EXAFS-SAXS-WAXS

Neville Greaves
Aberystwyth University
Aberystwyth SY23 3BZ
UK

Extended X-ray Absorption Fine Structure Spectroscopy - EXAFS

In recent years EXAFS spectroscopy has become increasingly important in glass science due to its ability to obtain information on the local structure of selected atomic species in complex, multi-component systems. It may be noted at the outset that NMR and EXAFS are both element-specific techniques. NMR is especially useful for identifying and quantifying multiple coordination environments or sites while EXAFS yields quantitative average nearest-neighbor (and in some cases next-nearest neighbor) distances and coordination numbers. EXAFS involves photo-excitation of an electron from a deep core state to a continuum state [1,2]. The photoelectron waves propagate outward from the excited atom and interfere with scattered waves from neighboring atoms, thus modulating the absorption cross-section [1]. Two regions are defined above the absorption edge. The strong oscillations which extend beyond the edge up to ~ 50 eV are the x-ray absorption near-edge structure (XANES) which involve the multiple scattering of excited photoelectrons and are determined by the geometrical arrangement of atoms in a local cluster around the excited atom. The XANES oscillations have rarely been utilized on a quantitative basis for determination of glass structure at the intermediate-range. The EXAFS oscillations are observable beyond ~ 50 eV. To separate the scattering and absorption processes in the photon absorption cross-section $\sigma(E)$ for an atom in a solid can be written as:

$$\sigma(E)=\sigma_0(E)[1+\chi(E)] \tag{1}$$

Where E is the X-ray photon energy, $\sigma_0(E)$ is the absorption cross-section for a free atom which is essentially featureless except for the edge jump and $\chi(E)$ is the EXAFS function representing the modulation in the photo-absorption rate due to scattering processes [1]:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)} \tag{2}$$

The EXAFS function $\chi(E)$ is usually expressed in terms of the photoelectron wavevector Q as $\chi(Q)$, where $Q = \frac{\sqrt{2m_e E_{KE}}}{\hbar}$ and E_{KE} is the kinetic energy of the photoelectron.   The measured EXAFS signal $\chi(Q)$ is a sum of contributions from all scattering events from *N* neighboring atoms of type β at an average distance R_β from the central photo-excited atom α and the standard plane wave expression for $\chi(Q)$ is [1,2]:

$$\chi(Q) = \sum_{\beta} \frac{-A(Q)}{Q} \frac{N}{R^2_{\beta}} |f_{\beta}(Q,\pi)| \exp\left(\frac{-2R_{\beta}}{\lambda}\right) \exp\left(-2\sigma^2 Q^2\right) \sin 2\left(QR_{\beta} + 2\delta + \phi\right) \quad (3)$$

The quantity $f_{\beta}(Q,\pi)$ is the amplitude of the electron backscattering factor for the atom β which is complex with phase ϕ, δ is the phase shift of the photoelectron introduced by the potential of the photo-excited atom and λ is the mean free path of the photoelectron. $A(Q)$ is the energy independent amplitude factor which is ≤ 1 and allows for processes which contribute to photo-absorption but not necessarily to EXAFS (e.g. multi-electron excitations) and σ^2 is the Debye-Waller factor which is the mean-square deviation in R_{β}. In contrast to the crystallography Debye-Waller factor, $<\mu^2>$, σ^2 measures the static and dynamic disorder relative to the excited atom. The quantities $f_{\beta}(Q,\pi)$ and δ can be derived either from *ab initio* calculations or from fitting the EXAFS spectra of suitably chosen model compounds with known atomic structure. The experimental $\chi(Q)$ is then fitted by varying R, N and σ to obtain the information regarding the number and type of nearest-neighbors atoms around and their distance from the central photo-excited atom. The Fourier transformation of $\chi(Q)$ then yields the partial structure factor for the central photo-excited atom. For reviews of EXAFS spectroscopy applied to glasses and liquids see [2,3].

Small angle x-ray scattering- SAXS

Scattering of x-ray or neutron at small angles provides information regarding structural or chemical heterogeneities over nanometer length scales. An excellent review of this technique can be found in the book by Glatter and Kratky [4]. Examples in this review for silica and silicate glasses can be found in Figures 7 and 20, respectively. At lowest Q values the scattered intensity, *I(Q)*, is given by

$$I(Q) = I(0)\exp\left(-\frac{R_g^2 Q^2}{3}\right) \quad (4)$$

where Q is the scattering vector $4\pi\sin\theta/\lambda$, 2θ is the scattering angle and λ is the x-ray or neutron wavelength. R_g is the radius of gyration, measuring the average radius of the particles R, and if these are spherical $R_g = \sqrt{\frac{3}{5}}R$. *I(0)* in eqn A25 can be obtained by extrapolation of *I(Q)* to *Q*=0. For monodispersed particles *I(0)* is related to their number, N_P, their average volume, V_P, and the electron density with respect to the matrix, $\Delta\rho_e$, viz.

$$I(0) = k\frac{N_P V_P^2}{N}(\Delta\rho_e)^2, \quad (5)$$

where *N* is the number of atoms in the sample, $\Delta\rho_e$ is the particle electron density contrast and *k* is a scaling constant. Given that $<\Delta\rho^2>/\rho_0^2 = <\Delta\rho_e^2>/\rho_e^2$, *I(0)* measures the contrast in density between particles and the surrounding matrix.

