RMC Run Report	Material: CCl_4 Cfg. Size: 10240 atoms
Data: 1 neutron	RMC Options: FNC
Run Date: March 2002	Code rmc_fi

Study of data vs. constraints effects with liquid CCl4

Guillaume Evrard[1],
Research Institute for Solid State Physics and Optics,
Hungarian Academy of Sciences, Budapest P.O. Box 49, H-1525, Hungary

1 Introduction

Due to the structure of the Metropolis algorithm, the RMC method produces configurations with *maximum disorder* within the constraints applied (including the χ^2, *i.e.* the data). Constraints such as distances of closest approach (cut-offs) and fixed neighbours constraints (FNC's) are essential to impose some realistic order to the configuration. However, it can be expected that this additional *a priori* information is redundant with the data.

The main purpose of this series of runs was to assess the importance of this redundancy. In short, we wanted to find, if possible, what kind of information is specifically brought by the data, and in which region of the Q-range it might be situated.

The material chosen for this test was liquid CCl4. This molecule has the advantage that it can be (geometrically) well defined by a set of FNC's, in other words, the *a priori* information made up by the FNC is particularly important.

The original data was a set of neutron diffraction data from the Budapest diffractometer[1]. The initial Q range was 0.55 to 9.15 Å^{-}1 in 100 points irregularly sampled.

In order to discriminate (if possible at all) between effects of algorithmic constraints (such as cut-offs and FNC's) and experimental data (especially the Q-range), I defined a 3×3 'constraints grid' with 3 Q-range extensions (9.15, 6.9 and 4.975 Å^{-1}) and 3 FNC's (C-Cl allowed distances in the ranges [1.71,1.85], [1.69, 2.00], and [1.69, 2.19]). The comparison of RMC runs results would, in principle, bring some information about the specific effect of the different constraints.

[1]E-mail:evrard@power.szfki.kfki.hu

2 The 9 runs

Common run parameters for all the runs were:

- 10240 atoms (*i.e.* 2048 molecules),
- density: 0.0319 atoms per cubic Angstrom,
- cubic cell size: 1/2 edge= 34.23522 Å,
- r-spacing 0.1 Å,
- move range for all atoms: 0.1 Å.
- cut-offs 3.3, 1.69 and 2.7 Åfor C-C, C-Cl and Cl-Cl respectively
- the σ (data standard deviation) was set to 0.001.

We must note that a previous attempt with a larger value of σ (0.005) failed to produce good fits to the data. Therefore I had to reduce this value to 0.001 in order to have RMC calculated data 'stick' to the experimental data.
The other run parameters appear in Tab. 1

The starting configurations for each run were configurations obtained from previous runs (with σ=0.005), which had failed to fit the data, but were definitely 'close' to the good configurations.

Unfortunately, information concerning the ratios of acceptance for the moves was not kept. But most presumably, the usual 'rule of thumb' to attempt to have 0.5 for both (tried/generated) and (accepted/tried) ratios was applied.

Since the code used was **rmc_fi**, there is no trace kept of the evolution of the run, and one cannot be sure that the convergence had been reached at the end of the runs. The runs duration seem quite short from that point of view. It is certain, however, that

Run	Q_{max} (data points)	C-Cl FNC	Cl-Cl FNC	duration (hours)
11	9.15 (100)	1.71 - 1.85	2.7 - 3.1	18*
12	9.15 (100)	1.69 - 2.00	2.7 - 3.3	24*
13	9.15 (100)	1.69 - 2.19	2.7 - 3.5	24*
14	6.9 (85)	1.71 - 1.85	2.7 - 3.1	23*
15	6.9 (85)	1.69 - 2.00	2.7 - 3.3	23*
16	6.9 (85)	1.69 - 2.19	2.7 - 3.5	23*
17	4.975 (70)	1.71 - 1.85	2.7 - 3.1	23*
18	4.975 (70)	1.69 - 2.00	2.7 - 3.3	22*
19	4.975 (70)	1.69 - 2.19	2.7 - 3.5	22*

Table 1: Data range, FNC's and duration for the 9 runs.

the decrease of the χ^2 was not 'visible' from the raw display update of **rmc_fi** when the run were stopped.

