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| <h1>RMC Run Report</h1> | Material: Cl₂ |
| | Cfg. Size: 2000 atoms |
| Data: 1 neutron | RMC Options: FNC |
| Run Date: April 2002 | Code rnc_fi |

Study of data vs. constraints effects with liquid Cl₂

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1 Introduction

This series of runs is a part of a more general study of the relative effects of *a priori* RMC algorithmic constraints, such as distances of closest approach (cut-offs) and fixed neighbours constraints (FNC) and diffraction data (especially the Q -range) on the simulation results. These runs on Cl₂ follow investigations conducted with CCl₄.

As for CCl₄, our main purpose is to test to which extent data and constraints are redundant, and what information relevant to the structure is specifically brought by which constraint (data or algorithmic).

The material chosen for this test was liquid Cl₂. The original data was a set of neutron diffraction data taken at Saclay[1], made of 74 points in the range 0.5 to 15.2 Å⁻¹.

2 The constraints grid

In order to discriminate (if possible at all) between effects of algorithmic constraints and experimental data (especially the Q -range), the strategy was to define a 4×4 ‘constraints grid’ with 4 Q -range extensions for the data and 4 FNC’s (Cl-Cl allowed distance range). The comparison of RMC runs results would thus, in principle, bring some information about the specific effect of the different constraints.

The 4 FNC constraints, from ‘loose’ to ‘strict’ were defined *a priori* as:

1. 1.97-1.99,
2. 1.96-2.00,
3. 1.93-2.03

4. 1.88-2.08

The different Q -ranges, were not defined initially, but after guesswork from two initial runs, also aimed at selecting the appropriate run parameters such as the σ (standard deviation) that controls the quality of the fit to the data, and the move amplitudes that dictate the acceptance ratios.

The configurations used contained 2000 atoms which is *very small* for such a simple system. This feature has to be kept in mind when analysing the $g(r)$: the high Q -range requiring a short Δr , the number of distances in the bins at short r is small, and therefore statistical fluctuations have to be acknowledged.

Starting ‘disordered’ configurations were obtained by running ‘hard sphere’ runs (*without data* from initially regularly ordered systems. The 2 initial runs (3 hours - for test purposes) were conducted with the following parameters

- cell size (1/2 edge of the cubic box) 20.77042 Å.
- number density 0.0279
- r spacing 0.083 Å.
- cut-off 1.9 Å.
- move amplitudes: 0.1 Å.
- FNC [1.97 - 1.99] and [1.96 - 2.00]

These values yielded rather high acceptance ratios (from 0.6 rising to 0.8) and poor fit quality (see Fig. 1). The σ value was subsequently adjusted to 0.001. From these results, the grid of constraints was defined for the 16 runs (see Tab. 1).

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|-------------------------|--------------|--------------|--------------|--------------|
| FNC \Rightarrow Cl-Cl | [1.97, 1.99] | [1.96, 2.00] | [1.93, 2.03] | [1.88, 2.08] |
| Q -range \downarrow | | | | |
| [0.5, 15.2] | run1a | run2a | run3 | run4 |
| [0.5, 10.0] | run5a | run6a | run7 | run8 |
| [0.5, 6.0] | run9 | run10 | run11 | run12 |
| [0.5, 4.0] | run13 | run14 | run15 | run16 |

Table 1: Input grid for the RMC runs. Horizontally: looser fixed neighbour constraint from left to right (lengths in Å). Vertically: shorter Q range from top to bottom (Q -values in Å⁻¹)

The four FNC intervals are centered around 1.98 Å, and with a width of 0.02, 0.04, 0.1 and 0.2 Å. The Q -ranges were obtained by chopping the high-end of the data (initially up to 15.2 Å⁻¹) at 10.0 Å⁻¹ (61 points), 6 Å⁻¹ (46 points) and 4 Å⁻¹ (36 points).

3 The 16 runs

The run parameters and durations appear in Tab. 2.

