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What can we learn by comparing experimental and theoretical-computational X-ray scattering data?

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ABSTRACT

In this letter we use X-ray scattering data of liquid water, as obtained by different experimental and theoretical-computational procedures, to address the problem of quantitative modeling of the scattering signal in liquids. In particular we investigate the accuracy of well optimized water models in reproducing top level X-ray experimental results and compare experimental data variations with the ones given by different theoretical-computational models. Results show that the experimental scattering data have an intrinsic noise which is comparable to the deviations of the theoretical-computational signals, hence suggesting that no reliable refinement based on scattering data is possible for such models.

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1. Introduction

The structure of liquid water has been the research subject of a lot of theoretical and experimental groups worldwide, for thirty years. The pioneering study of Narten and Levy [1], is commonly considered as providing a reliable and accurate description of X-ray diffraction of liquid water at room temperature, to be compared to related theoretical studies [2–5]. G. Hura et al. [6] performed a new X-ray diffraction study of liquid water under ambient conditions, which was subsequently [7,8] used, in conjunction with theoretical-computational data, to address the problem of modelling X-ray scattering data by a molecular simulation in order to obtain an accurate radial distribution function. In one of these articles [7] the authors state that the differences seen between their X-ray intensity profile and previously reported scattering curves (essentially the paper of Narten and Levy [1]) are significant, and hence utilize the detailed information of their scattering profile to obtain (empirically) new atomic scattering factors and select optimal water molecular models. Because of the discrepancy among the experimental results of such studies and the possible relevance for molecular modelling of X-ray data, we decided to accomplish new measurements with our EDXD (Energy Dispersive X-ray) diffractometer, which has proven to be particularly suited to study liquid and amorphous samples [9–17], to perform a detailed comparison with scattering data obtained by simulations and address the problem of evaluating the optimal water model and/or atomic scattering factors to be used in molecular simulations of X-ray scattering signal.

2. Theory

The scattering intensity for a given atomic configuration is defined by $I(\boldsymbol{S})=|F(\boldsymbol{S})|^2$ where the structure factor $F(\boldsymbol{S})$ due to a set of n atoms within a volume V is [18,19]

$$F(\boldsymbol{S}) = \sum_{j=1}^{n} f_j(S) e^{2\pi i \boldsymbol{S}\cdot\boldsymbol{r}_j} \tag{1}$$

with $\boldsymbol{r}_j$ the position vector of the jth atom, $\boldsymbol{S}$ the scattering vector, $S=|\boldsymbol{S}|$, $f_j(S)$ the jth atom scattering factor and $i=\sqrt{-1}$. Therefore the observed scattering intensity, corresponding to the intensity averaged by the atomic configurational distribution, may be written as

$$\begin{aligned}\langle I(\boldsymbol{S})\rangle &= \left\langle \sum_{j=1}^{n}\sum_{k=1}^{n} f_j(S) f_k(S) e^{2\pi i \boldsymbol{S}\cdot(\boldsymbol{r}_j-\boldsymbol{r}_k)} \right\rangle \\ &= \sum_j f_j^2(S) + \sum_j \sum_{k\neq j} f_j(S) f_k(S) \left\langle e^{2\pi i \boldsymbol{S}\cdot(\boldsymbol{r}_j-\boldsymbol{r}_k)} \right\rangle\end{aligned} \tag{2}$$

For a fluid state system where the distribution of each kth atom around a jth atom depends only on the radial distance of the two atoms and not on the angular orientation, we have

$$\begin{aligned}&\sum_j \sum_{k\neq j} f_j(S) f_k(S) \left\langle e^{2\pi i \boldsymbol{S}\cdot(\boldsymbol{r}_j-\boldsymbol{r}_k)} \right\rangle \\ &= \sum_j \sum_{k\neq j} f_j(S) f_k(S) \int \rho_{jk}(\boldsymbol{r}_{jk}) e^{2\pi i \boldsymbol{S}\cdot\boldsymbol{r}_{jk}} d\boldsymbol{r}_{jk} \\ &= \sum_j \sum_{k\neq j} f_j(S) f_k(S) 2\pi \int_0^{\infty} r_{jk}^2 \rho_{jk}(r_{jk}) dr_{jk} \int_0^{\pi} \sin\theta e^{2\pi i S r_{jk}\cos\theta} d\theta\end{aligned} \tag{3}$$

