



# Reverse Monte Carlo investigations concerning recent isotopic substitution neutron diffraction data on liquid water



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## ABSTRACT

Although liquid water has been studied for many decades by (X-ray and neutron) diffraction measurements, new experimental results keep appearing, virtually every year. The reason for this is that neither X-ray nor neutron diffraction data are trivial to correct and interpret for this essential substance. Since X-rays are somewhat insensitive to hydrogen, neutron diffraction with (most frequently, H/D) isotopic substitution is vital for investigating the most important feature in water: hydrogen bonding. Here, the two very recent sets of neutron diffraction data are considered, both exploiting the contrast between light and heavy hydrogen,  $^1\text{H}$  and  $^2\text{H}$ , in different ways. Reverse Monte Carlo structural modeling is applied for constructing large structural models that are as consistent as possible with all experimental information, both in real and reciprocal spaces. The method has also proven to be useful for revealing where possible small inconsistencies appear during primary data processing: for one neutron data set, it is the molecular geometry that may not be maintained within reasonable limits, whereas for the other set, it is one of the (composite) radial distribution functions that cannot be modeled at the same (high) level as the other three functions. Nevertheless, details of the local structure around the hydrogen bonds appear very much the same for both data sets: the most probable hydrogen bond angle is straight, and the nearest oxygen neighbors of a central oxygen atom occupy approximately tetrahedral positions.

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## 1. Introduction

Liquid water, as it is the basis of life on Earth, is the most common, everyday liquid. It is the simplest compound of two universal elements, hydrogen and oxygen ( $\text{H}_2\text{O}$ ), and is the second most frequent molecule in the Universe. In spite of these, water is still an amazing substance with unique properties: it has phase, density, thermodynamic and other physical anomalies [1]. Hence it is not surprising that water has been, and still is the most researched liquid. (For a comprehensive summary, see e.g. the collection of references in [1]).

In order to understand its properties (and anomalies!), it is necessary to comprehend the microscopic structure of liquid water. There are numerous studies in the literature using different spectroscopy and scattering techniques: X-ray [2–4] and neutron scattering [5–8], X-ray absorption spectroscopy (XAS) [9–12], X-ray emission spectroscopy (XES) [13–16] or small-angle X-ray scattering experiments (SAXS) [17,18]. To interpret the experimental results many models and computer simulation works have been performed (see e.g. [5,19–22] and references therein).

Though there have been many investigations, there is not a reassuring consensus present about the structure of water. For example,

even the concept of tetrahedral arrangement of 4-fold coordinated water molecules, that had been widely accepted earlier, has been challenged and an asymmetric distribution of twofold-coordinated molecules was suggested [9]. The proposed structural organization, with hydrogen-bonded chains and rings of water molecules in a weakly hydrogen-bonded disordered network, is still controversial (see e.g. [23,24]). As an interesting addition to the ongoing debate concerning coordination numbers, Skinner et al. report an ‘isosbestic point’, a distance at which the integrated O–O coordination number is independent of temperature [25].

Diffraction measurements are the obvious means for structure determination. X-ray diffraction can be useful for determining the oxygen–oxygen (and, to some extent, oxygen–hydrogen) correlations [25], but this technique is not too sensitive for hydrogen. Since neutron scattering lengths are different for the hydrogen isotopes, neutron diffraction with H/D isotope substitution is, in principle, suitable for the separation of the hydrogen–hydrogen and hydrogen–oxygen correlations (if one accepts the approximation that the structure of water depends only weakly on the isotopic composition). In practice, however, the correction of the measured scattering data is extremely difficult due to the strong incoherent and inelastic scattering of neutrons by protons ( $^1\text{H}$ ). There is still not a generally applicable way to remove such effects from the measured data (see, e.g., [5,19,26]). This is why structural modeling [27,28] has played an important role [5,8,19] in the history of structure studies on liquid water.

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One of the possibilities that can be useful for interpreting the corrected diffraction data sets is to prepare three-dimensional atomic (structural) models that are consistent with all of the input data sets. The Reverse Monte Carlo (RMC) method [27] is a perfect tool for this purpose. RMC also allows one to check whether it is possible to prepare physically meaningful particle configurations that match corrected experimental data (see Ref. [29]); i.e., the method (under certain conditions) may serve for providing a kind of ‘first aid support’ to measured diffraction data.

In this work we have studied two sets of very recent neutron total scattering structure factors (TSSF) and the corresponding radial distribution functions. One of them [8], referred to as ‘Case 1’ throughout, presented diffraction measurements on four mixtures of light and heavy water; the partial radial distribution functions (PRDF) were also provided. The other study [7], indicated as ‘Case 2’ in the following, is based on neutron diffraction measurements with oxygen isotope substitution. From these measurements the authors obtained linear combinations of the O–O and O–H (or O–D) partial structure factors. They presented radial distribution functions obtained by Fourier transformations, as well.

Two important differences between the two sets of neutron diffraction experiments should be mentioned explicitly:

- (1) Data for ‘Case 1’ have been gathered at a spallation neutron source (ISIS, UK), whereas experiments connected to ‘Case 2’ were performed on a steady-state reactor based instrument (ILL, France); this difference has a profound effect on the methods and complexity of data treatment (see Refs. [8,7]).
- (2) Since it was not stated otherwise in Ref. [8], standard values of the atomic coherent scattering lengths were assumed for data in ‘Case 1’, whereas for ‘Case 2’, they were taken from the original publication [7]. The coherent scattering lengths applied throughout this work are quoted in Table 1.