Apart from the trial runs (1 and 2), runs 5 and 6 were not satisfying because the starting configuration did not satisfy the FNC's (due to some error in manipulating the files). This led to spurious unacceptable peaks in the $g(r)$ below the lower FNC limit. These two runs had to be performed again (yielding runs 5a and 6a).

Run durations were of the order² of 24 hours. This was very probably more than enough for the size of the systems. Systematic intermediate checks of the χ^2 value showed that the χ^2 did not evolve significantly at least in the last 7 hours of the runs.

4 Results

4.1 In Q space

The fits to the experimental data used in each run are very good, which is not surprising since the rather small σ value (0.001).

The resulting configurations were used to compute calculated structure factors on the longest available range (up to 15.2 Å⁻¹). As for CCl₄, the total structure factor (TSF) can be recovered beyond the cut-off in the data. Although at the detailed level, the cut-off can be seen as a sudden departure of the calculated TSF from the experimental data curve

(see Fig 2).

4.2 In r -space

It must be stressed that in RMC, the partial pair correlation functions (PCF's) are calculated from the configurations. Therefore, any uncertainties or limitations on the $g(r)$ thus obtained are due to the size of the configuration box, and *not* to the truncation in Q space, as would be the case with direct inversion.

On a rough level, all derived PCF's agree with each other, there is no significant change for the different sets of data and constraints used in the simulation (see Fig. 3).

The small configuration size forbids the examination of the $g(r)$'s on a too detailed level. For instance, the number of distances involved in the first intermolecular peak (at 3.7 Å⁻¹) is about 650. However, one can confirm that the FNC's define the intramolecular peak (see Fig. 4).

These results confirm that the information brought by the high end of the $S(Q)$ data and the FNC are partly redundant. This can be explained: the $S(Q)$ features at high Q are defined by the geometry of the molecules, and this geometry (when known) is implemented in RMC via the FNC's. Note however that if there are *intermolecular* features on the same distance range as the *intramolecular* distances, then the additional information brought by the high Q range is essential.

References

- [1] Bellissent M.C.

²Several runs were done in parallel on a 2 processor 440 Mhz PC

| Run | Q_{\max} (data points) | σ | Cl-Cl FNC | Cl-Cl cutoff | duration (hours) |
|-----|-----------------------------|----------|-------------|--------------|------------------|
| 1 | 15.2 \AA^{-1} (74) | 0.008 | 1.97 - 1.99 | 1.9 | 3 |
| 2 | 15.2 \AA^{-1} (74) | 0.008 | 1.96 - 2.00 | 1.9 | 3 |
| 1a | 15.2 \AA^{-1} (74) | 0.001 | 1.93 - 2.03 | 1.9 | 24 |
| 2a | 15.2 \AA^{-1} (74) | 0.001 | 1.88 - 2.08 | 1.9 | 24 |
| 3 | 15.2 \AA^{-1} (74) | 0.001 | 1.97 - 1.99 | 1.9 | 24 |
| 4 | 15.2 \AA^{-1} (74) | 0.001 | 1.88 - 2.08 | 1.88 | 24 |
| 5 | 10 \AA^{-1} (61) | 0.001 | 1.97 - 1.99 | 1.9 | 24 |
| 5a | 10 \AA^{-1} (61) | 0.001 | 1.97 - 1.99 | 1.9 | 24 |
| 6 | 10 \AA^{-1} (61) | 0.001 | 1.96 - 2.00 | 1.9 | 24 |
| 6a | 10 \AA^{-1} (61) | 0.001 | 1.96 - 2.00 | 1.9 | 24 |
| 7 | 10 \AA^{-1} (61) | 0.001 | 1.93 - 2.03 | 1.9 | 28 |
| 8 | 10 \AA^{-1} (61) | 0.001 | 1.88 - 2.08 | 1.88 | 28 |
| 9 | 6 \AA^{-1} (46) | 0.001 | 1.97 - 1.99 | 1.9 | 38 |
| 10 | 6 \AA^{-1} (46) | 0.001 | 1.96 - 2.00 | 1.9 | 38 |
| 11 | 6 \AA^{-1} (46) | 0.001 | 1.93 - 2.03 | 1.9 | 38 |
| 12 | 6 \AA^{-1} (46) | 0.001 | 1.88 - 2.08 | 1.88 | 24 |
| 13 | 4 \AA^{-1} (36) | 0.001 | 1.97 - 1.99 | 1.9 | 24 |
| 14 | 4 \AA^{-1} (36) | 0.001 | 1.96 - 2.00 | 1.9 | 24 |
| 15 | 4 \AA^{-1} (36) | 0.001 | 1.93 - 2.03 | 1.9 | 24 |
| 16 | 4 \AA^{-1} (36) | 0.001 | 1.88 - 2.08 | 1.88 | 24 |

