

SUMMER STUDENT REPORT

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X-ray cross-correlation analysis: local structure of water

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I. Introduction

Despite the simplicity of the water molecules, liquid water has a number of unusual properties, such as the maximum density in the liquid phase, high surface tension, high boiling point and heat of vaporization. Water plays an important role in biological systems, so that the knowledge of the structural properties of water is important for a better understanding of the biophysical processes at the molecular level.

In the ordinary crystalline ice I_h water molecules form a periodic hexagonal structure with tetrahedral arrangements of oxygen atoms. During melting of ice only about 15% of the hydrogen bonds are breaking, so that one can expect that tetrahedral-like structures may exist in water on the short-range scale.[1] Unfortunately, the structural studies of water did not go far beyond the measurements of the small-angle scattering (SAXS) and analysis of pair-correlation functions. At the present moment the "tetrahedral" model TIP5P of water is in the best agreement (among other models) with the experimental radial distribution function obtained in neutron diffraction experiment.[2] The recent development of the free-electron lasers with ultra-short pulses and high brilliance opens new possibilities to study the structure of liquids.

Here we develop a method which can provide information on local structure of water going beyond the pair distribution function analysis. We perform simulations of x-ray scattering experiment in transmission geometry (Fig. 1). Coherent x-ray beam scatters from a disordered system of tetrahedral clusters, which we consider as a simplified model of water. For the analysis of the diffraction patterns we use the angular x-ray cross-correlation analysis.

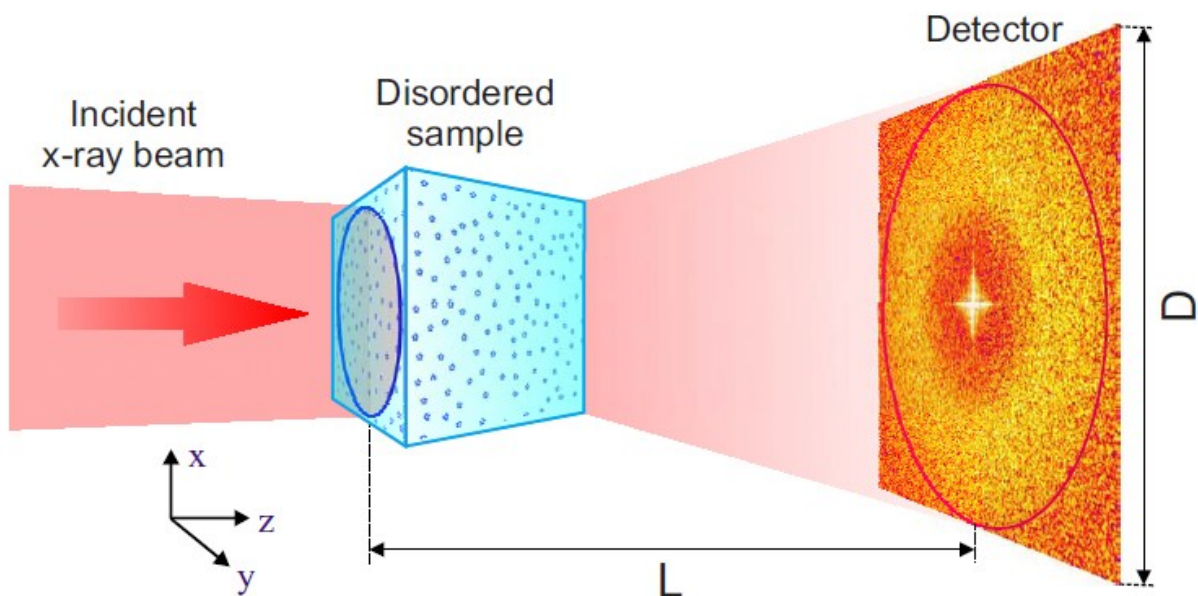


Figure 1. X-ray scattering experiment in transmission geometry

II. Theory

We consider a three-dimensional disordered system composed of tetrahedral clusters (Fig.2). In the case when the number N of clusters in the sample is large, diffraction patterns can only be used for the calculation of the radial distribution function, since the Fourier components of the intensity $I^n(q)$ with $n>0$ have vanishing values. However, if the number of clusters in the sample is small, one can extract the structural information about a single cluster performing the cross-correlation analysis of a sufficiently large number of diffraction patterns.[3]

The angular cross-correlation function (CCF) is defined as follows [4,5,6]:

$$C_q(\Delta) = \langle I(q, \phi) I(q, \phi + \Delta) \rangle_\phi - \langle I(q, \phi) \rangle_\phi^2 \quad (1)$$

where $I(q, \phi)$ is the scattered intensity, q is the magnitude of the scattering vector \mathbf{q} , ϕ and Δ , are the angular coordinates, and

$$\langle I(q, \phi) \rangle_\phi = \frac{1}{2\pi} \int_0^{2\pi} I(q, \phi) d\phi \quad (2)$$

is the angularly averaged intensity.

