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Cross-correlation analysis of x-ray scattering from oxygen clusters

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Abstract. Development of methods for the analysis of the structure of non-crystalline materials at the nanoscale is an important challenge for materials research with x-rays. Here, we present the results of modelling of x-ray scattering from a disordered system composed of oxygen tetrahedral pentamers. We apply x-ray cross-correlation analysis to the simulated x-ray data and show that the intensity cross-correlation functions can extract information about the local structure of the system.

1. Introduction

The standard analysis of x-ray scattering data from disordered systems such as liquids, colloids and molecules in solution, or atomic clusters in gas phase did not yet go far beyond the study of radial distribution functions extractable from the average intensity profile. Using such an approach no directional information about molecular or atomic arrangements in the system can be directly accessed. In contrast to this, it has recently been demonstrated [1–6] that the x-ray cross-correlation analysis (XCCA) of diffraction patterns from disordered systems can provide direct information on the local symmetry and the structure of these systems. This approach is based on the intensity cross-correlation functions (CCFs) introduced by Kam [7].

Application of XCCA to the scattering data from a two-dimensional (2D) disordered system of particles demonstrated a successful reconstruction of the structure of an individual particle [4, 6]. At the same time, for a three-dimensional (3D) disordered system the same problem has been solved only if additional *a priori* knowledge was used [5]. Therefore, development of direct, self-consistent approaches for the recovery of the local structure of a 3D disordered system remains a challenge.

As a step towards the solution of this problem we present the results of simulations of x-ray scattering experiments from disordered systems composed of oxygen tetrahedral pentamers (figure 1). The structure of the oxygen pentamer corresponds to the tetrahedral arrangement of water molecules in a so-called Walrafen pentamer [8], that is one of the favorable models of water that reproduces the results of x-ray and neutron scattering experiments [8-12]. We perform the XCCA of the obtained diffraction patterns and show that the Fourier spectra of the CCFs contain information on local structure of a disordered system that is not accessible in the standard small-angle x-ray scattering (SAXS) experiment.

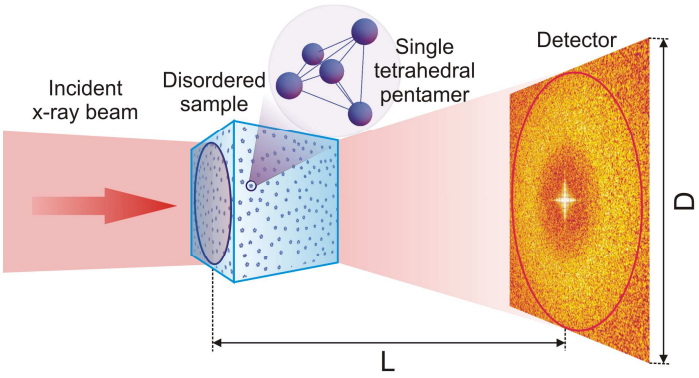

Figure 1. Geometry of the diffraction experiment in transmission geometry. The incident x-ray beam illuminates a disordered sample composed of oxygen tetrahedral pentamers.

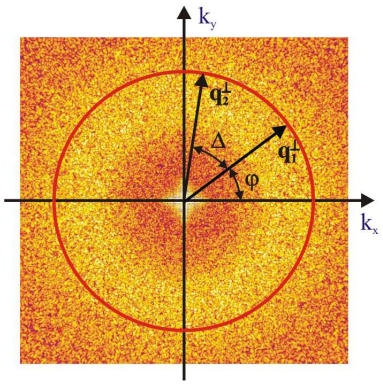

Figure 2. Typical diffraction pattern and definition of the momentum transfer vectors.

2. X-ray cross-correlation analysis

We consider here a scattering experiment on a three-dimensional (3D) disordered system composed of N oxygen pentamers (figure 1). In our model we assume a uniform distribution of the orientations of the clusters. The interference of the scattered amplitudes from different clusters in the system is neglected corresponding to the dilute limit approximation. In this case the total scattered intensity $I(\mathbf{q})$ at the momentum transfer vector $\mathbf{q}$ from N clusters can be considered as a sum of intensities $I_i(\mathbf{q})$ scattered from individual clusters, $I(\mathbf{q}) = \sum_{i=1}^{N} I_i(\mathbf{q})$. It has been demonstrated [2,3,6], that if the number N of clusters in a system is small, one can apply XCCA to extract information about the structure of a single cluster using an average of CCFs over a large number M of diffraction patterns.

