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A Method for the Resolution of Composite Radial Pair Distribution Functions

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The superposition of distances between different types of atom pairs in experimental pair radial distribution functions of vitreous systems, makes it difficult to interpret such functions. As the present note will show, it is possible to circumvent this difficulty in favourable cases.

In a system consisting of J different species of atoms, there are $(J + 1) J/2$ ways to combine atom species in different pairs. (For instance: $J = 2$ species of atoms, A and B, will give the three pairs A-A, A-B and B-B). An atomic center radial distribution curve from a composite system with J different kinds of atoms may therefore be considered composed of the $(J + 1) J/2$ individual distribution curves of each possible pair of atoms. These individual distribution curves may thus in principle be determined from $(J + 1) J/2$ independent and relevant measurements. (In some cases it may be found useful to treat a polyatomic system as two-atomic, lumping all but one type of atoms into a single category. Only three independent intensity curves are then needed.)

Independent measurements may be obtained when the relative scattering efficiency of the different species of atoms can be altered. This can be done by: 1) using different types of radiation, e.g. X-rays, neutrons, or electrons, 2) using one kind of radiation at different wavelengths,

taking advantage of the dispersion, 3) using isomorphic (or isotopic substitution with neutrons) of one species of atoms in the structure. To take advantage of this additional information, we shall derive the appropriate expression for the scattered intensity from an amorphous system as a function of the structure and the scattering efficiency of the different atomic species.

The atomic form factor (or scattering efficiency), f_j , of the j 'th species of atoms under specified scattering conditions will be written as the complex quantity:

$$f_j = f_j^0 + \Delta f_j' + i \Delta f_j''$$

The number of atoms of species j is taken to be n_j so that the total number of atoms, N , in a system with J different kinds of species, is given by:

$$N = \sum_{j=1}^J n_j$$

The amplitude, A , of radiation scattered by this system is:

$$A = \sum_{j=1}^J \sum_{m=1}^{n_j} f_j \exp(2\pi i \mathbf{q} \mathbf{R}_{jm})$$

where \mathbf{q} is the scattering vector and \mathbf{R}_{jm} is a vector defining the position of the m 'th atom of species j .

To obtain the intensity of the scattered radiation, we note that

$$\begin{aligned} AA^* &= \sum_{j=1}^J \sum_{m=1}^{n_j} f_j \exp(2\pi i \mathbf{q} \mathbf{R}_{jm}) \sum_{k=1}^J \sum_{n=1}^{n_k} f_k^* \\ &\exp(-2\pi i \mathbf{q} \mathbf{R}_{kn}) \\ &= \sum_{j=1}^J \sum_{k=1}^J \sum_{m=1}^{n_j} \sum_{n=1}^{n_k} f_j f_k^* \exp[2\pi i \mathbf{q} (\mathbf{R}_{jm} - \mathbf{R}_{kn})] \end{aligned}$$

Introducing:

$$r = |\mathbf{R}_{jm} - \mathbf{R}_{kn}|$$

for the distance between atom jm and kn , and:

$$s/2\pi = |\mathbf{q}| = 2 \sin \theta / \lambda$$

for the length of the scattering vector, θ being the scattering angle and λ the wave length, and averaging over all directions in space (see, e.g., Viervoll¹), we obtain

$$\begin{aligned} I(s) = \overline{AA^*} &= \sum_{j=1}^J \sum_{k=1}^J \sum_{m=1}^{n_j} \sum_{n=1}^{n_k} [(f_j^0 + \Delta f_j') \\ &(f_k^0 + \Delta f_k') + \Delta f_j'' \Delta f_k''] \frac{\sin sr}{sr} \end{aligned}$$

Let us for simplicity assume that the particular pair of any atom with itself ($r = 0$) is not counted in the above summation.