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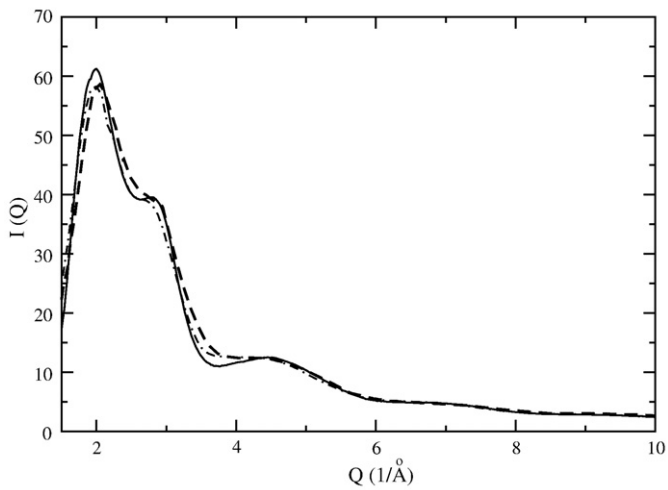

Fig. 1. Comparison of different experimental scattering data: our data (solid line), Hura et al. [6] (dashed line), Narten et al. [1] (dashed-dotted line).

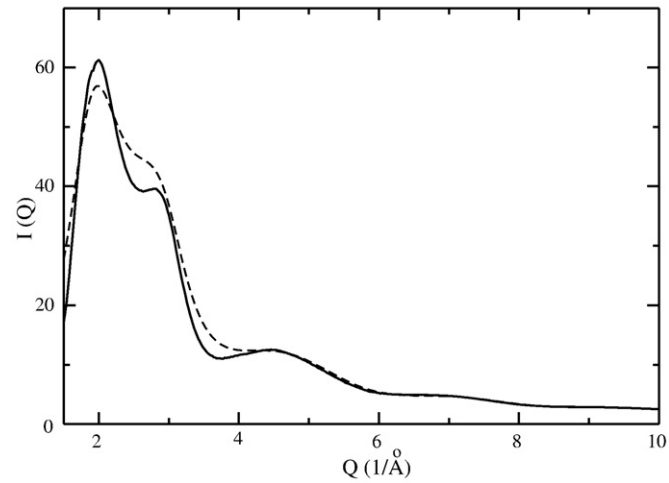

Fig. 2. Comparison of our experimental scattering data (solid line) with the theoretical signal as provided by the SPCE simulation at 300 K, utilizing the usual (free atoms) atomic scattering factors (dashed line).

where $\boldsymbol{r}_{jk}=\boldsymbol{r}_j-\boldsymbol{r}_k$, $r_{jk}=|\boldsymbol{r}_{jk}|$, $S\ r_{jk}\cos\theta=\boldsymbol{S}\cdot\boldsymbol{r}_{jk}$ and ρ_{jk} is the probability density of the j, k atomic couple relative position. Hence, by setting $q=2\pi r_{jk}\,S\cos\theta$, we readily obtain

$$\sum_j\sum_{k\neq j} f_j(S)f_k(S)2\pi\int_0^\infty r_{jk}^2\,\rho_{jk}(r_{jk})dr_{jk}\int_0^\pi \sin\theta\, e^{2\pi i S r_{jk}\cos\theta}d\theta$$

$$=\sum_j\sum_{k\neq j} f_j(S)f_k(S)2\pi\int_0^\infty r_{jk}^2\,\rho_{jk}(r_{jk})dr_{jk}\int_{-2\pi r_{jk}S}^{2\pi r_{jk}S}\frac{e^{iq}}{2\pi r_{jk}S}dq \tag{4}$$

$$=\sum_j\sum_{k\neq j} f_j(S)f_k(S)4\pi\int_0^\infty r_{jk}^2\,\rho_{jk}(r_{jk})\frac{\sin(2\pi r_{jk}S)}{2\pi r_{jk}S}dr_{jk}$$