For convenience we use the designation $I(\mathbf{q}) \equiv I(|\mathbf{q}^{\perp}|, \varphi; q^{z})$, where the momentum transfer vector $\mathbf{q}$ is defined in terms of its components $\mathbf{q}^{\perp}$ and q^{z} that are perpendicular and parallel to the direction of the incident x-ray beam, and φ is an azimuthal angle of $\mathbf{q}^{\perp}$ (figure 2). The two-point CCF is defined at each $\left|\mathbf{q}_1^{\perp}\right| = \left|\mathbf{q}_2^{\perp}\right|$ as follows [1-7]

$$C_q(\Delta) = \left\langle I(|\mathbf{q}^{\perp}|, \varphi; q^{z}) I(|\mathbf{q}^{\perp}|, \varphi+\Delta; q^{z}) \right\rangle_{\varphi} - \left\langle I(|\mathbf{q}^{\perp}|, \varphi; q^{z}) \right\rangle_{\varphi}^{2}, \quad (1)$$

where Δ is the angular coordinate, and $\left\langle I(|\mathbf{q}^{\perp}|, \varphi; q^{z}) \right\rangle_{\varphi} = 1/(2\pi) \int_0^{2\pi} I(|\mathbf{q}^{\perp}|, \varphi; q^{z}) d\varphi$ defines the angular average. The Fourier series of the scattered intensity $I(|\mathbf{q}^{\perp}|, \varphi; q^{z})$ and of the CCF $C_q(\Delta)$ are defined as $I_q^n = \frac{1}{2\pi} \int_0^{2\pi} I(|\mathbf{q}^{\perp}|, \varphi; q^{z}) \exp(-in\varphi) d\varphi$ and $C_q^n = \frac{1}{2\pi} \int_0^{2\pi} C_q(\Delta) \exp(-in\Delta) d\Delta$, respectively. The Fourier components C_q^n and I_q^n are related according to the expression [2-4]

$$C_q^n = \left| I_q^n \right|^2. \quad (2)$$

In the case of a dilute sample, the Fourier components of intensity can be written as [2,3]

$$I_q^n = \left| f(q) \right|^2 \sum_{k=1}^{N} \sum_{m,l}^{N_o} \exp(-i\, q^{z} z_k^{ml}) J_n(|\mathbf{q}^{\perp}| \cdot \left| \mathbf{r}_k^{lm\perp} \right|) \exp(-in\, \phi_{\mathbf{r}_k^{lm\perp}}), \quad (3)$$

where $f(q)$ is the atomic form factor of oxygen, the summation over index k is performed over N clusters in the sample, the summation over indexes l and m is performed over N_o oxygen atoms in

the k -th cluster, $\mathbf{r}_k^{lm} = (|\mathbf{r}_k^{lm\perp}|, \phi_{r_k^{lm\perp}}; z_k^{lm})$ is the vector connecting two oxygen atoms in the k -th cluster with its components that are perpendicular and parallel to the direction of the incident x-ray beam similar to a vector $\mathbf{q}$, and $J_n(x)$ is the Bessel function of the first kind of integer order n.

3. Results

We simulated an x-ray scattering experiment (see figure 1) with the following parameters: x-ray wavelength λ=1.0 Å, detector size D = 24 mm (with a pixel size of p = 80 μm), sample-detector distance L = 25 mm. The samples were composed of different numbers N of oxygen clusters. The regular pentamer (see figure 1) was defined by a O-O distance of 2.82 Å between the central oxygen atom and each atom in a vertex, and a tetrahedral angle 109.47° typical for water [9].

We demonstrate results of the calculations of the Fourier spectra $\langle C_q^n \rangle_M = 1/M \sum_{m=1}^{m} (C_q^n)^m$ averaged over a sufficiently large number of realizations of a system, where the spectrum for each m-th realization was directly determined using equations (2) and (3). Such spectra statistically converge to their average values for a sufficiently large number M enabling a reliable determination of the local structural contribution of a single cluster from a large x-ray dataset [2,3].

The Fourier spectra $\langle C_q^n \rangle_M$ averaged over M=10^4 diffraction patterns for the case of N=10 clusters in the system are presented in figure 3. Calculations were performed for a regular pentamer for the case of a the flat (a) and a curved (b) Ewald sphere. Calculations for the case of a flat Ewald sphere were performed by setting the z-component of the momentum transfer vector to $q^z = 0$. The results shown in figure 3(c) demonstrate the statistical convergence of the spectra after averaging over a sufficiently large number M of diffraction patterns. The spectra $\langle C_q^n \rangle_M$ calculated for a single cluster N=1 in the system, and for a system containing N=100 clusters (not presented here), converge to the same functional dependence on q. Therefore, the results do not depend on the number N of particles in the system, but are just scaled by N.

The effect of a distortion of the regular pentamer on the Fourier spectra of the CCF is demonstrated in figure 4. The difference spectra $\langle C_q^n \rangle_M^{\text{diff}} = \langle C_q^n \rangle_M^{\text{dist}} - \langle C_q^n \rangle_M^{\text{reg}}$ were calculated for the case when a single atom in a cluster was shifted by 5% [figure 4 (a), (b)] and by 10%, [figure 4 (c), (d)] and when all atoms were randomly displaced by 5% of the O-O distance [figure 4(e),(f)]. Here, $\langle C_q^n \rangle_M^{\text{reg}}$ corresponds to the spectra calculated for the regular pentamer, and $\langle C_q^n \rangle_M^{\text{dist}}$ to the distorted one.