We performed Reverse Monte Carlo modeling, in order to (a) learn about the internal consistency of these new, much improved scattering data and (b) find structural models that would be consistent with the entire data sets, including the *r*-space information, simultaneously.

## 2. Reverse Monte Carlo modeling

Reverse Monte Carlo (RMC) modeling has been described in many publications in detail [30–33], so here only a brief description is necessary. RMC is an inverse method to obtain large three-dimensional structural models that are consistent with the supplied (experimental and/or theoretical) data sets (TSSF-s and/or (P)RDF-s). It can be used in conjunction with any quantity that can be expressed directly from the atomic coordinates. By moving particles randomly in the simulation box, the difference between the experimental (or ‘quasi-experimental’, see, e.g., [34] and RMC model structural quantities (e.g. structure factors) is minimized. As a result, particle configurations are obtained that are consistent with all the input data. From the particle configurations, further structural characteristics (coordination numbers, nearest neighbor distances, bond angle distributions, etc...) may be calculated. Over the past nearly three decades, RMC has been successfully applied to a wide variety of systems, from simple liquids (see, e.g., the review of McGreevy [30]), through metallic [35] and covalent [36] glasses,

**Table 1**  
Coherent atomic scattering lengths used for neutron data of ‘Case 1’ [8] and ‘Case 2’ [7] (in fm).

	$b_{\text{natO}}$	$b_{18\text{O}}$	$b_{\text{D}}$	$b_{\text{H}}$
Case 1	5.803	–	6.671	–3.7406
Case 2	5.805	6.005	6.619	–3.7409

**Table 2**  
Minimum and maximum O–H and H–H intramolecular distances used in fixed neighbor constraints and intermolecular closest approach distances (cutoff distances) between atoms (in Å).

	O–O	O–H	H–H
Intramolecular distances realistic molecule	–	0.95–1.02	1.50–1.62
Intramolecular distances ‘elastic’ molecule	–	0.78–1.15	1.36–1.71
Intermolecular distances all models	2.3	1.5	1.6

simple [37,38] and hydrogen-bonded [19] molecular liquids, as well as for characterizing disordered crystalline structures [39,40].

The method is also suitable for establishing whether various input data sets are consistent with each other: if they are then they can be fitted simultaneously within their uncertainties [34]. If, on the other hand, not each element of the input set is consistent with the others then it is possible to tell which element is problematic: an approach proposed and tested recently [41] for input data consisting of TSSF-s and PRDF-s is applied in this work.

Here the RMC++ code [32] was used to obtain structural models. The cubic simulation boxes contained 6000 atoms (2000 molecules), the atomic number density was  $0.1 \text{ \AA}^{-3}$ , the simulation box length was 39.1 Å. In order to keep the atoms together in the molecules during the calculations the ‘fixed neighbor constraints’ (FNC) option was applied [31]. This algorithm connects two hydrogen atoms and their oxygen central atom permanently via their identity numbers (defined for the atomic configuration file). For the realization of this constraint, the O–H and H–H intramolecular distances were kept between minimum and maximum values: the values for the various FNC combinations tested are shown in Table 2. Intermolecular closest approach (‘cutoff’) distances between atoms were chosen as indicated in Table 2.

Simulations were started from a random configuration where only the cutoff distances and the fixed neighbor constraints were in effect (‘hard sphere’ model). The number of accepted moves was about  $1-2 \times 10^7$  in each calculation.  $\sigma$  parameters (essentially, control parameters for the different data sets that influence the tightness-of-fit, cf. Ref. [31]) were decreased progressively during the simulation runs, resulting in a gradually improving fit to the target functions. Final  $\sigma$  values are listed in Tables 3 and 4. Note that these tables also provide information on the sets of input data applied in the various RMC calculations: for Case 1 (data from Ref. [8]), always at least 7 target functions (4 TSSF-s, 3 intermolecular PRDF-s) were considered, whereas for Case 2 (data from Ref. [7]), 4 functions (two in *Q* and two in *r* space, each a kind of ‘composite’) were approached.

## 3. Results and discussion

### 3.1. Case 1: H/D isotopic substitution

Four total scattering structure factors of four mixtures of light and heavy water were considered, as seen in Fig. 2 of Ref. [8]. The four compositions are: pure D<sub>2</sub>O, pure H<sub>2</sub>O, and two mixtures of light and heavy water with  $x = 0.5$  (denoted as ‘HDO’) and  $x = 0.64$  (denoted as ‘Null’) ( $x$  is the mole fraction of light water in the mixture). In the case of the

**Table 3**  
 $\sigma$  parameters and R-factors for the different data sets in Case 1.

	$\sigma$	R – Case 1a	R – Case 1b	R – Case 1c
$g_{\text{OO}}(r)$	0.02	6.2	6.1	6.1
$g_{\text{OH}}(r)$	0.02	5.9	4.6	5.1
$g_{\text{HH}}(r)$	0.02	4.1	3.0	4.1
$g_{\text{HH}}^{\text{intra}}(r)$	0.02	–	–	15.4
$F_{\text{D}_2\text{O}}(Q)$	0.0075	14.4	9.0	8.2
$F_{\text{HDO}}(Q)$	0.002	18.0	18.2	18.7
$F_{\text{Null}}(Q)$	0.00045	27.0	27.0	27.0
$F_{\text{H}_2\text{O}}(Q)$	0.001	16.0	7.4	8.8

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