with the neutron beam at the top of the sample volume. This cell has been designed for the 1.02-cm wide \times 1.27-cm high collimated neutron beam of the GLAD instrument (Figure 1[h]). For a taller neutron beam, a proportionally longer cell should be used to insure that the barrier does not intrude into the beam at the higher pressures.

Figure 4 presents neutron diffraction data for fully-deuterated methanol obtained with the all-hydraulic pressure system. Methanol is prototypical of hydrogen-bonded systems (both liquid and glass) where the short- and medium-range structure can be probed by varying the external pressure on the system. The data in Figure 4 are the normalized intensities from the low-angle detector grouping of GLAD. They illustrate the relative ease with which the pressure effects can be followed when the floating barrier separates the deuterated methanol sample from the working pressure fluid. It is apparent that at 0.62 GPa the intermediate-range order of methanol is changed. For example, the repeat distance at 3.6 \AA in real space ($2\pi/Q$) has decreased; i.e., shifted to higher Q (see Figure 4). A complete study of the pressure dependence of

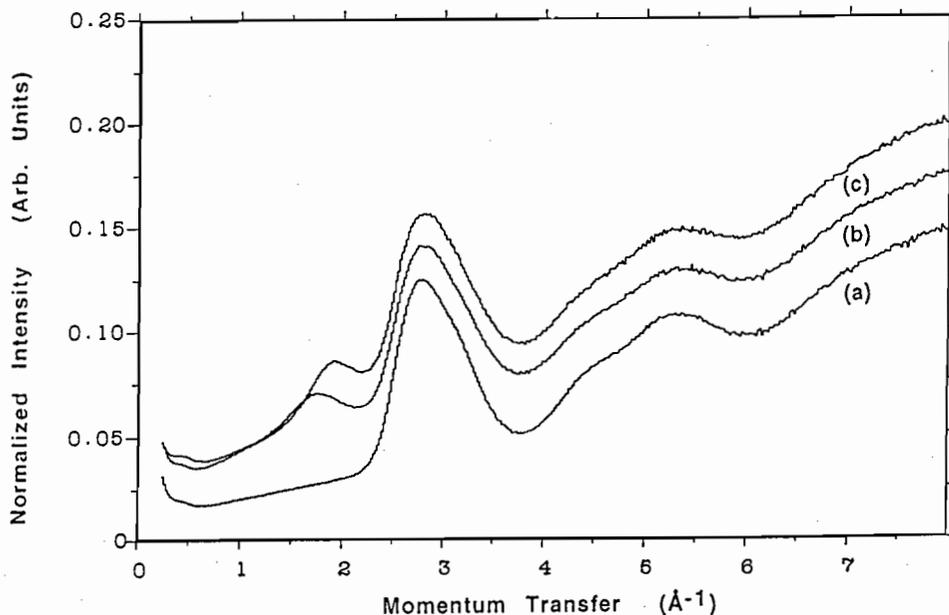


Figure 4 Neutron diffraction intensity for: (a) The empty 7075-T6 aluminium alloy pressure cell. (b) Fully-deuterated methanol, CD_3OD , in the pressure cell at ambient pressure. (c) Fully-deuterated methanol, CD_3OD , in the pressure cell at 0.62 GPa.

the structure of methanol involving fully- and partially-deuterated samples is in progress.

SUMMARY

A safe, simple, all-hydraulic pressure system is described for neutron scattering from glass or liquid samples at 0.7 GPa. The central feature of the design is a novel floating barrier. The barrier isolates the hydraulic working fluid from the glass or liquid sample in the neutron beam. The effectiveness of the system is demonstrated by neutron diffraction spectra of fully-deuterated methanol at ambient pressure and at 0.62 GPa.

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References

1. S. Susman, K. J. Volin and R. C. Liebermann, *Physics Chem. Glasses* **31**, 144 (1990).
2. S. Susman, D. L. Price, K. J. Volin, R. J. Dejus and D. G. Montague, *J. Non-Cryst. Solids* **106**, 26 (1988); S. Susman, K. J. Volin, D. G. Montague and D. L. Price, *J. Non-Cryst. Solids* **125**, 168 (1991).
3. S. Susman, K. J. Volin, D. G. Montague and D. L. Price, *Phys. Rev.* **B43**, 11076 (1991); S. Susman, K. J. Volin, D. L. Price, M. Grimsditch, J. P. Rino, R. K. Kalia, P. D. Vashishta, G. Gwanmesia, Y. Wang and R. C. Liebermann, *Phys. Rev.* **B43**, 1194 (1991).
4. G. W. Nielson and S. Cummings, *Revue Phys. Appl.* **19**, 803 (1984).
5. Leco Corporation, Tem-Press Division, Blanchard Street Extension, P.O. Box 390, Bellefonte, Pennsylvania, USA.
6. Enerpac Group, Applied Power Inc., Butler, Wisconsin, USA.
7. Sensotec Inc., 1200 Chesapeake Avenue, Columbus, Ohio, USA.
8. J. D. Jorgensen, *et al.*, *Physica* **C171**, 93 (1991).
9. R. K. Crawford, J. M. Carpenter, R. Dejus, J. R. Haumann, R. Kleb, D. G. Montague, D. L. Price and S. Susman, Proceedings of ICANS-XI, International Collaboration on Advanced Neutron Sources, KEK, Tsukuba, Japan, October 22-26, 1990, pp. 820-829.