| RMC Run Report | Material: $H_2O$<br>Cfg. Size: 6000 atoms |
|---|---|
| Data: 2 neutrons, 1 X-ray | RMC Options: FNC |
| Run Date: July 2002 | Code rmc_fi |

# Data $Q$-range vs. constraints, and neutron vs. X-ray diffraction data in RMC-modelling of liquid water

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## 1 Objective

The main purpose of this series of runs was to assess the importance of the extent of the $Q$ range in diffraction data for the modelling of liquid water.
Water has the advantage that its molecule can be (geometrically) well defined by a set of FNC's (the O-H and the H-H distances), which constitute an important *a priori* information.
The original data was composed of three data sets:

1. 1 neutron diffraction data set (DHO, 60 points ranging from 0.99 to 9.5 $Å^{-1}$)[1].

2. 1 neutron diffraction data set ($D_2O$, 110 points ranging from 0.99 to 31.18 $Å^{-1}$)[2].

3. 1 X-ray data set ($H_2O$, 79 points ranging from 0.99 to 16.15 $Å^{-1}$)[3]

Note that since we used **rmc_fi**, the data had been re-sampled at the same $q$ values on overlapping regions.
It must also be noted that the X-ray data set was used as a neutron data set: form factors were neglected and the sensitivity of the X-Ray data to the hydrogen atoms was set to zero. That means in short, that we know (or we decide) a priori that the X-ray data set provides direct information on the repartition of the molecular centres (O atoms) only.
In order to evaluate the importance of the extent of the $Q$-range in the data, the strategy is to make several runs with chopped-off data sets, and then to examine possible differences in the resuting configurations.
The different data constraints used in the runs appear in Tab. 1.

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## 2 The 5 runs

Common run parameters for all the runs were:

- 6000 atoms (*i.e.* 2000 molecules),
- density: 0.099 atoms per cubic Angstrom,
- cubic cell size: 1/2 edge= 19.64002 Å,
- r-spacing 0.1 Å,
- move range for all atoms: 0.1 Å.
- cut-offs 2.5, 0.9 and 0.9 Åfor O-O, O-H and H-H respectively
- the $\sigma$ (data standard deviation) was set to 0.001, 0.0015, and 0.0015 for the DHO, $D_2O$ and $H_2O$ sets respectively.

N.b.: change of amplitudes (multiplicative renormalization) were not allowed for sets 2 and 3, but were authorized for set 1.
The starting configurations for each run were configurations obtained from previous runs. They were 'not too far' to the final solutions, although a completely disordered configuration (resulting from a 'hard-sphere' run without data) would have worked as well (as was proved by a later test).

Following the usual 'rule of thumb', move parameters were set so that the acceptance ratios were approximately 0.5 for both (tried/generated) and (accepted/tried).

Since the code used was **rmc_fi**, there is no trace kept of the evolution of the run, but the runs duration practically ensures that convergence was reached

| Run | $Q_{max}$ | number of data points | duration (hours) |
|---|---|---|---|
| 1 | 9.5 | 60 | 3×20 |
| 2 | 7.02 | 53 | 3×20 |
| 3 | 4.5 | 44 | 3×20 |
| 4 | 2.65 | 33 | 3×20 |
| 5 | 9.5 * | 60 | 3×20 |

Table 1: Data range and duration for the 5 runs. * the X-ray data were droppped in run 5.

(durations was most probably 3 times 20 hours for all of them, my logbook indicates 60 hours for runs 2 and 3)

# 3 Results

The resulting configurations have been used to extend the $Q$ range for calculated data to the maximum range of 9.50 Åfor all runs (see Fig.1).

The first conclusions reached from the results in Fig.1, are that in the $Q$ region where data were used for the run, the fit is rather good. This is not entirely satisfying for DHO after 4 $Å^{-1}$, but it must be noticed that even calculated data from runs 1 and 5 (*i.e.* with the largest $Q$ range) display the *same* departure from the experimental curve in this region (this could be a problem with the data, as there is no such a problem with the $D_2O$ data set).

The second conclusion is that the main features of the total structure factors for neutron diffraction experiments are recovered beyond the cutoff (except for run 4). This indicates that the information brought by the modelling assumptions and the constraints are redundant with the information contained in the suppressed $Q$ regions. Since this is not true for run 4, we can say that on the contrary, the data below 4.5 $Å^{-1}$ contains specific information absent from the *a priori* constraints.