Introducing the indeces l, m running over the atom types in the system, we may rewrite the last equation as

$$\sum_l\sum_m f_l(S)f_m(S)4\pi\int_0^\infty r_{lm}^2\frac{\sin(2\pi r_{lm}S)}{2\pi r_{lm}S}\sum_{j=1}^{n_l}\sum_{k=1}^{n_m}\left(1-\delta_{lm}\delta_{jk}\right)\rho_{jk}(r_{lm})dr_{lm}=$$

$$\sum_l\sum_m f_l(S)f_m(S)4\pi\int_0^\infty r_{lm}^2\frac{\sin(2\pi r_{lm}S)}{2\pi r_{lm}S}n_l\,\rho_m\,g_{lm}(r_{lm})dr_{lm} \tag{5}$$

$$\rho_m\,g_{lm}(r_{lm})=\frac{1}{n_l}\sum_{j=1}^{n_l}\sum_{k=1}^{n_m}\left(1-\delta_{lm}\delta_{jk}\right)\rho_{jk}(r_{lm}) \tag{6}$$

where n_l, n_m are the l and m atom type numbers (with hence the indeces j, k now running only over the corresponding atoms), $\rho_m=n_m/V$ is the bulk density of the m atom type, δ_{lm}, δ_{jk} are the Kroenecker terms for the l, m and j, k indeces and

$$\rho_m\,g_{lm}(r_{lm})=\frac{1}{n_l}\sum_{j=1}^{n_l}\sum_{k=1}^{n_m}\left(1-\delta_{lm}\delta_{jk}\right)\rho_{jk}(r_{lm}) \tag{7}$$

$$n_m=4\pi\int_0^\infty r_{lm}^2\,\rho_m\,g_{lm}(r_{lm})dr_{lm} \tag{8}$$

is the radial distribution function providing the m atom type density around a l type atom at radial distance r_{lm}.

Therefore, using the mathematical relation [18]

$$4\pi\int_0^\infty r_{lm}^2\frac{\sin(2\pi r_{lm}S)}{2\pi r_{lm}S}\rho_m dr_{lm}=\delta(S) \tag{9}$$

with $\delta(S)$ the Dirac function, and considering a proper radial distance upper limit R such that for $r_{lm}\geq R[g_{lm}(r_{lm})-1]\cong 0$, we may write for $S\neq 0$

$$\frac{\Delta\langle I(\boldsymbol{S})\rangle}{V}\cong$$

$$\sum_l\sum_m f_l(S)f_m(S)\rho_l\rho_m 4\pi\int_0^R r_{lm}^2\frac{\sin(2\pi r_{lm}S)}{2\pi r_{lm}S}[g_{lm}(r_{lm})-1]dr_{lm} \tag{10}$$

$$\Delta\langle I(\boldsymbol{S})\rangle=\langle I(\boldsymbol{S})\rangle-\sum_{j=1}^{n}f_j^2(S) \tag{11}$$

The last equation might be used to evaluate the scattering intensity in general, once each $g_{lm}(r_{lm})$ is known. However, we may further proceed by splitting each $g_{lm}(r_{lm})$ into its intramolecular $\hat{g}_{lm}(r_{lm})$ and intermolecular $\tilde{g}_{lm}(r_{lm})$ parts (i.e. $g_{lm}=\hat{g}_{lm}+\tilde{g}_{lm}$) and considering that for a rigid molecule like water

$$4\pi\,\rho_l\rho_m r_{lm}^2\hat{g}_{lm}(r_{lm})=\frac{N}{V}\sum_{j=1}^{\hat{n}_l}\sum_{k=1}^{\hat{n}_m}\left(1-\delta_{lm}\delta_{jk}\right)\delta\left(r_{lm}-r_{jk}\right) \tag{12}$$

Table 1
Root mean square relative deviations between different X-ray scattering experimental data for liquid water at ambient conditions (290–300 K)

	Exp. data [1]	Exp. data [6]	Exp. data (this work)
Exp. data [1]	0.000	0.049	0.037
Exp. data [6]	0.049	0.000	0.061
Exp. data (this work)	0.037	0.061	0.000

