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

Study of data vs. constraints effects with liquid CCl4. Part II

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1 Introduction

This series of run is a sequel to a former study[1] of data *vs.* constraints effects with CCl4. This first study lead to the conclusion that constraints, especially fixed neighbours constraints (FNC) which define the molecular geometry, and the high-end of the Q range of the diffraction data are at least partly redundant. In order to assess more precisely the nature of this redundancy, a second series of runs was designed as follows.
A set of artificial data was built from a previous RMC-obtained configuration (run11 of previous study). The Q range for the artificial data was extended to the -not necessarily realistic- value of 40 $Å^{-1}$. Six runs were subsequently made using identical FNC's (the 'loosest' of our first series) but with input 'virtual' data sets chopped-off at different Q ranges.

2 The runs

The common 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,
- 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
- fixed neighbour constraints: [1.69, 2.19] for C-Cl, and [2.7, 3.5] for Cl-Cl.
- the σ (data standard deviation) was set to 0.001.

The varying run parameters appear in Tab. 1. Note that due to the extended Q range, the width of the histogram bin had to be adjusted for each run. Indeed, for the sake of statistical accuracy, the wider Δr the better, however, in order to compute calculated data up to the range $Q_{\max}$, Δr must satisfy

$$\Delta r \leq \frac{2\pi}{5Q_{\max}}. \quad (1)$$

The values Δr chosen for each run were therefore the largest acceptable values.

2.1 Evolution of the χ^2

Initial test with the configuration issued from the previous run11, *i.e.* the very configuration that was used to produce the artificial data set yielded extremely low acceptance ratios (about 1% in general and never more than 4%). The χ^2 value was understandably very low (about 1.7 per data point), and therefore the explanation for this behaviour can be that the algorithm is stuck in the 'very best' possible solution, and is therefore very reluctant to move away from it.

The starting configuration was then changed to the resulting configuration of the previous run19 (with loose constraints and shortest data range, i.e. maximally disordered). The starting behaviour of the algorithm was familiar: high χ^2 (450), decreasing sharply, with acceptance ratios about 1/2. After 5 hours, the χ^2 had dropped to 50, but the acceptance ratios to about 0.05. After 20 hours, the χ^2 wa about 30 and the acceptance ratio about 0.01.

One can attempt the following explanation: the starting configuration allowed a quick convergence to a solution. The constraints (*i.e.* the data only,

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Run	Q-range (data points)	Δr step (Å)	duration (hours)
21	[0.55, 40] (409)	0.032	20
22	[0.55, 30] (309)	0.042	20
23	[0.55, 25] (259)	0.05	15
24	[0.55, 20] (209)	0.063	15
25	[0.55, 15] (159)	0.084	15
26	[0.55, 10] (109)	0.1	15

Table 1: Data range, histogram bin width and duration for the 6 runs.

Run (no data)	C-Cl FNC	Cl-Cl FNC
run0hs	[1.71, 1.85]	[2.7, 3.1]
run1hs	[1.69, 2.19]	[2.7, 3.5]

Table 2: hard-sphere run parameters

since the FNC's are loose) are too strong to allow many moves away from it. It is possible that the σ value of 0.001 is indeed very strict for such a large Q range. The move amplitude (0.1 Å) can be also reduced to increase the ratios. the question remains if that kind of behaviour is particular to this system or typical for all RMC runs. Possible sequels to this study might include the release of the 'fit to the data' constraint (*i.e.* increase the σ), and/or decrease of the move amplitudes, and see how the χ^2 and the acceptance ratios evolve.

2.2 'hard-sphere' runs

Two additional runs without data were performed with 'strict' and 'loose' FNC's (see tab.2) in order to assess the contribution of the FNC only, or alternatively the contribution of the lower part of the Q-range.

3 Results

Figure 1 shows the total structure factors, and Fig. 2 the partial pair correlation functions.

The results of the runs indicate that there is not much information gained by extending the Q range beyond 15 Åat most for this system. Differences between Q-ranges in input appear only in the sharpness of the *intra*molecular peak. The *inter*molecular features are hardly affected at all.

Results of the 'hard-sphere' runs appear in Fig.3. very remarkably, The C-C and C-Cl partials do not seem affected by the absence of the data. In other words, FNC's and distances of closest approach are enough to define the C-C and C-Cl partials. The data show themselves in the PCF's only by creating a slight intermolecular 'bump' at about 3.8 ÅCl-Cl partial, or rather by separating the first *inter*molecular peak from the *intra*molecular peak).

It must be kept in mind however that the PCF's do not represent *all* the information that is available from the RMC configuration. It is possible that investigating additional features (like distribution of angles) might reveal other differences yielded by the different inputs.

References

[1] RMC Report.

Run files:

- **on PC**: in folders `run21`, `run22`, `run23`, `run24`, `run25`, `run26`, `run0hs`, `run1hs`
  access path: `C:\Guillaume\ccl4`.
- **on iBook**: in folders `run21`, `run22`, `run23`, `run24`, `run25`, `run26`
  access path: `DataHD:Budapest:RMC Workshop:ccl4 RMCA data vs const:run folders`.