Table 2: Data range, FNC's and duration for the 18 runs.

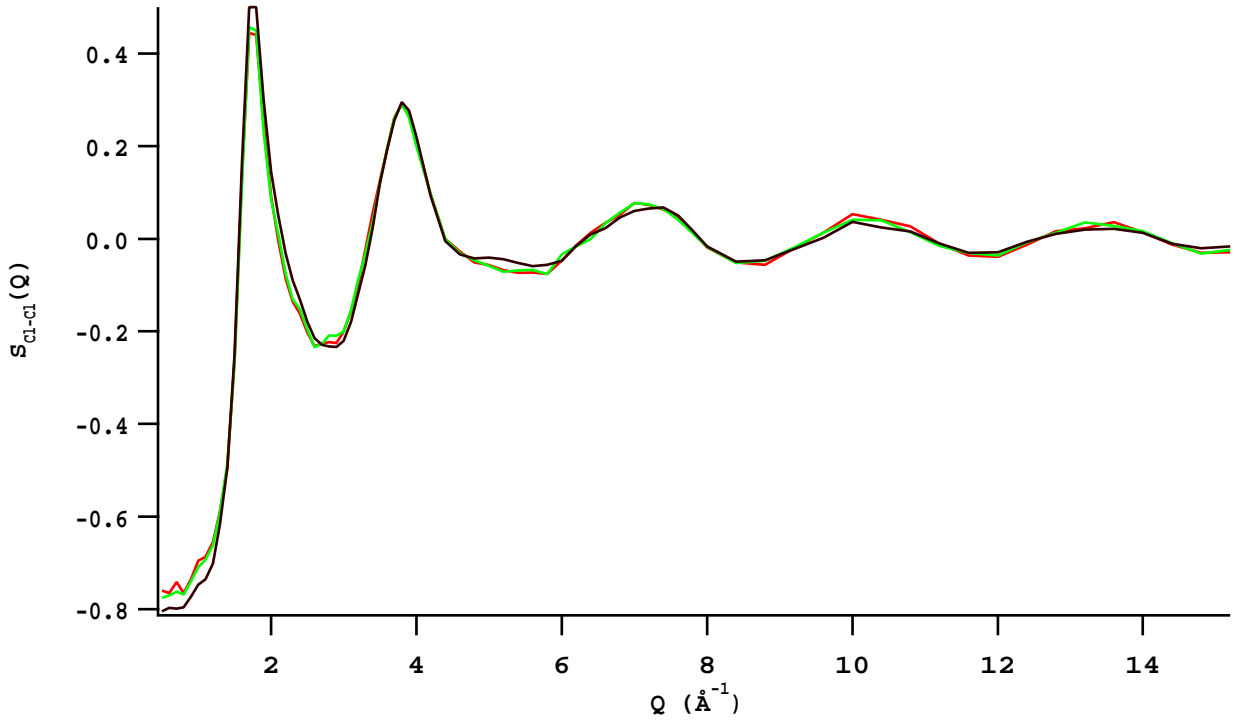


Figure 1: Experimental and RMC total structure factors for trial runs 1 and 2. Notice the low quality of the fit due to the 'large' σ value (0.008).