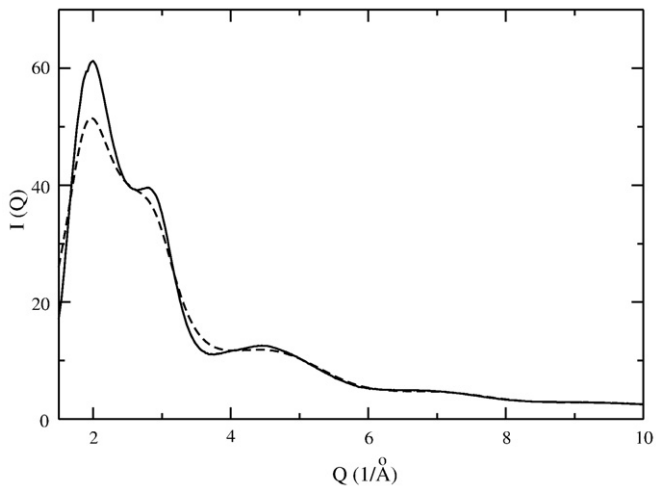

Fig. 3. Comparison of our experimental scattering data (solid line) with the theoretical signal as provided by the SPCE simulation at 300 K, utilizing the modified atomic scattering factors (MASF) introduced by Hura et al. [6] (dashed line).

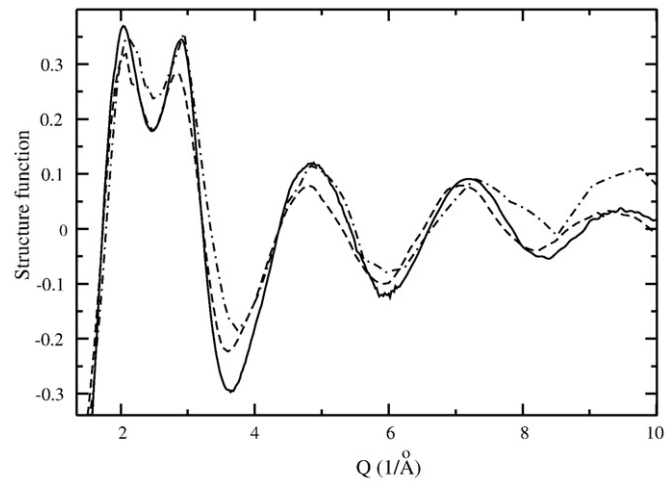

Fig. 4. Comparison of experimental structure functions: our data (solid line), Hura et al. [6] (dashed line), Narten et al. [1] (dashed-dotted line).

with N the number of molecules and $\hat{n}_l, \hat{n}_m$ the number of atoms, in a single molecule, for the l and m atom types respectively. Hence, we have

$$\frac{\Delta\langle I(\boldsymbol{S})\rangle}{V} \cong \frac{N}{V}\sum_l\sum_m f_l|(S)f_m(S)\sum_{j=1}^{\hat{n}_l}\sum_{k=1}^{\hat{n}_m}(1-\delta_{lm}\delta_{jk})\frac{\sin(2\pi r_{jk}S)}{2\pi r_{jk}S} + \sum_l\sum_m f_l(S)f_m(S)\,\rho_l\,\rho_m 4\pi\int_0^R r_{lm}^2\frac{\sin(2\pi r_{lm}S)}{2\pi r_{lm}S}\left[\tilde{g}_{lm}(r_{lm})-1\right]dr_{lm} \tag{13}$$

We used this last equation with $R=12$ Å and $\tilde{g}_{lm}$ as provided by MD simulations of a set of water molecular models, to obtain the signal per molecule to be compared to the experimental data.