To analyze the CCF it is convenient to use the Fourier series,

$$C_q^n = \frac{1}{2\pi} \int_0^{2\pi} C_q(\Delta) e^{-in\Delta} d\Delta \quad (3)$$

Fourier components of the CCF Eq.(3) are related to the Fourier components of the intensity,

$$C_q^n \sim |I^n(q)|^2 \quad (4)$$

where

$$I^n(q) = \frac{1}{2\pi} \int_0^{2\pi} I(q, \phi) e^{-in\phi} d\phi \quad (5)$$

The Fourier components of intensity can be represented as the sum of two terms, associated with different types of correlations in the system [7,3]:

$$I_n(q) = (i)^n \sum_{k_1, k_2=1}^N L_{k_1, k_2}^n(q) = (i)^n \left[\sum_{k=1}^N L_k^n(q) + \sum_{k_1 \neq k_2}^N L_{k_1, k_2}^n(q) \right] \quad (6)$$

where

$$L_k^n(q) = |f(q)|^2 \sum_{m, l=1}^{N_s} e^{-iq^z z_{ml}} J^n(q^\perp |r_k^\perp|) e^{-in\phi_{r_k^\perp}^{lm}} \quad (7)$$

is the first term that contains contributions of individual clusters, and the second term

$$L_{k_1, k_2}^n(q) = |f(q)|^2 \sum_{m, l=1}^{N_c} e^{-iq^z z_{ml}} J^n(q^\perp |r_{k_1, k_2}^{\perp ml}|) e^{-in\phi_{r_{k_1, k_2}^{\perp ml}}} \quad (8)$$

contains contributions from the correlations between different clusters.

Here $f(q)$ is the form factor of the oxygen atom, summations over k , k_1 and k_2 are performed over different clusters, summations over m and l are performed over atoms in the clusters, r is the projection of the vector connecting the particles on the plane perpendicular to the x-ray beam, z is the distance between the particles along the direction of the x-ray beam; J^n is the Bessel function of the first order. Further, we will consider the cases of the flat and curved Ewald sphere; for the flat Ewald sphere q^z is equal to zero.

In the results of simulations presented here we, for simplicity, we neglect the interference of the scattered radiation from the different clusters and consider only the structural term Eq.(7) in Eq.(6). This approximation corresponds to the scattering from a dilute system. We also do not consider the scattering from hydrogen atoms, as they give a very small contribution to the total intensity as compared to oxygen atoms.

III. Modeling

The program for simulations was written in C++ for parallel computing on computer cluster, and Wolfram Mathematica was used for visualization of the results. In our calculations, we modeled the scattering of x-rays with a wavelength of 1 Å from tetrahedral oxygen clusters (Fig. 2).

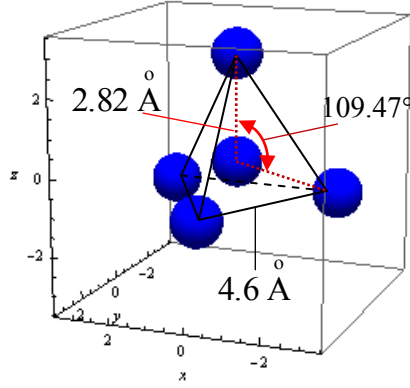


Figure 2. Tetrahedral oxygen cluster.

The distance between the central atom and the vertex is 2.82 Å, the same as in the TIP5P model of water. To generate the orientations of the clusters we used Euler angles rotations in the x-convention (Fig. 3). To generate a uniform distribution of orientations of clusters, we used the following formulae for Euler angles, $\alpha = 2\pi u$, $\gamma = 2\pi u$, $\beta = \arccos(2u - 1)$, where $u = [0,1)$ is a uniformly distributed random number.