The third conclusion concerns the X-ray data. We have to keep in mind that in our run setup, this data derives only from the O-O partial. It is obvious from the X-ray fit of Fig. 1 that in the absence of experimental (X-ray data), the O-O partial is not constrained. Contrary to the neutron data sets (where features of the experimental curves are recovered beyond the cutoff), as soon as the experimental constraints are released (cutoff in the X-ray data set) the fit departs from the experimental curve. This indicates that the neutron data set do not bring significant information about the O-O partial.

In r-space, the partial pair correlation functions confirm this feature (Fig. 2). The information gained from run 1 is lost in run 4 (cut-off at 2.6 $Å^{-1}$) for all partials. Keeping the full $Q$-range but suppressing the X-ray data set (run 5) yields the same loss of information for the O-O partial, while the others are almost left intact.

In short, the findings of this series of runs are:

- no accurate information about the O-O partial can be obtained without the X-ray data.
- data beyond $Q$=4.5 $Å^{-1}$ are partly redundant with RMC constraints.

# References


[1] Thiessen W.E., Narten A.H., *J. Chem. Phys.* **77**, 2656 (1982).

[2] Soper A.K., Bruni F., Ricci M.A., *J. Chem. Phys.* **106**, 247 (1997).

[3] Narten A.H., Levy H.A., *J. Chem. Phys.* **55**, 2263 (1971).


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Run files:

- **on PC**: in folders `run 1`, `run 2`, `run 3`, `run 4`, `run 5`
  access path: `C:\Guillaume\h20`.

- **on iBook**: out files only access path: `DataHD:Budapest:RMC Workshop:h20/d20:result files`.