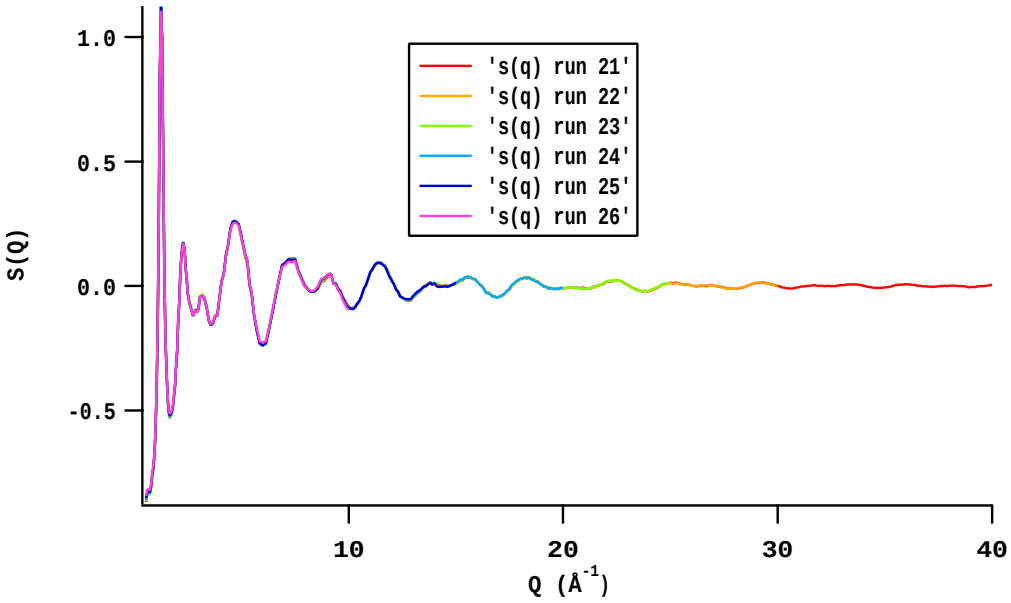

Figure 1: Calculated total structure factors for runs 21-26.