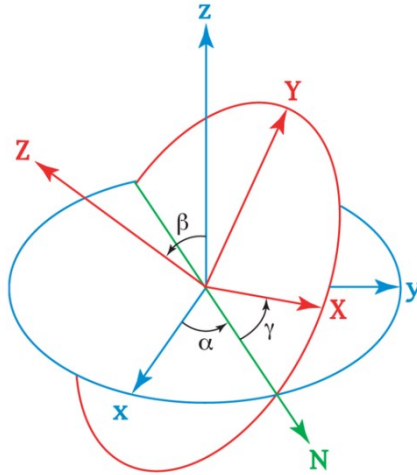


Figure 3. Euler angles rotations in the x-convention.

IV. Results

Figure 4a shows first nine Fourier components of the cross-correlation function simulated for a sample containing a single cluster. We perform the averaging

$$\langle C_q^n \rangle_M = \frac{1}{M} \sum_{m=1}^M \{C_q^n\}^m \quad (9)$$

of the spectrums obtained from particles in different orientations over a large number M diffraction patterns. Fig. 4 show the spectrums obtained after averaging over $M=1$, 10 and 10000 diffraction patterns. After averaging over many diffraction patterns the spectrum converge to some fixed form (Fig 4c) which is characteristic for a given structure of a cluster.

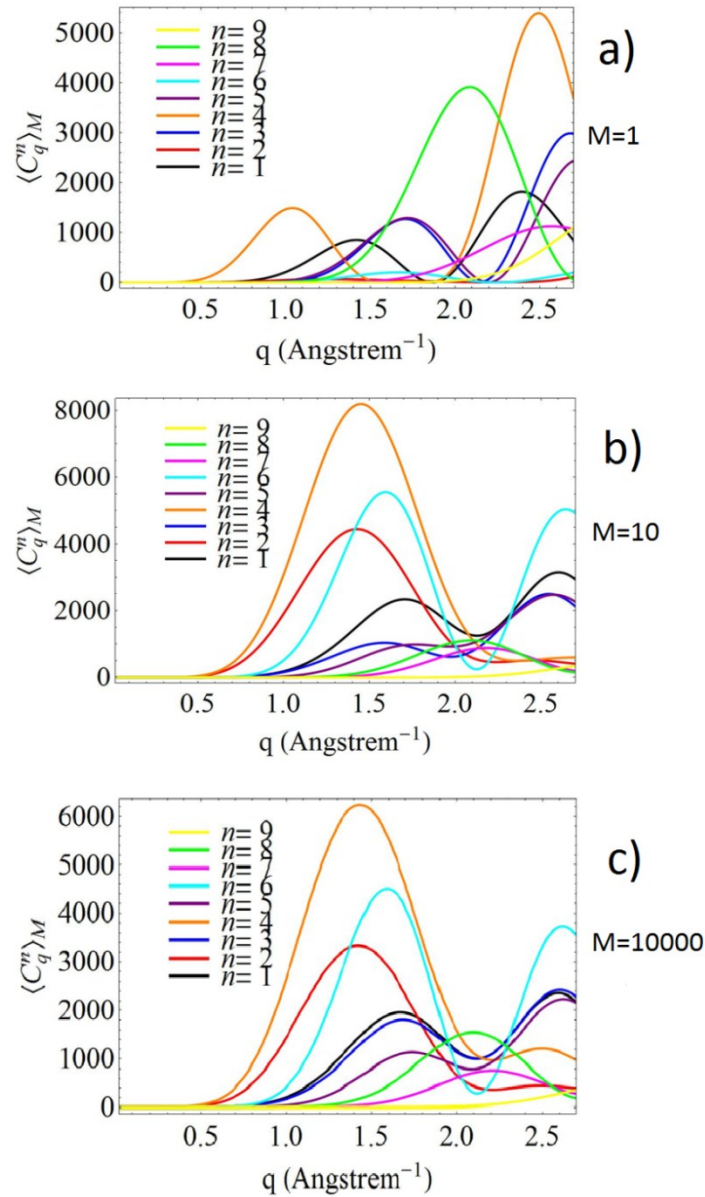


Figure 4. The spectrums obtained after averaging over a) $M=1$, b) 10 and c) 10000 diffraction patterns.

In Fig.5 the evolution of the $\langle C_q^n \rangle_M$ spectra as a function of the number of the averaged diffraction patterns M is shown for N=1, 10,100. According to Fig.5 when the number of samples used in the averaging is less than M=1000 the spectra are changing considerably. As the number M growth the fluctuations of $\langle C_q^n \rangle_M$ become smaller and for M=10000 the results converge with the error less than 1%.