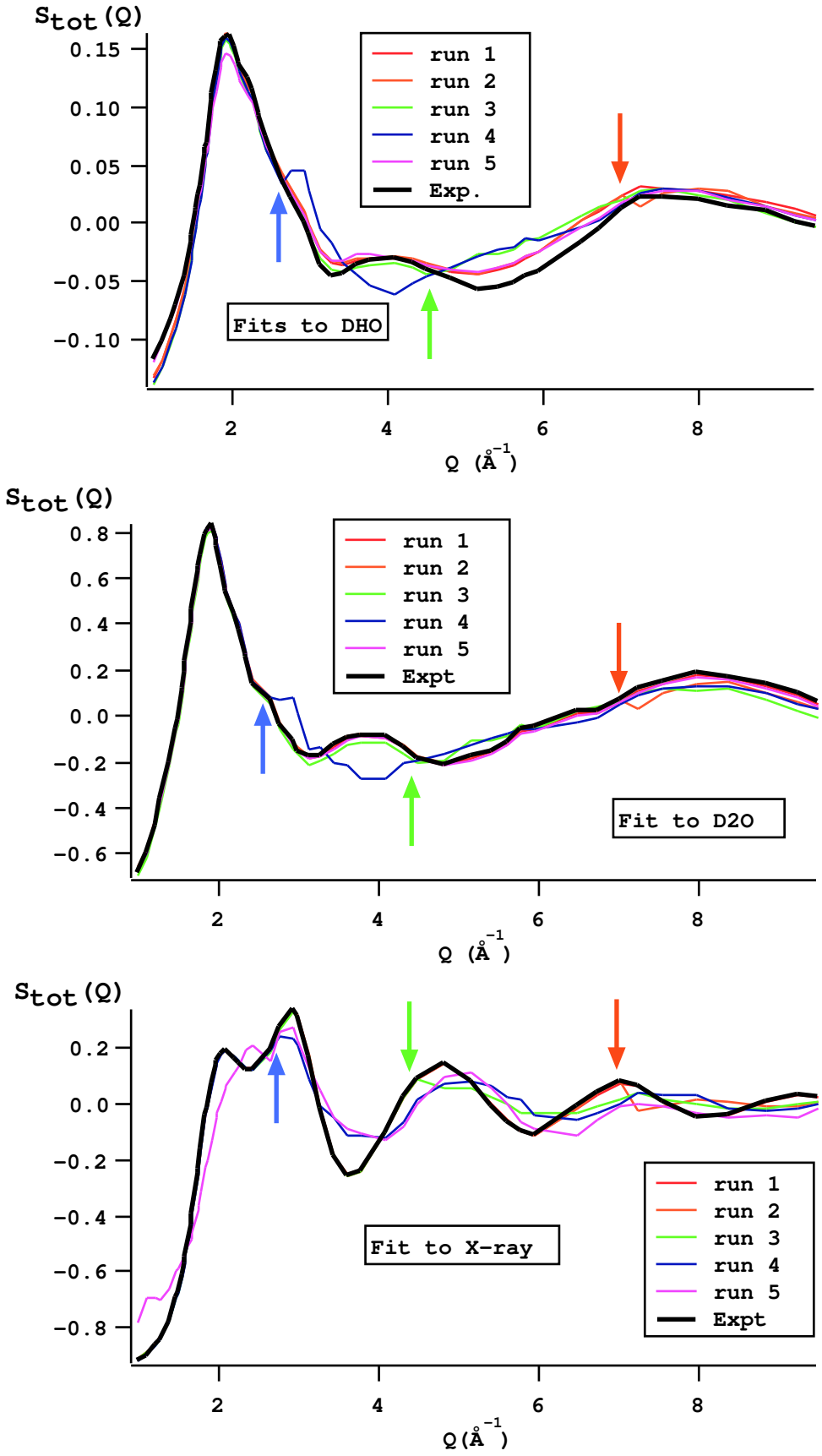


Figure 1: Experimental and RMC total structure factors for DHO (top) D2O (middle), and X-ray (bottom) data sets. The arrow points to the $Q$-range cutoff used for runs 2, 3 and 4. The X-ray data was not used in run 5

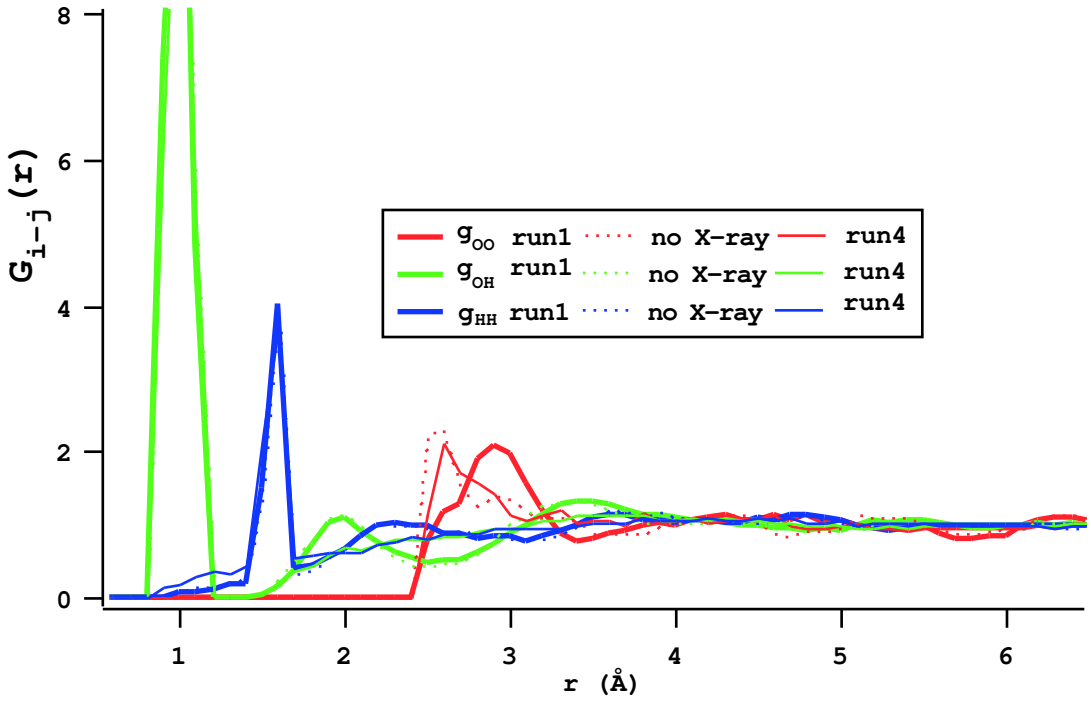


Figure 2: The partial pair correlation functions derived from runs 1, 4 and 5.