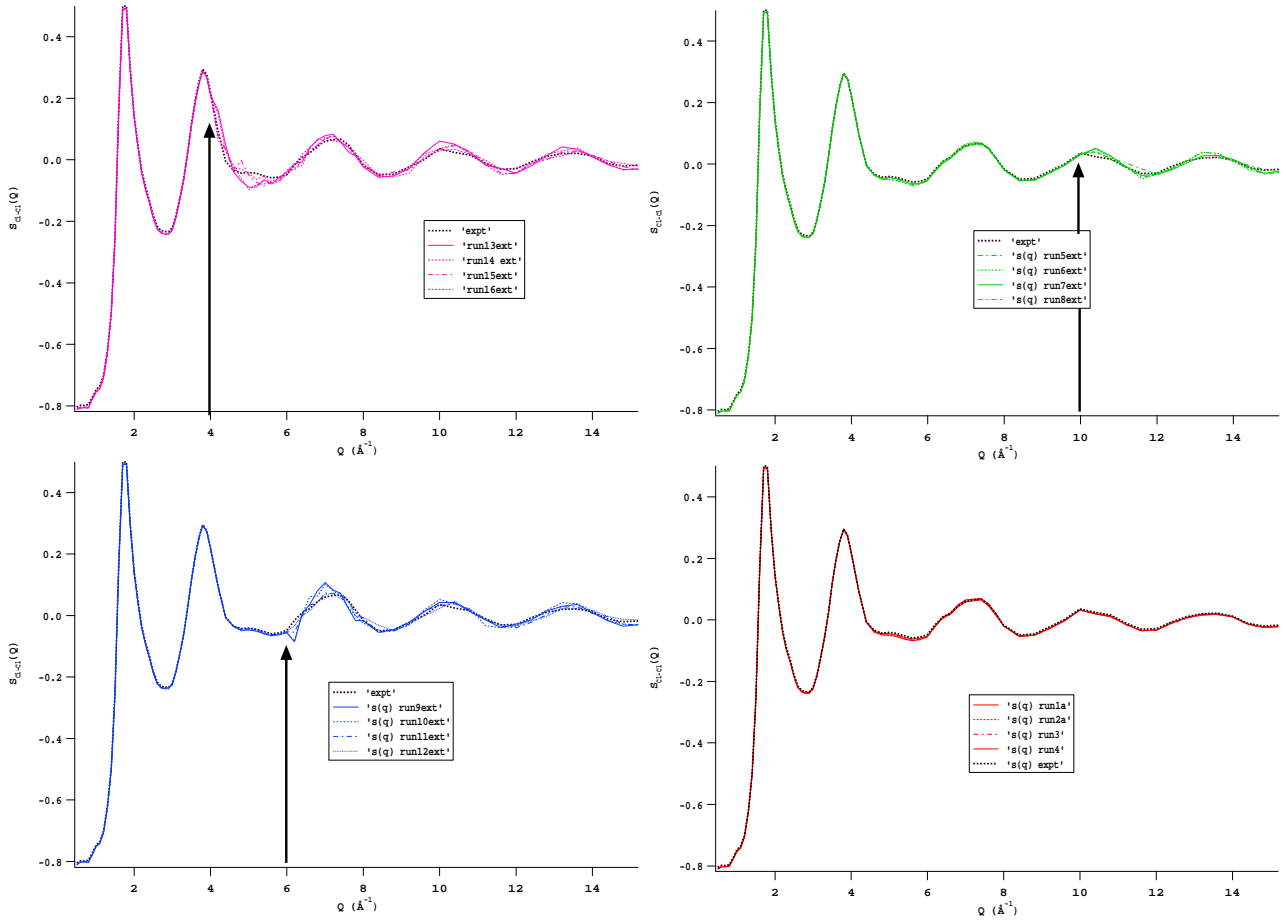


Figure 2: Experimental and modelled total structure factors grouped by Q -range used in the RMC runs. The arrows point at the cut-offs in Q -range.

