We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

6,600 Open access books available
177,000 International authors and editors
195M Downloads

154 Countries delivered to
TOP 1% Our authors are among the most cited scientists
12.2% Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
Chapter

Pressure Inhomogeneities across Large Samples Using Gas Pressure Media at Low Temperatures

Juscelino Batista Leão

Abstract

In-situ inert gas high pressure vessels for neutron scattering for pressures of up to 1.0 GPa, and temperatures as low as 1.5 K, pose a particular problem due to the $P \times T$ phase diagram of the pressure media. Hydrostatic pressure under constant pressure and volume, passing through the pressure versus temperature phase diagram ($P \times T$) of the gas to achieve low temperatures (1.5 K < $T$ < 30 K) will cause an overall pressure reduction at base temperatures of at most 25% of the pressure read at the $P \times T$. A methodology for pressurization to ensure minimal pressure loss as temperature falls below the pressure media phase change and at the same time minimizing pressure inhomogeneity throughout the length of the sample is presented within this work. The technique proved to reduce the isochore loss of pressure by a factor of 5. Moreover, for the first-time direct experimental quantitative evidence of the reduction in pressure inhomogeneities across large samples is reported here, and the average inhomogeneity reduction in pressure across top and bottom of a 45 mm long sample is better than a factor of 3.

Keywords: pressure, hydrostatic, neutron scattering, helium, pressure gradient

1. Introduction

There has been a constant interest in high-pressure neutron scattering studies involving the in-situ application of pressure [1–9]. Techniques vary depending on many factors not limited to type of scattering, pressure vessel construction, and pressure transmitting media (PTM) (see Klotz [1] for a literature review on the subject). Neutron scattering is a powerful tool to investigate both the structure and the dynamics of molecules; however, neutron scattering under pressure poses special challenges associated with the need of large sample volumes to obtain acceptable signal-to-noise ratio in reasonable time; pressure vessels design safety; sample pressure determination; as well as PTM considerations to name a few.

Neutron scattering under pressure ($P < 2.5$ GPa) typically requires bulky samples as a result of large neutron beam line cross sections. With the exception of neutron experiments involving pressures beyond 2.5 GPa (where other pressure intensifying methods may be better tailor to the measurement at the cost of counting time and
signal-to-nose ratio), most experiments using gas as the pressure medium benefit from samples where large amounts are available. Powder samples are easily adaptable to pressure vessels that can provide a maximum in beam cross section. Single crystal samples may employ co-alignment of a number of specimens [10] or take advantage of unusually large crystals [11].

Pressure vessel construction must take into consideration extensive and conservative calculations in order to mitigate risk to personnel and facilities [12–15]. Moreover, a standard operating procedure (SOP) is essential for the safe operation of all high pressure apparatus. It must include engineered and administrative controls for the mitigation of operational risk. Notwithstanding the design and SOP, the high pressure equipment must be submitted to frequent maintenance analysis and procedures.

Not only engineered, but also administrative controls must be in place when determining a pressure vessel operational maximum pressure range. Codes and regulatory bodies differ from country to country and between neutron scattering facilities. The interpretation to these codes also differs between the researcher and their respective safety officers. Therefore, it is in the best interest of the experimental community that, at a minimal, some regulatory guidelines must be followed in the design, testing, and operation of pressure systems. Experiment scheduling problems may rise when a certain pressure apparatus for neutron scattering is to be taken from one facility and used at another. The hazard assessment procedure is a necessary time consuming process intrinsically tied to the safe operation of the system.

Monoblock thick-wall cylindrical vessels are often used in neutron scattering for the 360° available scattering window but pose difficulties in resolving vessel integrity after normal operating temperature and pressure cycling over time. During the manufacturing process in this design, the vessel undergoes autofrettage. The internal pressure is raised above the elastic limit of the construction material without reaching failure and, as a consequence, the inner part of the unloaded cylinder is left under tangential tension while the outer part is left under tangential compression after an initial pressurization well above the final vessel working pressure. Nevertheless, the residual stresses over many temperature and pressure cycles lack quantitative data in general. This issue may be resolved using neutron diffraction (ND) residual stress mapping as a non-invasive long term quality control procedure [16].