In the high Q range of the small angle scattering the scattered intensity is given by the relation:

$$I(Q) = K_1 + \frac{K_2}{Q^p} \quad (6)$$

where K_1 is the so-called thermal background, K_2 is the Porod constant and p is a parameter influenced by the dimensionality and the surface roughness of the scattering particles. At intermediate angles scattering originates from the interior of particles and p reveals the bulk dimensionality, typically falling between 2 and 3. Finally at the end of the SAXS Q range, scattering from the interfaces between the particles and their surroundings dominates. For smooth three-dimensional particles $p=4$ whereas for rough surfaces or where there are interface density gradients the exponent is smaller. Note that few real sytems are purely fractal over all length scales. Nanostructure can often be nested, with different dimensionallity and interface character emerging as the length scale probed by the incident radiation decreases with increasing Q. A recent demonstration of the wealth of nanostructural information obtainable from SAXS can be found in [5].

X-ray scattering- WAXS

The basic theoretical frameworks of the neutron and x-ray scattering techniques are outlined below. The interested reader is referred to the books by Lovesey and James for a complete treatment [6,7]. For a recent review of these techniques applied to glasses see Fischer, Barnes and Salmon [8]. In the case of neutron or x-ray scattering experiments, like those for silica glass shown in Figure 6, the short, intermediate and long -range structural information for glasses is contained in the Radial Distribution Function (RDF), $J(r)$ or the correlation function $J(r)/r$ illustrated for silica in Figure 5(a). Experimentally $J(r)$ is derived from the measured scattered intensity by Fourier transforming the x-ray or neutron structure factor $S(Q)$, where Q is the scattering vector $4\pi\sin\theta/\lambda$, 2θ is the scattering angle and λ is the x-ray or neutron wavelength. The scattered x-ray intensity $I(Q)$ from an assemblage of atoms of different types is given by:

$$\mathrm{N.I(Q)} = \sum_{\alpha=1}^{N} W_\alpha^2 + S(Q) + I_{inc}(Q) \tag{7}$$

Where N is the number of formula units in the scattering volume of the sample and W_α is the average X-ray or neutron cross section for each type of atom . In the case of X-rays W_α is real and decreases monotonically with increasing Q except at core level absorption edges where it becomes complex with considerable dispersion in the real and imaginary parts.   For neutrons W_α is almost Q-invariant but differs considerably between the different isotopes. For the majority of experiments the contrast in W_α inherent in anomalous X-ray scattering is not exploited whilst in neutron scattering W_α is averaged over the concentrations of the different isotopes present. The second term in equation (7) represents interference scattering from different atoms and contains all the structural information in terms of spatial distribution of constituent atoms. The first term, on the other hand, is the sum of scattering from individual atoms and the third term is the incoherent scattering. Following polarization, absorption and normalization correction of $I(Q)$ the first and third terms of equation (7) must be subtracted from experimentally measured $I(Q)$ as they contain no structural information.

The resulting interference function is known as the structure factor and is typically designated as $S(Q)$. For a glass or liquid with two atom types α and β (e.g. Si and O in the case of SiO_2):

$$S(Q) = \sum_{\alpha}^{N} \sum_{\beta}^{N} W_\alpha W_\beta S_{\alpha\beta}(Q) \tag{8}$$

where the double summation covers the partial structure factors $S_{\alpha\beta}(Q) = \dfrac{\sin Qr_{\alpha\beta}}{Qr_{\alpha\beta}}$ between all pairs of atoms, $S_{\alpha\alpha}$, $S_{\beta\beta}$ and $S_{\alpha\beta}$, $r_{\alpha\beta}$ is the distance between atoms α and β. Often $W_\alpha W_\beta$ is replaced by $W_{\alpha\beta}$ the average cross section for atoms α and β, weighted according to the composition. The Radial Distribution Function (RDF) can be obtained from $S(Q)$ by Fourier transformation according to:

$$J(r) = \frac{2r}{\pi} \int_0^\infty [Q\{S(Q)-1\}\sin Qr]dQ + 4\pi\rho_0 r^2 \qquad (9)$$

where ρ_0 is the physical density. The positions of the peaks in $J(r)$ give the radii of the different shells of atoms surrounding the average atom and the area measured under the peaks gives the coordination numbers for the different shells of atoms. An alternative form of RDF is often used in the literature which is $T(r)=J(r)/r$.