3. Methods

We performed our experiments using the non-commercial energy-scanning diffractometer built in the Department of Chemistry of the University of Rome La Sapienza. Detailed description of both instrument and technique can be found elsewhere [11,15]. Transmission geometry has been employed and the white Bremsstrahlung component of the radiation emitted by a tungsten tube working at 50 kV and 40 mA was used. Scattered intensities for the samples and for the empty cell were measured at seven different angles (26.0, 15.5, 8.0, 3.5, 2.0, 1.0 and 0.5 degrees). This choice allowed us to cover a wide range of the scattering variable $Q=2\pi S$, namely between 0.12 and 17 $Å^{-1}$. The measuring time was set so as to obtain a minimum of 300,000 counts per experimental point for $Q<5$ $Å^{-1}$ and 1,000,000 counts for $Q>5$ $Å^{-1}$. This large amount of counts can be achieved in a limited period of time with EDXD (with respect to ADXD), resulting in a significant improvement of signal to noise ratio at high angles. The primary beam intensity was measured directly, by reducing the tube current to 10 mA at zero scattering angle without the sample. Transmission of the samples was measured under the same conditions. Both quantities are needed to carry out necessary corrections to observed scattered intensities. After correction of experimental data for escape peak suppression [11,15], the various angular data were combined and the re-scaled intensity, in electron units (e.u.), was normalized to provide the intensity per molecule. Such correction was performed using our program DIF1, purposely written. The collected and corrected experimental data were hence used to obtain the signal per molecule as defined in the theory section.

The MD simulations were performed using Gromacs software package [20], modified to use the isokinetic temperature coupling [21]. The trajectories of 6ns (the first ns was considered as equilibrature and hence disregarded) were obtained using a time step of 2fs. Short range interactions were evaluated within 0.9 nm cut off radius and the long range electrostatics was calculated using the Particle Mesh Ewald (PME) method, with 34 wave vectors in each dimension and a 4th order cubic interpolation. A simulation box of 256 water molecules at 55.32 mol/l was used for all the simulations. The models used for the water were the Simple Point Charge (SPC) [23] and its extension (SPCE) [22]. Such models, parametrized on basic thermodynamic properties, provide a proper description of liquid

Table 2
Root mean square relative deviations between X-ray scattering data obtained by MD simulations (300 K) of different water models and experimental data

	SPC	SPCE	SPCE MASF
Exp. data [6]	0.045	0.049	0.038
Exp. data (this work)	0.038	0.042	0.055

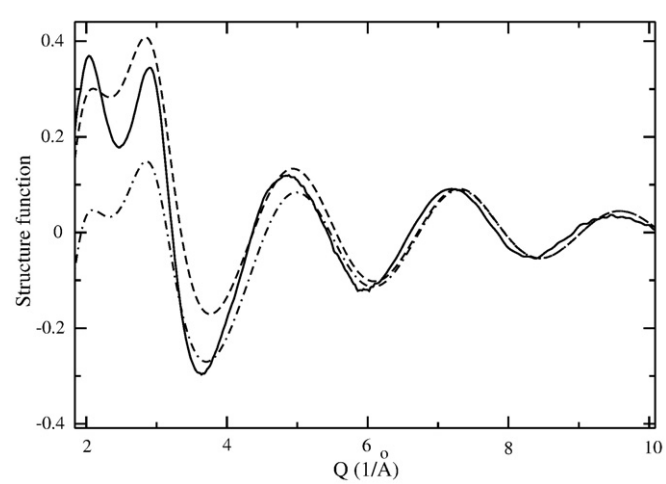

Fig. 5. Comparison of our experimental structure function (solid line) with the theoretical signal as provided by the SPCE simulation at 300 K using the usual (free atoms) atomic scattering factors (dashed line) and the modified atomic scattering factors (MASF) introduced by Hura et al. [6] (dashed-dotted line).

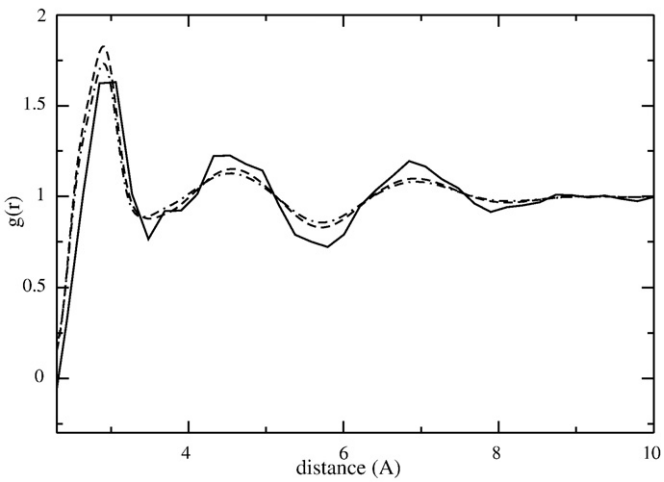

Fig. 6. Comparison of the "effective" radial distribution functions obtained via transforming the experimental (solid line) and the SPCE structure functions using the free atoms atomic scattering factors (dashed line) and the modified atomic scattering factors (MASF) introduced by Hura et al. [6] (dashed-dotted line).