Many neutron scattering experiments under pressure focus on the study of first order phase transition properties, and thus require refined precision in the pressure determination. Unquestionably, in the range of pressures reaching 1.5 GPa, noble gases are particularly desirable as PTM. And among these, helium is by far the gas of choice [13]. The use of gases as PTM in such experiments must also take into consideration the pressure media phase transition at low temperatures. Homogeneous hydrostatic conditions are paramount for such experiments, and this is obtained fairly straightforward for measurements where the gas media is in the temperature regime above its melting point in the $P \times T$ diagram (Figure 1).

However, for experiments where temperatures and pressures dip into the solid media phase, the problem of pressure inhomogeneity across large samples becomes obvious [11]. While the media present at temperatures above the $P \times T$ are in the gas phase, the media inside the pressure vessel solidifies as its temperature traverses the $P \times T$ curve. In this scenario the pressurization is typically done still in the gas phase by maintaining the temperature of the entire system just above the $P \times T$ melting curve for helium ($PT_{He}$). Once the target pressure is achieved, while in the gas phase, the temperature of the pressure vessel is allowed to drop passing through the freezing point. This cooling under constant pressure ($P_C$) attempts to minimize pressure
Pressure inhomogeneities but it is responsible for pressure losses due to helium gas-solid phase change [13]. Sherman and Stadtmuller reported a pressure loss of 20% at 0.1 GPa [14]. There is mention, in literature, of the possibility for pressure differences across a sample [14]; however, to best knowledge, this has not been documented experimentally elsewhere. Pressure inhomogeneities across large samples are of significant importance for experiments, such as in the pressure-temperature phase diagram of URu$_2$Si$_2$ in helium [11] for example, where the mapping of first-order phase changes is significantly sensitive to pressure.

Another consideration for such neutron scattering experiments under pressure is the accuracy and precision of the pressure measurement. Again, in the $P \times T$ case where the PTM is held in the gas phase, the pressure measurement can be achieved fairly easily through the use of various commercially available gauges [12] as long as the hydrostatic condition is unimpeded by a possible “blockage” within the length of the capillary tube that links the pressurizing device to the pressure vessel. The scenario changes once the pressure measurement temperature crosses the solid phase in the $P \times T$ diagram. The pressure loss as the temperature drops from the melting point for helium is well known and understood [13, 14] in terms of the media isochores. Nevertheless, as mentioned previously, the pressure loss due to the volumetric changes in the PTM must be tabulated with the help of secondary pressure gauges. The accuracy in pressure measurements depends greatly on the gauge used. There are primary gauges that measure the force applied on a precise area, secondary gauges that depend on the change of a certain property of the gauge that then can be translated into a pressure, and fixed points that propagate the precision of the fixed point measured. The topic of pressure gauges and accuracies is extensive and better suited elsewhere. For the pressure range at hand, the accuracy of the measurements is high [17] across the different gauges; however, the reliance on a single technique for measurement has its drawbacks.

For the case where it is not possible to use optical pressure gauges and measurements other than room temperature, the use of fixed point calibration provides reliable data with small loss in accuracy. Due to its high degree of structural anisotropy, HOPG is a good choice for pressure calibration in neutron scattering experiments using an autofrettage monoblock vessel for pressures up to 15 GPa. The carbon atoms
within the two-dimensional hexagonal lattice structure of HOPG are bound by strong covalent bonds, in contrast to much weaker bonding between adjacent planes [18].

Here it is discussed a methodology for pressurization using He as PTM in neutron scattering experiments to minimize the pressure loss in experiments that require temperatures below the pressure media phase change. At the same time minimizing pressure inhomogeneity throughout the length of the sample. Direct evidence of stacking pressure inhomogeneities presented here have not been addressed nor quantified until now. Pressure measurements for first-order phenomena are greatly influenced by these pressure differences since neutron scattering measurements provide an illumination area average [19]. Pressure difference across large samples were significantly reduced following the novel procedure here demonstrated.

