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Report:

A major difficulty with liquid diffraction at high pressure is the large background signal generated by the pressure vessel. In large-volume cells this can be overcome using energy-dispersive diffraction and careful spatial filtering of the scattered radiation, [1] or using angle-dispersive diffraction and precise Soller slits. [2] Unfortunately, low-Z compressible liquids and gases are much easier to study in diamond-anvil cells (DACs) and neither approach is possible with the much smaller sample volumes required for DAC studies. Thus, we are pleased to report the first successful measurements of the structure factor, radial-distribution function, and density of liquid water at room temperature up to 1.1 GPa by angle-dispersive x-ray diffraction.

We loaded high-purity water into specially-modified membrane-diamond-anvil cells (MDACs) [3] with large-angle access $2\theta_{\max} = 36^\circ$. The diamond-anvil seats were made of boron to give high x-ray transmission over the full aperture of the MDAC. We performed angle-dispersive x-ray diffraction on the ID09 and ID30 beam-lines at the ESRF.

The proper determination of the reference background spectra is the most difficult aspect of making and analyzing these measurements. We attempted to minimize the background signal by using thick samples (up to 100 μm) and thin diamond anvils (down to 500 μm), but diffuse scattering from the diamonds was still

dominant by more than an order of magnitude. Great care must be exercised in collecting the reference spectra with the gasket-hole shape, size, and position identical to that used for the liquid spectra. Scattering from the diamond anvils takes the form of: i) Bragg scattering, which is easily removed by digitally masking the image integration; ii) Compton scattering, which is assumed to be independent of pressure and temperature; and iii) temperature-diffuse scattering (TDS), which is far more insidious due to its temperature dependence and anisotropy, necessitating a separate reference spectra for each sample temperature. To simplify the collection of appropriate background spectra, we developed a procedure for utilizing solid-sample reference spectra. [4] The most difficult aspect of using solid-sample references involves properly treating the sample TDS.

Since the diffuse scattering in a DAC experiment is dominated by background, our analysis was necessarily different than for most liquid-diffraction experiments where background scattering is minimized. Thus, we employed an iterative analysis method that allowed the correction of systematic uncertainties in the Krogh-Moe, [5] Norman [6] normalization factor, the scaling factor, and the form factor. This iterative method is an extension to molecular liquids of the method introduced by Kaplow et. al [7] and will be completely described elsewhere. [4] During this analysis we found it possible (and necessary) to directly determine the density.

Figure 1 shows our determination of the density for liquid water at 295 K plotted against the Saul and Wagner equation of state. [8] The excellent agreement between our measurements and the equation of state suggest that our analysis rests on a sound foundation, and that it is possible to measure the density of low- Z liquids by x-ray diffraction to $\sim 3\%$ accuracy in diamond-anvil cells. This is the first time that density measurements of liquids have been reported by x-ray diffraction at high pressure, and it opens exciting new possibilities for directly measuring the equation of state of liquids.

To illustrate the accuracy of our method we present a comparison of our results for ambient-pressure water with recent x-ray [9] and neutron [10] diffraction experiments, as well as a first principles simulation [11] in figure 2. The dominant peak in our radial distribution function $g_{mol}(r)$ at $r = 0.28$ nm is too broad, too weak, and at too high r compared to the other results (figure 2a). However, we believe that these inconsistencies can be explained by our finite Q_{max} since the other experiments were analyzed to explicitly eliminate the Q_{max} problem. [4] All the subsequent peaks in $g_{mol}(r)$ are in excellent agreement. In figure 2b we show the structure factor $S_{mol}(Q)$. We find that our determination of $S_{mol}(Q)$ is in excellent agreement with the other experimental structure factors. The small discrepancy in the relative and total intensities of the primary doublet is entirely consistent with a small (<0.05 GPa) applied pressure.