It may be noted here that $J(r)$ is a one-dimensional representation of a three-dimensional structure, hence the isotropic nature of the sample is implicitly assumed. In simple network glasses, though local structure – nearest neighbour distances and coordination numbers – is often unequivocally and accurately measured. In multicomponent systems another limitation of RDFs (and the diffraction technique in general) is that all $\alpha\beta$ pairs contribute and their deconvolution in $J(r)$ becomes extremely difficult. This can be removed in principle by exploiting different cross sections W_α of the same atom type and differencing to extract partial structure factors. The techniques of anomalous X-ray scattering and isotopic substitution neutron scattering can disentangle local structure and often intermediate range order in more complex glasses but are difficult and time consuming to perform. Intermediate range order and ring statistics which are embedded in X-ray and neutron scattering are best analysed using computer simulation methods like Molecular Dynamics (*vide infra*) and Reverse Monte Carlo (RMC) techniques. In RMC simulations the atomic positions in a three-dimensional model are iterated to obtain the closest agreement with experiment. RMC can incorporate several independent measurements, like X-ray scattering, neutron scattering and also EXAFS. The partial structure factors and correlation functions can be readily extracted.

Combing EXAFS, SAXS and WAXS
Combining EXAFS with SAXS and WAXS is an instrumentation challenge involving dispersive or fast scanning monochromators and rapid 1D and 2D detectors [9]. EXAFS and WAXS were first demonstrated using a curved crystal dispersive arrangement, a PDA and a curved 1D detector [10]. Translating slits were used to separate out a non-dispersive beam for WAXS – EAXS and WAXS being measured in tandem. Subsequently SAXS and WAXS were combined with a non-dispersive curved monochromator each measured simultaneously, a quadrant detector being used to capture the SAXS [11]. Later WAXS was combined with EXAFS using a rapidly scanning monochromator (QuEXAFS) [12]. EXAFS SAXS and WAXS have seldom been measured in the same experiment but could be. The utility of all using all three probes of local structure and nanostructure to follow materials processing is described in ref [5]. Indeed the main advantage of combined X-ray techniques – particularly EXAFS-WAXS is for in situ experiments like following catalysts under operating conditions, for example [13]. The most recent example of SAXS and WAXS was the detection of polyamorphism at ultra high temperature in refractory liquids [14].

References

1. SAYERS, D.E., STERN, E.A. AND LYTLE, F.W.,1971, *Phys. Rev. Lett.*, **27**, 1204-1207.
2. GREAVES, G.N., 1990, in: *Glass Science and Technology*, ed. Uhlmann, D.H. and Kreidl, N. (New York: Academic Press), p.1-76.
3. BROWN, G.E., FARGES, F. and CALAS, G., 1996, in: *Structure, Dynamics and Properties of Silicate Melts*, ed. Stebbins, J.F., McMillan, P.F. and Dingwell, D.B.(Reviews in Mineralogy Vol 32, Mineralogical Society of America), p317-410.
4. GLATTER, O. AND KRATKY, O., 1982, *Small Angle X-ray Scattering* (London: Academic Press)
5. BRAS, W., GREAVES, G.N., OVERSLUUIZEN, M., CLARK, S.M. and EECKHAUT, G., 2005, *J. Non-Cryst. Solids* **351**, 2178-2193.
6. LOVESEY, S.W., 1984, *Theory of Neutron Scattering from Condensed Matter*, *Vols. 1&2* (Oxford : Clarendon Press)
7. JAMES, R.W., 1953, *X-ray Crystallography* (New York: Wiley).
8. Fischer, H.E., Barnes, A.C. and Salmon, P.S., 2006, Rep. Prog. Phys. **69**, 233- 299.
9. G.N. Greaves, C.R.A. Catlow, G.E. Derbyshire, M.I. McMahon, R.J. Nelmes and G. van der Laan Nature Materials 2008, 7, 827-830.
10. Couves J W, Thomas J M, Waller D, Jones R H, Dent A J, Derbyshire G E and Greaves G N Nature, 354, 465-468 (1991)
11. Bras W, Derbyshire G E, Ryan AJ, Mant G R, Felton A, Lewis R A, Hall C J and Greaves G N Nucl. Instr. and Methods. A326, 587-591 (1993)
12. Sankar G, Wright P A, Srinivasa N, Thomas J M, Greaves G N, Dent A J, Dobson B R, Ramsdale C A and Jones R H, J. Phys. Chem. 97, 9550-9554 (1993)
13. G.N. Greaves, M.C. Wilding, S. Fearn, D. Langstaff, F. Kargl, S. Cox, O. Majérus, Q. Vu Van, C.J. Benmore, R. Weber, C.M. Martin, L. Hennet *Science* 2008, 322, 566-570.