2. Experimental details

A systematic approach to resolving the issue of pressure inhomogeneity requires replicating and quantifying the pressure differences across a sample under typical conditions. There is mention, in literature, of the possibility for pressure differences across a sample due to the irregular formation of helium crystals [14]; however, this has not been documented experimentally. Once quantified, a procedure to minimize these average pressures is demonstrated.

A typical neutron scattering experiment under gas pressure consists of a gas pressure intensifier (or “booster”) capable of increase the pressure of a gas cylinder to orders of magnitude. Connecting such “booster” to a pressure vessel requires a pressure gas line robust enough, and yet offering low thermal sink from room temperature. Moreover, the pressure vessel and a small portion of the pressure line must also be inserted onto a cryostat that can provide the heat removal necessary to cool the pressure vessel to the desired temperature.

The apparatus consisted of a monoblock aluminum alloy Al 7075-T6 pressure vessels (Figure 2) [20]. The vessel was designed with a working pressure of 0.65 GPa, 1.5 cm$^3$ sample volume, and having a 69% neutron transmission at 2 Å. *In-situ* pressurization was achieved using helium as the pressure media. High pressure was achieved using a commercially available two-stage helium intensifier [21]. The pressure vessel was connected to the intensifier through a high-pressure capillary brazed to a pressure plug and contained a line heater (LH) wound through the entire length of the cryostat sample well down to the immediate sample vessel connector. A commercially available cryostat, or top-loading closed cycle refrigerator (TLCCCR), was used to cool the sample down from room temperature to 4 K [20].

The sample measured consisted of three uniformly shaped pyrolytic graphite (HOPG) single crystals each measuring 10 mm × 5 mm × 3 mm and placed onto an aluminum sample holder designed as to hold each of the crystals with the c-direction normal to the neutron beam while maintaining each with a rotation off-set of 10° from one another. The sample holder containing the samples was loaded into the pressure vessel and sealed. The pressure vessel was flushed with helium and connected to the cryostat sample center stick containing the pressure capillary connection form the intensifier. Once the sample centering stick was lowered into the cryostat, a small amount of helium gas (~15 MPa) was then allowed to fill the system from the intensifier to the sample vessel. The sample was cooled to 80 K overnight and pressurized to 0.65 GPa.

Single crystal ND measurements performed in the ĉ scattering plane were conducted at the NIST Center for Neutron Research, using the BT-4 triple-axis...
spectrometer [22] operated in diffraction mode, employing an incident wavelength of \( \lambda = 2.35 \text{ Å} \) (14.7 meV) defined by pyrolytic graphite PG(002) crystals at both the monochromator and analyzer positions.

ND data for each of the HOPG crystals were obtained by rotating the TLCCR between each 10° off-sets without disturbing neither the temperature, nor the pressure in the vessel. Thus, three measurements were conducted for each temperature in both the cooling under constant volume (\( V_C \)) and cooling under constant pressure (\( P_C \)) conditions.

3. Discussion

A modified version of the Murnaghan equation [23] (Eq. (1)) was used to explore the relation between the pressure (\( P \)) and the lattice constant (\( r \)) along one of the HOPG crystal axes. For any given temperature.

\[
P = \left( \frac{\beta_h}{\beta} \right) \left( \frac{r}{r_0} \right)^{-\beta} - 1
\]

\[\text{(1)}\]
Where $\beta_0^{-1} = 37.1(5)$ GPa is the linear compressibility at ambient pressure, and $\beta' = 14.4(7)$ [24] is the pressure derivative of the linear compressibility. The axial compression coefficients of graphite vary greatly among references [25–30], this is partially due to the methodology used in determining the modulus for graphite. The measurement techniques that depend on pressure measurement themselves tend to be highly susceptible to propagation in errors. Using explosive-generated pressures these moduli were determined through empirical shock wave and particle velocity experiments by Coleburn [24]. This was particularly interesting since the results were, according to the author, in close agreement with other pressure-gauge independent results. Moreover, good agreement was observed while determining the vessel pressure at temperatures ≥70 K using the pressure gauge reading and Eq. (1) (Figure 3).