water thermodynamics hence suggesting their ability to reproduce liquid water structural behaviour.

4. Results

In Fig. 1 we compare our experimental scattering data with data published in previous papers [1,6]. The figure clearly shows that the three experimental data sets are very close in the right tail and present larger deviations in the principle peak region. Such data variations may be quantitatively expressed by the root mean square relative deviations (RMSRD) reported in Table 1, indicating moderate but not negligible variations. Interestingly, our experimental scattering profile is closer to Narten et al. data [1], although obtained with a rather different procedure. Such results strongly suggest the presence of an intrinsic noise in the experimental scattering data corresponding to a mean deviation of roughly 3–6%. It must be noted that uncertainty in a single scattering experiment is typically well below 1%, being essentially due to the number of counts measured at each angle-energy. The relatively large noise observed when comparing different experiments (see Table 1) is determined by the different experimental procedures used, requiring different conversion and correction methods to obtain the scattering intensity from the measured counts. We also compare in Figs. 2 and 3 our experimental scattering data with the theoretical scattering signals (see Theory section) as obtained by the MD simulation of the extended simple point charge [22] (SPCE) water model, utilizing either the usual atomic scattering factors or their modification (MASF) as proposed by Hura et al. [6]. These two figures again show very similar right tails for all the curves considered, with moderate deviations present in the principle peak region. Interestingly, such variations are comparable to the ones observed for the three different experimental data sets, although a bit enhanced and more localized in the principle peak. In Table 2 we show the RMSRD of these theoretical curves with respect to Hura et al. and our experimental data, including the comparison with the theoretical data provided by the MD simulation of the simple point charge [23] (SPC) model utilizing the usual atomic scattering factors. RMSRD values in this last table are indeed fully comparable to the ones of Table 1, quantitatively confirming that deviations of these models are, in average, within the experimental noise. Comparison of structure functions instead of scattering intensities, Figs. 4 and 5, provides similar results and evaluation of the "effective" radial distribution function as obtained via transformation of the structure functions, as given in the work of Brunner et al. [24], of our experimental data well matches the corresponding theoretical curves (Fig. 6) also calculated by the same method. Note that in the figures as well as in the tables we considered the 1.5–10 $Å^{-1}$ Q range as for $Q \geqslant 10$ no relevant signal is present and for $Q \leqslant 1.5$ both the experimental data and MD based theoretical signals are not fully reliable, and the obtained radial distribution functions, essentially equivalent to the Oxygen–Oxygen radial distribution, are typically affected by relevant errors due to truncation in the inverse space [25].

5. Conclusions

In this letter we compared three experimental scattering data sets with three different theoretical scattering signals, as obtained by MD simulations of SPCE and SPC water models using either the usual atomic scattering factors or the modified atomic scattering factors (MASF) of Hura et al.. Results indicate that the variations of the theoretical data, as provided by the use of these related but different water models and/or the inclusion of MASF, are roughly comparable to the differences of the experimental data sets. Such experimental data variations are likely to be connected to the intrinsic noise of the scattering signal (RMSRD within 3–6%) rather than to a systematic error of the experimental procedures used, and therefore it does not seem fully reliable to use the small variations of the theoretical-computational scattering signals with respect to an experimental data set to select the optimal water model and/or to optimize (empirically) the atomic scattering factors. Such results imply that well optimized liquid water molecular models like SPC and SPCE, although parametrized on basic thermodynamic properties not involving diffraction data, have reached a level of description of the structural properties (SPC and SPCE) and of the dielectric and diffusion properties (SPCE) which can hardly be improved further, unless the experimental scattering data decrease relevantly their noise.

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