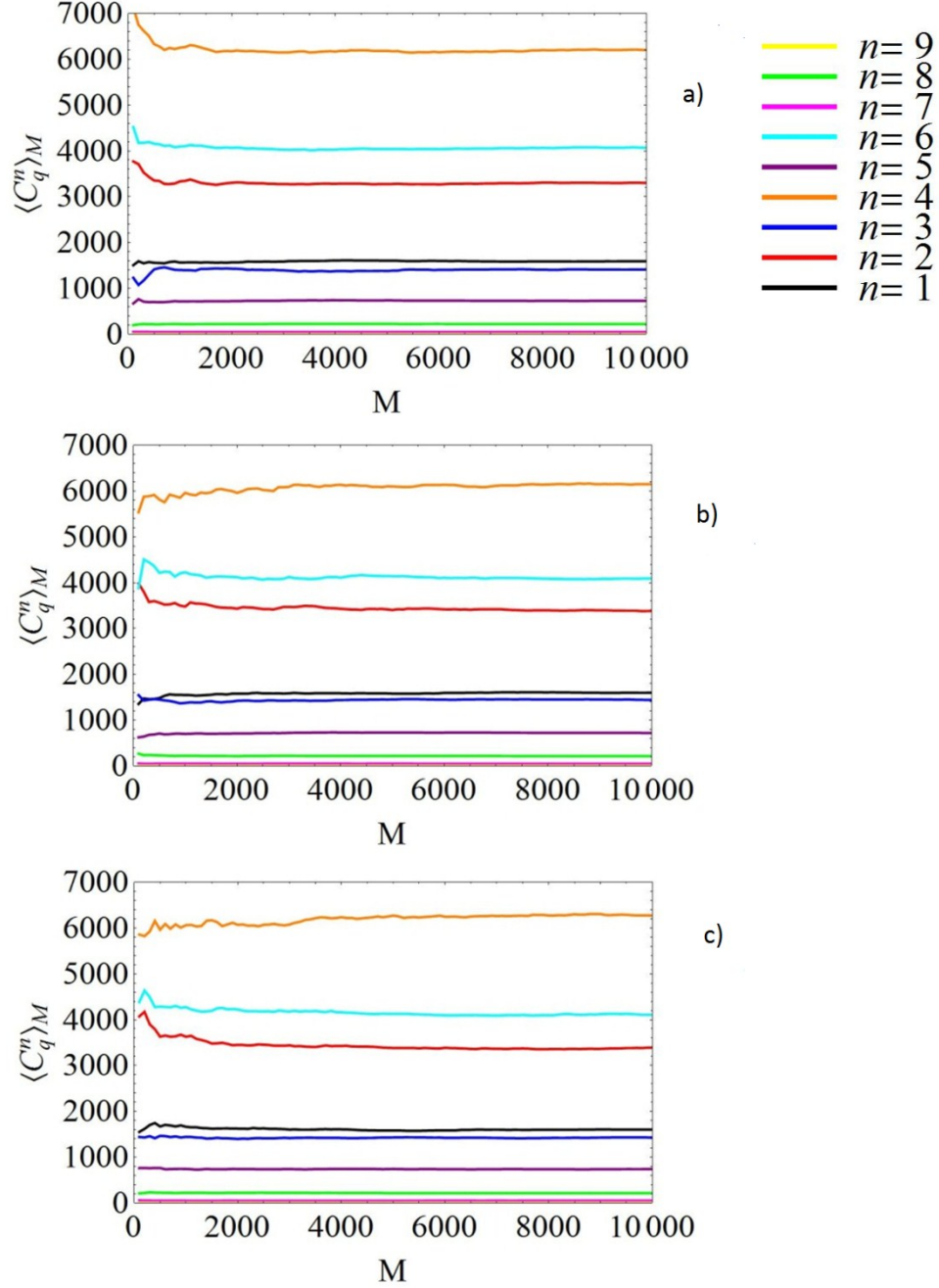


Fig 5 The averaged Fourier components $\langle C_q^n \rangle_M$ calculated at $q = 1.47 \text{ \AA}^{-1}$ calculated for different numbers of clusters in the sample a) N=1, b)N=10, c)N=100 $\langle C_q^n \rangle_M$ were normalized as $1/N$. For different number of clusters in the sample the spectra are identical.