The results for the room temperature pressurizing intensifier gauge reading and the calculated pressure from the $\hat{c}$ -direction lattice parameters for HOPG were in excellent agreement (±2 MPa). After cooling the pressure vessel to 80 K (still above the $PT_{He}$), the system was then pressurized to 0.65 GPa under constant volume. The vessel temperature was allowed to equilibrate for 30 minutes before each diffraction pattern was collected. The data in Figure 3 for pressure measurements above the $PT_{He}$ and their calculations from the ND spectra are in close agreement with the pressure readings while the sample was under hydrostatic conditions. The $\hat{c}$ -direction lattice parameters were measured for each of the HOPG crystals at ambient pressure ($P_0$) and maximum pressure ($P_{0.65}$) for temperatures above and below the $PT_{He}$. For the temperature range below the $PT_{He}$, the vessel was pressurized at a temperature above and close to the melting curve of He. Pressure and diffraction data were collected for $V_C$ and $P_C$ conditions.

Figure 3 also shows the results for all temperatures measured from 80 K down to 4 K. The pressure intensifier gauge ($P_{Gauge}$) monitored the hydrostatic pressure.
transmitted through the connecting pressure capillary. Once the pressure LH was turned off, \(P_{\text{Gauge}}\) as expected demonstrated the behavior consistent of a PTM “ice” blockage; that is, the pressure stabilized at a reading within the pressure immediately above the \(PT_{\text{He}}\) down to the base temperature.

Results for pressures below \(PT_{\text{He}}\) are shown to be distinct (Figure 3). While pressurizing and cooling under constant volume (\(V_C\)) the pressures calculated using the ND data confirm the behavior described by Sherman and Stadtmuller [14] and show a significant overall drop in pressure staring at 40 K and steadily increasing down to the lowest temperature (4 K). Readily it is observed that as the vessel is cooled from 60 to 40 K there is a divergence in pressures within the vessel partially due to crossing the \(PT_{\text{He}}\) (this is also observed in the pressure intensifier gauge reading). For the case of cooling under constant volume (\(\Delta P_{\text{VC}}\)) the pressure gradient is of the order of 25% and substantiates the isochore correction calculations done by Spain and Segall [13].

To minimize the isochore loss of pressure, subsequent pressurization was done under cooling at constant pressure (\(P_c\)) by following a rigorous procedure to ensure that during pressurization the helium solidifying at the bottom of the vessel will be formed at a pressure as close as possible to the solid helium nearest the “He ice” blockage in the system. In this case of cooling under constant pressure (\(\Delta P_{\text{PC}}\)) the data shows that the overall pressure loss on solidification of the helium within the sample space was reduced to 5% overall (Figure 3).

Finally, results of the direct evidence of pressure inhomogeneities across the vessel’s sample space are shown and quantified in Figure 3 and Table 1, respectively. For the first-time direct experimental quantitative evidence of the pressure inhomogeneities across large samples is reported. The average inhomogeneity reduction in pressure between top and bottom of a 45 mm long sample is better than a factor of 3.

Neutron scattering proved to be the defining probe technique to unravel these results. By mounting three HOPG samples off-set in degrees of rotation, the pressures within the vessel could be tabulated across the three distinct regions of the sample space by using Eq. (1).

The total pressure inhomogeneity for cooling at constant pressure (\(\text{TPI}_{\text{PC}}\)) at a given temperature is compared with the total pressure inhomogeneity for cooling at constant volume (\(\text{TPI}_{\text{VC}}\)) across the three HOPG single crystals (top, center, and bottom).