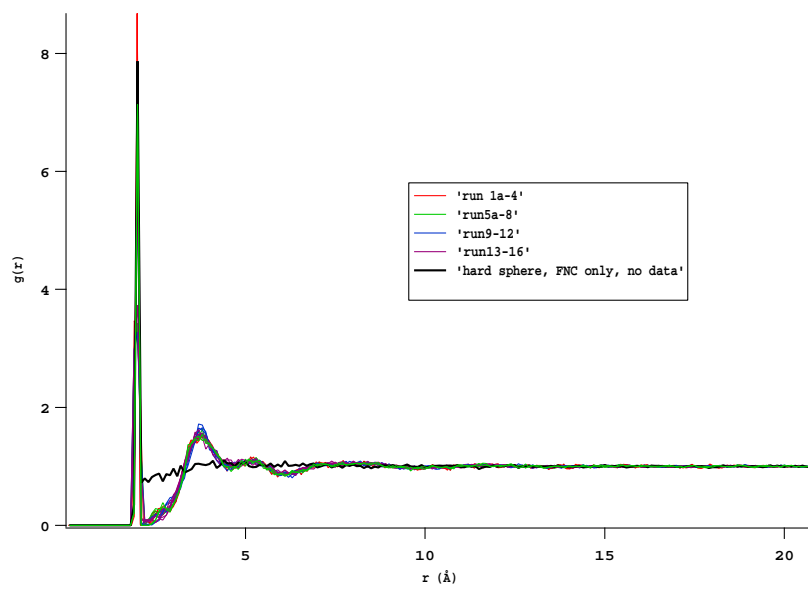


Figure 3: Partial pair correlation functions for all runs, and for the 'hard-sphere' starting configuration.

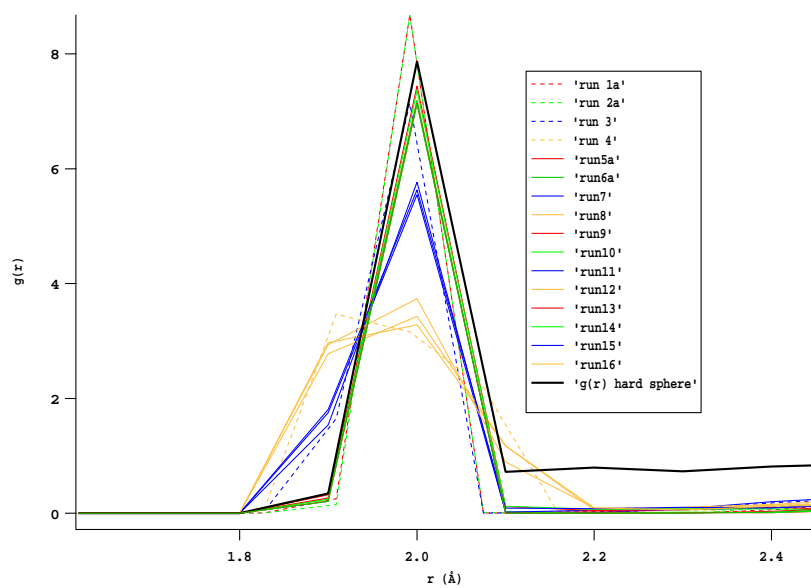


Figure 4: Intramolecular peak of the PCF. Note the grouping ‘by FNC’.

Run files:

- **on PC:** in folders run1a, run2a, run1, run2, run3, run4, run5, run6, run7, run8, run9, run10, run11, run12, run13, run14,run15, run16
access path: C:\Guillaume\c12.
- **on iBook:** in folders run1a, run2a, run1, run2, run3, run4, run5, run6, run7, run8, run9, run10, run11, run12, run13, run14,run15, run16
access path: DataHD:Budapest:RMC Workshop:C12:run files (see also extensions for the extended Q -range outputs).