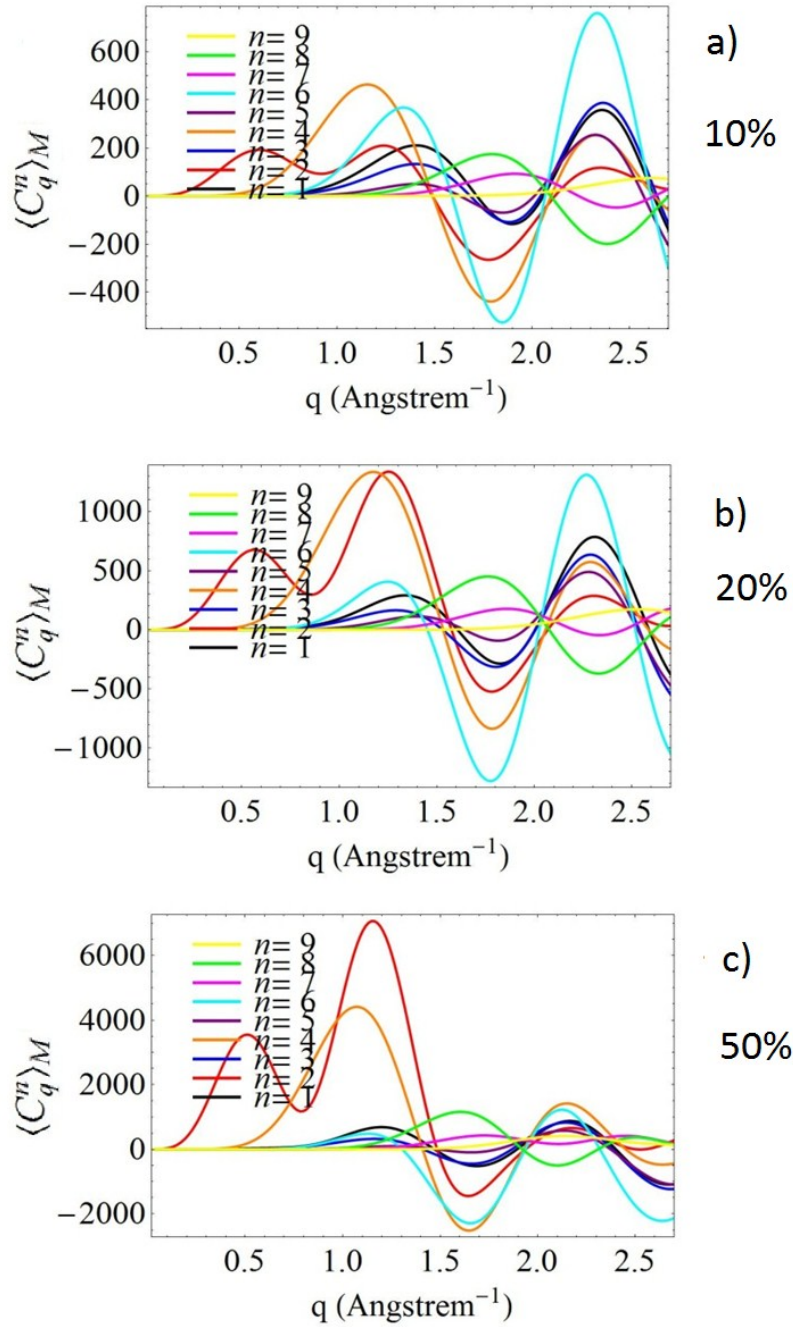


Figure 6. The difference between the $\langle C_q^n \rangle_M$ spectra of the regular and the distorted tetrahedron.

The results above were obtained for a regular tetrahedron. Now we consider the effect of tetrahedron deformation on the spectrum of the $\langle C_q^n \rangle_M$. We displace one of the atoms in the vertex of the tetrahedron by different magnitude and calculate the average spectra of the $\langle C_q^n \rangle_M$. Figure 6 shows the difference between the spectra of the regular and the distorted tetrahedron for the cases when the atom is displaced by 10% (5a), 20% (5b), 50% (5c) of the distance between two oxygen atoms.

V. Conclusions

- Fourier spectra of CCFs converge to the same form for different number of particles ($N=1, 10, 100$). Typically $M \sim 10000$ diffraction patterns are required to achieve convergence with the absolute error $\sim 1\%$;
- Small distortions of the cluster do not result in significant changes of the $\langle C_q^n \rangle_M$ spectra;
- $\langle C_q^n \rangle_M$ spectra are sensitive to the symmetry of the cluster. This can be used to identify the structure of the cluster from its $\langle C_q^n \rangle_M$ spectra.

VI. References

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