Inhomogeneities between the top and the bottom of a sample are, for the first time, quantified showing the importance of proper pressurization procedure.

A procedure to minimize this pressure drop caused by the phase change in the PTM (assuming helium) is then: (i) Firstly the pressurizing apparatus must contain a properly heated capillary line throughout the entire length of the sample stick to remove the risk of creating a helium ice plug during the procedure and monitor the capillary temperature maintaining it at least 30 K above the \(PT_{\text{He}}\) for the pressure

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>(\text{TPI}_{\text{PC}}) (GPa)</th>
<th>(\text{TPI}_{\text{VC}}) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.018(7)</td>
<td>0.006(9)</td>
</tr>
<tr>
<td>10</td>
<td>0.016(9)</td>
<td>0.005(1)</td>
</tr>
<tr>
<td>20</td>
<td>0.019(3)</td>
<td>0.008(8)</td>
</tr>
<tr>
<td>30</td>
<td>0.023(3)</td>
<td>0.001(8)</td>
</tr>
</tbody>
</table>

Table 1.
Pressure inhomogeneities shown for the range 4 K ≤ \(T\) ≤ 30 K.
target. Monitor three temperature sensors (one for the capillary line, one for the sample vessel and one for the cryostat temperature). (ii) Cool the sample to a temperature at most 10 K above the $P_{T_{\text{He}}}$. (iii) Pressurize the vessel to the target pressure (it is recommended to exceed the target pressure by 10% to allow for the pressure loss as the helium cools to the freezing temperature) to just above the $P_{T_{\text{He}}}$ to ensure the helium remains fluid. (iv) Cool the cryostat (while maintaining the capillary line temperature above $P_{T_{\text{He}}}$) under constant pressure to the $P_{T_{\text{He}}}$ It might be necessary to increase the temperature of the capillary at this point to maintain it at least 30 K above the $P_{T_{\text{He}}}$ (v) Freeze the helium slowly under constant pressure, and (approximately) constant volume conditions. While freezing the helium, allow the cryostat temperature to drop well below the $P_{T_{\text{He}}}$ and maintain the capillary LH providing heat to the system. This way the vessel begins cooling below the $P_{T_{\text{He}}}$ from the bottom and the top of the vessel connected to the capillary is held above $P_{T_{\text{He}}}$ This step is important to guarantee that helium ice is forming gradually inside the vessel and immersing the sample throughout its length more or less uniformly, thus minimizing the inhomogeneities in pressure as the helium ice forms. (vi) When the cryostat temperature reaches at least 15 K below the $P_{T_{\text{He}}}$ the capillary temperature is lowered at a rate of 0.5 K/min and continuing until freezing is complete. (vii) Cool slowly to the required temperature under constant volume conditions.

4. Conclusion

For the first time pressure inhomogeneities across large samples in neutron scattering experiments at low temperature are quantified and documented experimentally. A methodology was demonstrated to minimize these pressure inhomogeneities across large samples under pressure at low temperatures, when using helium as PTM, in low temperature neutron scattering experiments. The technique employed here using HOPG to determine pressure measurements corroborate, in the helium gas phase, with previously published calculations of helium isochores to good approximation and provided means to reduce the isochore loss of pressure by a factor of 5. As of the date of publication, this is the first-time direct experimental quantitative evidence of the reduction in pressure inhomogeneities across large samples is reported, and the average inhomogeneity reduction in pressure between top and bottom of a 45 mm long sample is better than a factor of 3.

Author details

Juscelino Batista Leão
NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland, USA

*Address all correspondence to: juscelino.leao@nist.gov

IntechOpen

© 2022 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
References


[23] Murnaghan FD. The compressibility of media under extreme pressures. Proceedings of the National Academy of Sciences. 1944;30(9):244-247. DOI: 10.1073/pnas.30.9.244


[27] Lynch RW, Drickamer HG. Effect of high pressure on the lattice parameters of diamond, graphite, and hexagonal boron nitride. The Journal of Chemical Physics. 1966;44:181