The double summation over all atom

pairs consisting of one atom of species j and one atom of species k can be replaced by an integration over a continuous pair distribution function. For this purpose a function $\varrho_{jk}(r)$ is introduced such that $\varrho_{jk}(r) dr$ is the number of atom pairs j and k separated by a distance falling between r and $r + dr$. The above equation may thus be rewritten:

$$sI(s) = \sum_{j=1}^J \sum_{k=1}^J [(f_j^0 + \Delta f_j') (f_k^0 + \Delta f_k') + \Delta f_j''] \\ \int_0^{\infty} \frac{\varrho_{jk}(r)}{r} \sin sr \, dr$$

The last integral defines a new function of s , $sX_{jk}(s)$, which is the Fourier transform of an individual pair distribution:

$$sX_{jk}(s) = \int_0^{\infty} \frac{\varrho_{jk}(r)}{r} \sin sr \, dr$$

From $X_{jk}(s)$ the unknown $\varrho_{jk}(r)$ may thus be obtained explicitly by the Fourier transform:

$$\frac{\varrho_{jk}(r)}{r} = \frac{2}{\pi} \int_0^{\infty} sX_{jk}(s) \sin sr \, ds$$

Hence if the $X_{jk}(s)$ functions can be extracted from the experimental material, our objective has been achieved. This extraction is possible if the scattering factor, f_j , of any atom in the structure can be altered relative to the others; *e.g.* by isomorphous substitution, change of radiation type or by anomalous scattering. If we choose to utilize anomalous X-ray scattering, for instance, we observe that the dispersion corrections $\Delta f'$ and $\Delta f''$ vary with the wavelength λ . Since the imaginary terms $\Delta f''$ for the X-ray case are not generally large enough to become important, the observed intensity function can be written

$$I(s, \lambda) = \sum_{j=1}^J \sum_{k=1}^J [f_j^0 + \Delta f_j'(\lambda)] [f_k^0 + \Delta f_k'(\lambda)] X_{jk}(s)$$

Measuring the intensity function $I(s, \lambda)$ for $(J + 1) J/2$ different and appropriate wavelengths and introducing theoretical values of f_j to obtain the coefficients of $X_{jk}(s)$, the above expression is transformed to a set of linear equations enabling us to determine the unknown $X_{jk}(s)$ and thus the individual pair distribution functions $\varrho_{jk}(r)$. (The linear equations must of course be solved separately for a large number of

closely spaced values of s to obtain an adequate numerical representation of $X_{jk}(s)$ for the Fourier transform.

The difference $\Delta f_j'(\lambda_1) - \Delta f_j'(\lambda_2)$ should be quite large, if useful results are to be expected. For a given element, the maximum difference ranges from 6% to 20% or more of the atomic number.^{2,3} The dispersion correction does not decrease as rapidly as f_j with increasing values of s , so these percentages are even more favourable at higher s -values.³ It is also possible to have large dispersion corrections at the high energy side of the absorption edge, which is of practical importance with liquid scattering.

A combination of anomalous scattering data with data from isomorphous substitutions will probably prove especially useful. Systems containing the lanthanides, for instance, are eminently suitable for such studies. Firstly cases of isomorphous substitutions should be easily found, and secondly the dispersion correction, which is less than 1% for $\text{MoK}\alpha$ -radiation, runs above 10% with $\text{CuK}\alpha$ -radiation for several of the lanthanides.³ Many other attractive systems could be quoted, however.

A crude use of isomorphous substitutions has been made in some studies of glass.⁴ A radial distribution curve has been subtracted from the corresponding curve of a sample where one element has been exchanged. This gives a so-called difference curve. The difference curve in all studies reported so far, has still consisted of a sum of several pair distribution functions so that unequivocal results have in no case been reached.⁴ Moreover, a simple interpretation of a difference curve presupposes that the scattering form factor functions for all the atoms involved differ only by a proportionality constant, a condition which is often poorly fulfilled. A more rigorous treatment according to the method suggested in this paper, therefore seems desirable.

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