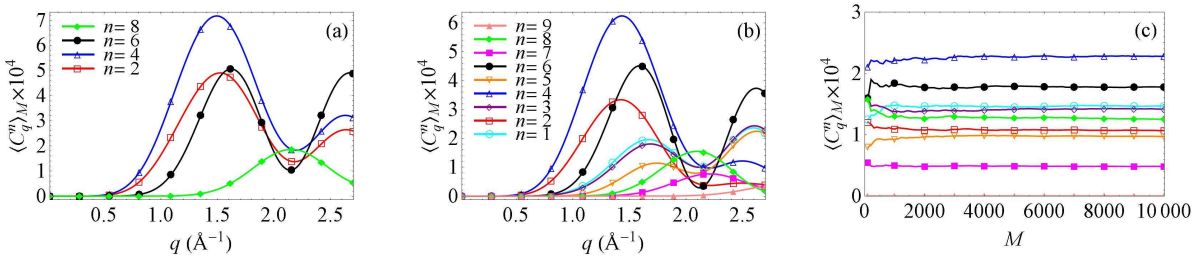

Figure 3. (a),(b) Fourier spectra $\langle C_q^n \rangle_M$ calculated for N=10 and averaged over M=10^4 diffraction patterns as a function of q for 1≤n≤9 for a flat (a) and a curved (b) Ewald sphere. In the case of a flat Ewald sphere only Fourier components with even n-values have nonzero values. (c) Convergence of $\langle C_q^n \rangle_M$ as a function of M calculated for the case of a curved Ewald sphere at a single value of q=1.9 Å^{-1} for 1≤n≤9.

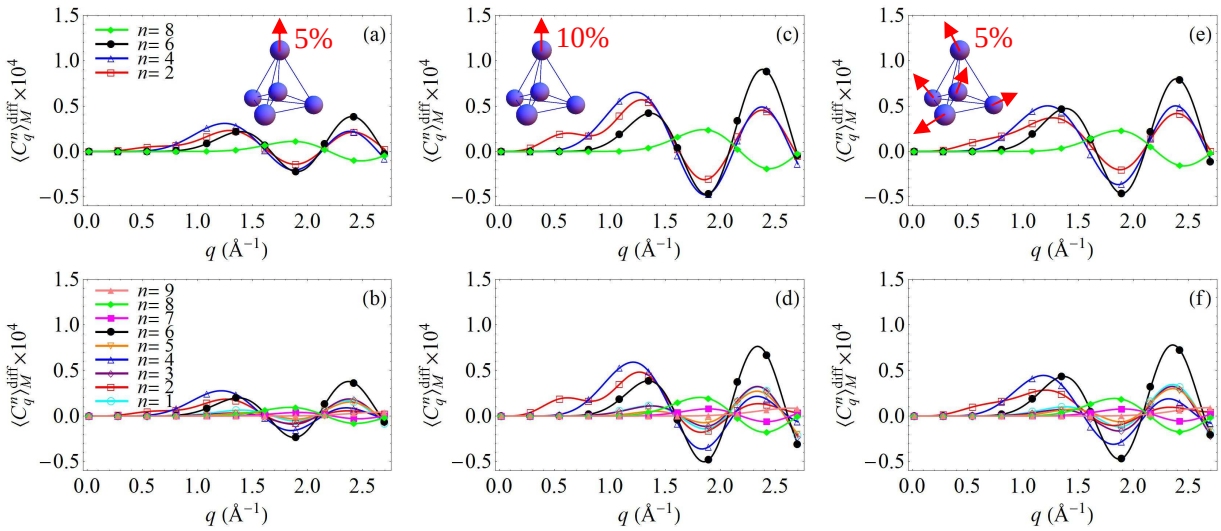

Figure 4. Difference spectra $\left\langle C_q^n \right\rangle_M^{\text{diff}}$ (see text) calculated for the different types of distortions of the regular oxygen pentamer for N=10, M=10^4 for the case of a flat (a), (c), (e) and a curved (b), (d), (f) Ewald sphere. Three cases were considered: (a), (b) a single atom is shifted by 5% and (c), (d) by 10% of the O-O distance (2.82 Å), (e), (f) all atoms are randomly displaced by 5% of the O-O distance.

4. Conclusions

Results presented here demonstrate the ability of XCCA to obtain information about the oxygen clusters with tetrahedral arrangement of oxygen atoms typical for water. The average Fourier spectra of the CCF can be used to identify the presence of this symmetry in liquids, particularly in water. Our results show, that small distortions of the oxygen pentamer do not lead to significant changes of the CCFs. This may help to identify an average local structure of water using experimentally determined CCFs. In our future research we are planning to investigate the influence of correlation effects [2-3] on the average spectra of the CCFs for dense systems such as water.

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