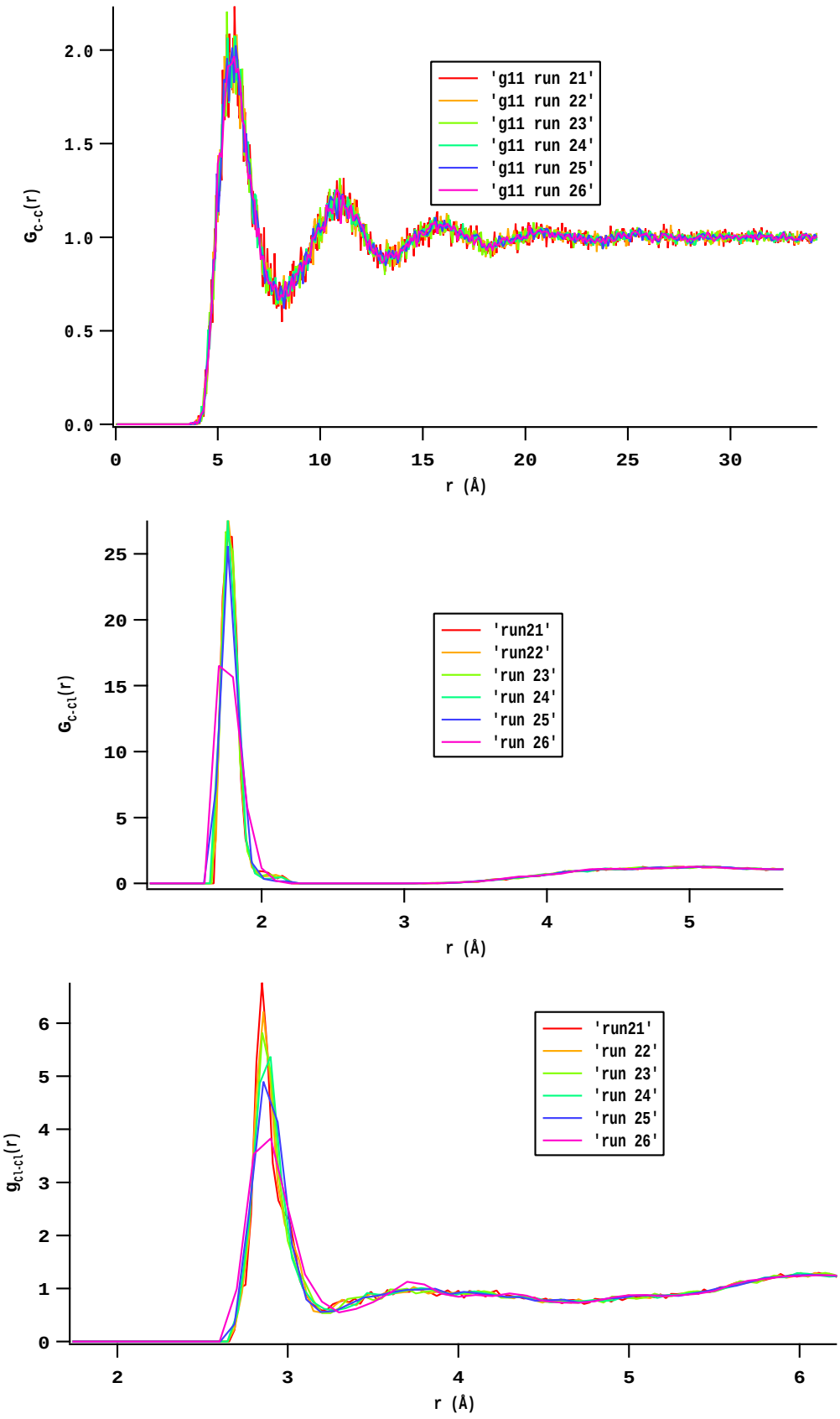

Figure 2: RMC pair correlation functions for runs 21-26.

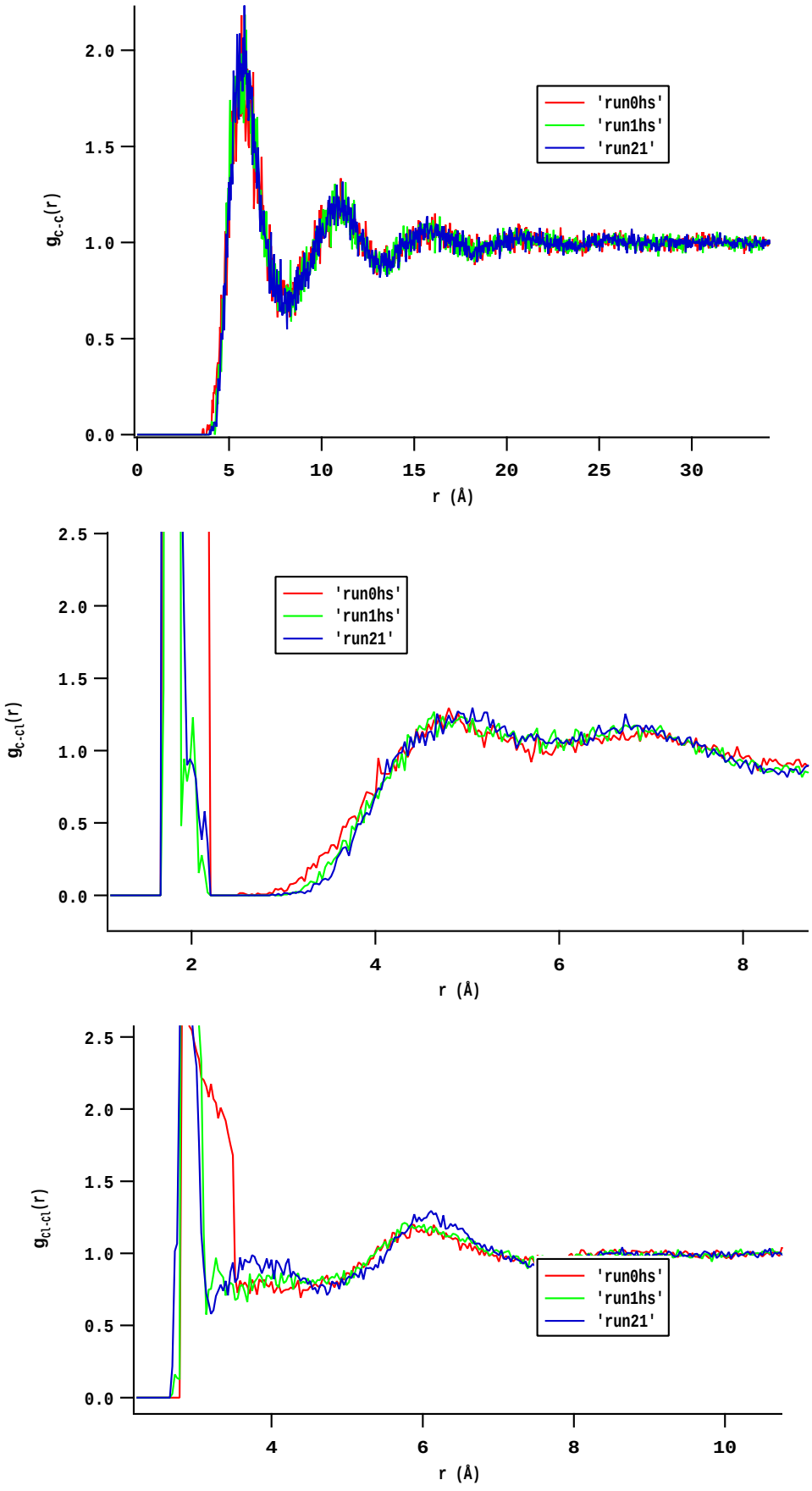

Figure 3: RMC pair correlation functions for runs 21-26.