3 Results

The reduction of σ from 0.005 to 0.001 has an immediate result: the fits to the experimental data show good agreement, although, by usual RMC standards, they are not excellent, which suggests (together with the rather short runs durations) that convergence was not fully achieved.
The resulting configurations have been used to extend the Q range for calculated data to the maximum range (see Fig.1) in order to check if the high Q range information could be recovered by the constraints. This is partly true, although the Q cutoff can be seen on the detailed level. The differences between the results of the various runs are only marginal.

What is more, it is likely that the effects of FNC's dominate over the effects of data. This feature can be guessed from the grouping of the C-Cl partials in the Q range 4 to 9 $Å^{-1}$ (see Fig.2). Indeed it appears that the C-Cl partial structure factors are more similar for the same FNC's, rather than for the same data. This could also mean that the data do not bring significant information for this partial, in the suppressed Q-range.
Complementary tests are needed to investigate further this aspect. Detailed analysis should appear elsewhere.

References

[1] Jóvári P. *et al. J. Chem. Phys.* **114**, 18 (2001).

Run files:

- **on PC**: in folders `run10`, `run11`, `run12`, `run13`, `run14`, `run15`, `run16`, `run17`, `run18`, `run19`
  access path: `C:\Guillaume\ccl4`.
- **on iBook**: in folders `run10`, `run11`, `run12`, `run13`, `run14`, `run15`, `run16`, `run17`, `run18`, `run19`
  access path: `DataHD:Budapest:RMC Workshop:ccl4 RMCA data vs const:run folders`.

