High energy x-ray diffraction from liquids and glasses.

Chris Benmore
Advanced Photon Source, Argonne National Laboratory.

X-ray diffraction studies have long been used to obtain information on the short and intermediate range structure of glasses, since the pioneering work of Warren [1] and co-workers in the 1930's. This is still the case. In the conference summary of the 10th International conference on the Structure of Non-Crystalline Materials in 2006, x-ray diffraction was identified as the main structural technique used by the participants. High energy x-ray diffraction is the latest generation of this popular method of determining glass structure. The high energy technique has it's origins with the seminal work of Egelstaff in the 1980's who used γ-ray diffraction to obtain liquid structure factors. The breakthrough however came in the mid-90's by Poulsen and Neuefeind [2], when they adapted this technique to synchrotron radiation using 100 keV x-rays. The technique has spread in the last decade and current synchrotron beamlines that routinely perform measurements on glasses include : Spring-8, Japan (BL04B2), Hasylab, Germany (BW5), ESRF (ID15B), APS, USA (1-ID high pressure, 11-ID-B time resolved, 11-ID-C liquid, glass, levitation).

There are two main advantages over conventional x-ray diffraction techniques when hard x-rays of ~100 keV are used in experiments on amorphous materials (i) the structure factors can be measured out to much higher momentum transfers, $Q>20Å^{-1}$ at smaller scattering angles $2\theta>20^{o}$, leading to higher real space resolution, and (ii) attenuation and multiple scattering effects are negligible for small samples i.e. $\sim 1mm^3$ [2,3]. This is because the photo-electrical absorption decreases as $\sim E^{-3}$ and scattering typically becomes the dominant process, under conditions similar to that of a transmission neutron diffraction experiment.

In the data analysis procedure the measured sample intensity is corrected for background, polarization, detector geometry, Compton scattering, attenuation and detector related corrections. The self scattering is removed and a pseudo-nuclear total x-ray structure factor, S(Q) obtained. Provided a wide range of reciprocal space is covered this function can be Fourier transformed into real space to provide an average probability function of all the atomic positions in the material called the radial or pair distribution function G(r) [4]. The G(r) function can be used to extract bond distances, local coordination numbers, average bond angles and provide a rigorous test of structural models. In addition, the first sharp diffraction peak at position Q_1 in the x-ray (or neutron) diffraction patterns is associated with the existence of intermediate or medium range order in glass with a periodicity of $2\pi/Q_1$ (although it's origin is still controversial). Medium range order has been defined as covering the region ~5-10Å, although longer 'extended chemical ordering' up to 40Å has also been found in network glasses.

High energy x-ray diffraction is very much a sister technique to neutron diffraction, and as for all glass studies, whenever possible should be combined with other

structural probes to obtain the most information. Limitations of the technique include that it is not element specific (like EXAFs) and information on low dopant ions (<1%) cannot be obtained. Fluorescence energies of elements in the sample should also be avoided. One of the strengths of high energy diffraction data lies in it's ability to provide a rigorous test of atomistic models from computer simulation such as molecular dynamics or density functional theory. It is also often used as a model constraint in inverse computer simulation techniques, such as Reverse Monte Carlo and Empirical Potential Structure Refinement. Despite the growth in popularity of high energy diffraction in the field of glass no thorough reviews yet exist, so the reader is directed to references 1-4. Future directions of high energy x-ray synchrotron radiation in glass research include high pressure studies [5,6], high and low temperature combined with containerless levitation techniques [7,8] and time resolved structural measurements around the glass transition.

References:

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