We have performed the first quantitative measurements of a liquid structure factor in a DAC—water up to 1.1 GPa. A fortuitous by-product of our analysis is that the bulk density of the liquid can be measured directly, thereby eliminating a free parameter in all previous high-pressure studies. The density we present is accurate to within about 3 % in liquid water. We have performed extensive tests of our analytical method and believe that our structure factors are highly accurate. [4]

- [1] Y. Katayama, T. Mizutani, W. Utsumi, O. Shimomura, M. Yamakata, and K. Funakoshi, *Nature*, 403, 170 (2000).
- [2] M. Mezouar, S. Bauchau, G. Blattmann, P. Faure, N. Rambert, and B. Sitaud, in preparation.
- [3] R. LeToullec, J. P. Pinceaux, and P. Loubeyre, *High Pres. Res.*, 1, 77 (1988).
- [4] J. H. Eggert, G. Weck, P. Loubeyre, M. Mezouar, submitted for publication.
- [5] J. Krogh-Moe, *Acta Cryst.*, 9, 951, (1956).
- [6] N. Norman, *Acta Cryst.*, 10, 370, (1957).
- [7] R. Kaplow, S. L. Strong, and B. L. Averbach, *Phys. Rev.*, 138, A1336 (1965).
- [8] A. Saul and W. Wagner, *J. Phys. Chem. Ref. Data*, 18, 1537 (1989).
- [9] G. Hura, J. M. Sorenson, R. M. Glaeser, and T. Head-Gordon, *J. Chem. Phys.*, 113, 9140 (2000). J. M. Sorenson, G. Hura, R. M. Glaeser, and T. Head-Gordon, *J. Chem. Phys.*, 113, 9149 (2000).
- [10] A. K. Soper, F. Bruni, and M. A. Ricci, *J. Chem. Phys.*, 106, 247 (1997).
- [11] E. Schwegler, G. Galli, and F. Gygi, *Phys. Rev. Lett.*, 84, 2429 (2000).

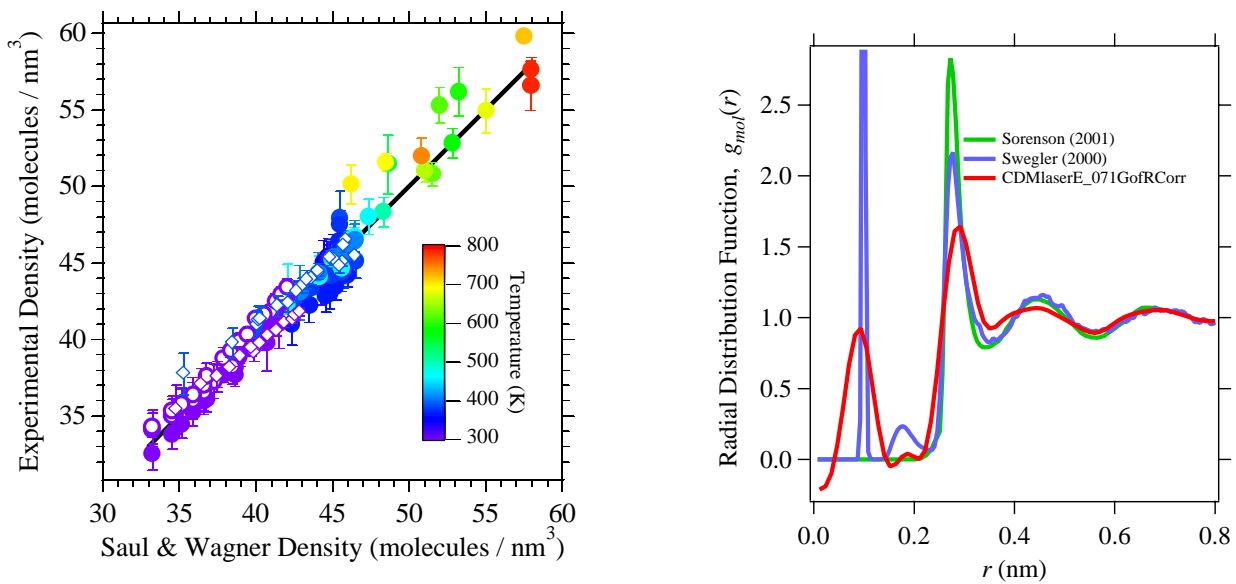


Figure 1: Our experimental determination of the density of liquid water at 295K plotted against the Saul Wagner equation⁸⁾.

Figure 2: Results of our experiments for ambient pressure water and comparison to recent experiments by Hura⁹⁾ and to first principle simulations by Schwegler¹¹⁾.