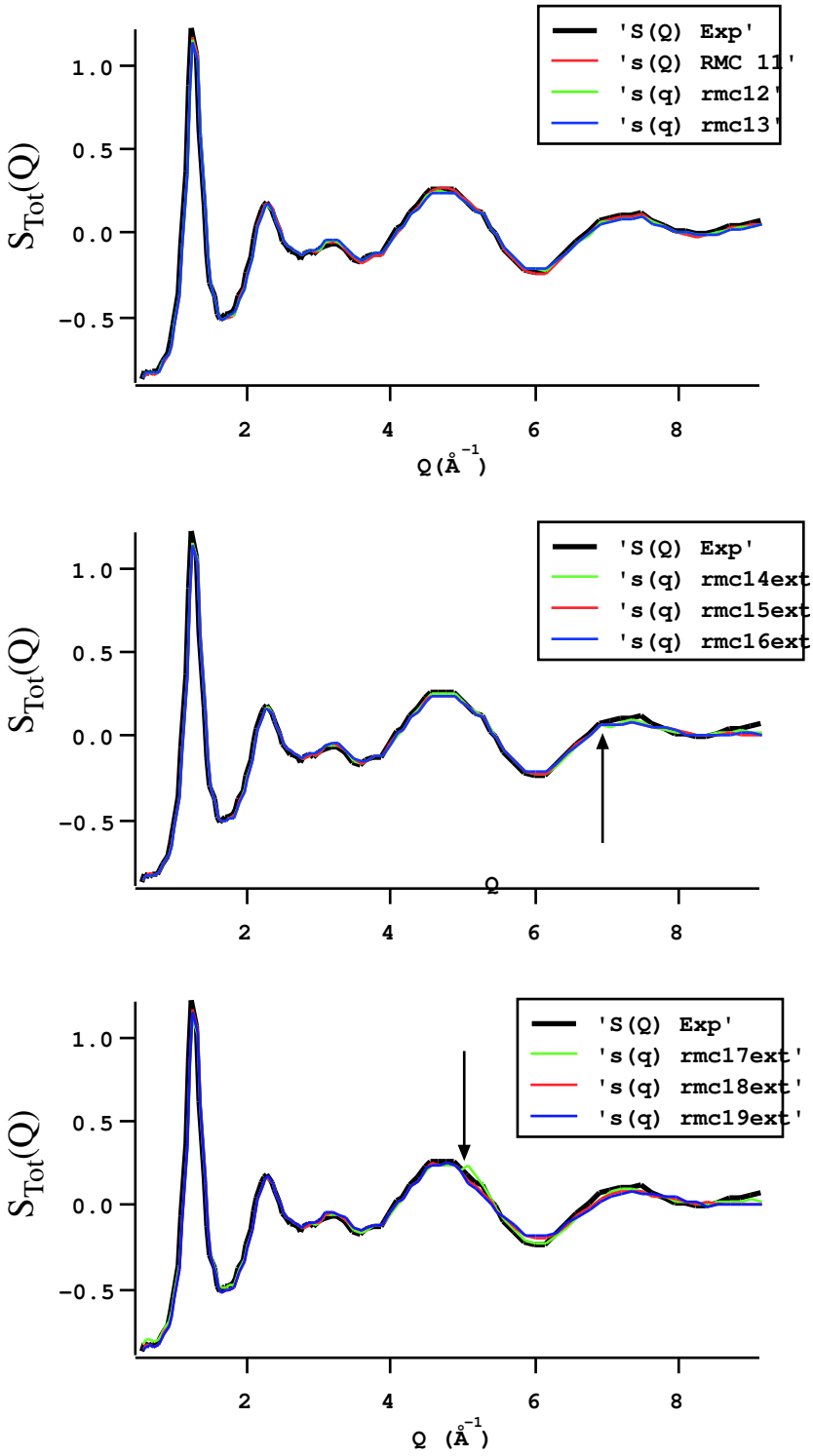

Figure 1: Experimental and RMC total structure factors for runs 11, 12, 13 (top), 14,15,16 (middle), 17, 18, 19 (bottom). The arrow points to the Q-range cutoff used for runs 14-19.

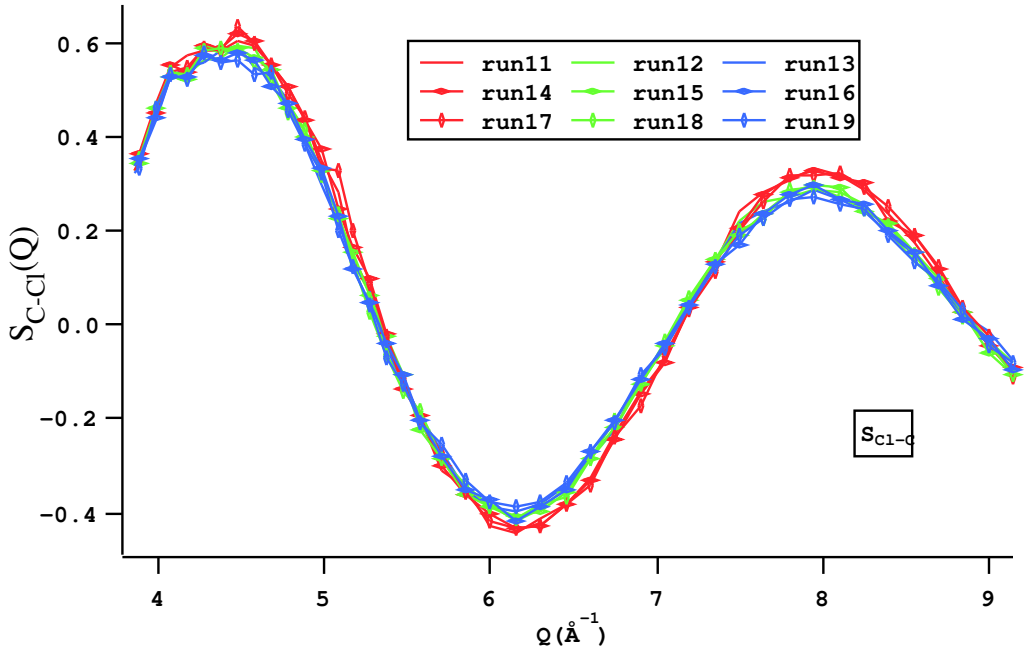

Figure 2: Experimental and RMC total structure factors for runs 11, 12, 13 (top), 14,15,16 (middle), 17, 18, 19 (bottom). The arrow points to the Q-range cutoff used for runs 14-19.