RMC PRACTICAL

Modelling the structure of crystalline AgBr

All the files needed for this practical, including programs, are found in the file **`rmca_agbr.zip`**. Extract them all into the same directory. You should have the following:

```
confplot.exe
convol.exe
coord.exe
crystal.exe
mcgr_31.exe
rmca.exe
rmcplot.exe
show.exe
agbr_cryst.dat
agbr_cryst_fq.dat
agbr_cryst_0.dat
agbr_mcgr.dat
agbr_mcgr_0.dat
agbr_slad.fq
```

The general approach in this practical is as follows:

- Various relevant distances will be determined from *G(r)* which is obtained from the experimental *F(Q)* using the MCGR program
- A start configuration for AgBr will be created and then modified by the RMCA program while fitting to *G(r).*

The times given in this practical, for running MCGR and RMC is real time and <u>NOT</u> CPU time. The times may have to be increased on a slow computer. The outputs you get, will probably not be identical to the outputs in this example.

1. The model is based on the neutron scattering data measured at the SLAD diffractometer NFL, Studsvik. This is in the file **agbr_slad.fq**. Plot it with the program **show**.

```
File format (RAW, TEXT, DATA)? data
Full File name: agbr_slad.fq
Blocks no: 1 to 1 exists.
> d 1
```

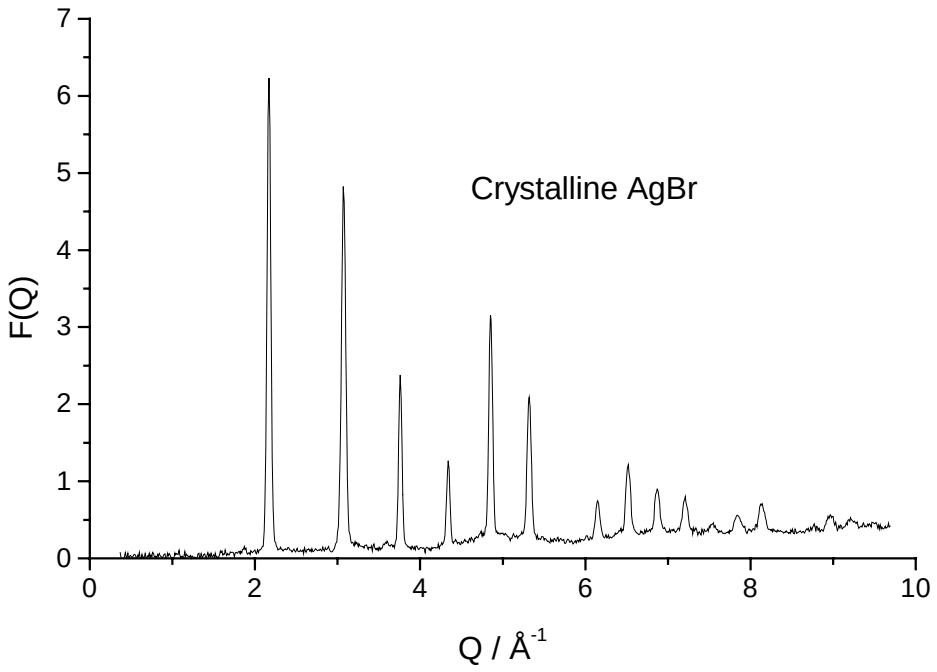
Now you should have a plot on the screen.

To plot with other limits

```
> d 1 Xlow Xhigh Ylow Yhigh
```

To exit

```
> e
```



2. *G(r)* is produced using the MCGR program. The control data are in **agbr_mcgr_0.dat**. Use an editor (like Wordpad) to look at the control data.

```
AgBr 300K
.false.         ! rerun
.true.          ! plot
1000
0.0414          ! density
.false.         ! generate partials
1               ! no of partials
1               ! no of zero constraints
1 0 2.2         ! cut-offs
0.1             ! delta
7 100.          ! mr rmax
.false.         ! save
.false.         ! converge only
1               ! no of positivity constraints
1 0 100.1       ! Positivity constraint
0               ! no of coordination constraints
.true.          ! smoothing
3
1
0.2 100.1
.false.         ! resolution
200             ! printing
40,5            ! time limits
1 0             ! no of data sets
agbr_slad.fq
1 1000          ! points to fit
0.0             ! const to subtract
0.404           ! coeff.
0.01            ! sigma
.false.         ! renormalise
.true.          ! background
1               ! Nparm
.false.         ! magnetic
agbr_mcgr
```

Because we have a crystalline sample with sharp Bragg-peaks that have to be resolved *G(r)* will be calculated out to large *r*-values (100 Å). Run the program **mcgr_31** and give **agbr_mcgr_0.dat** as input file. This will take 40 minutes, saving the intermediate results every 5 minutes. On the screen you can see how χ^2 decreases as the fitted *F(Q)* approaches the experimental *F(Q)*. You will also see two windows, one containing the fit to *F(Q)* and the other window containing the corresponding *G(r)*.The *r* spacing in *G(r)* will be 0.0926 Å because the maximum *Q* value in the original data is 9.69 $Å^{-1}$ (see MCGR manual) which gives an *r* space resolution of $2\pi/45 \sim 0.65$ Å, giving 7 *r* points across the resolution width (5-7 points are recommended). Expected $\chi^2 \sim 4$.

3. While this is running you can start making the initial configuration for the RMC model. We will make a configuration of 5*5*5 unit cells. The cell parameter is 5.78136 Å. We use the program **crystal**:

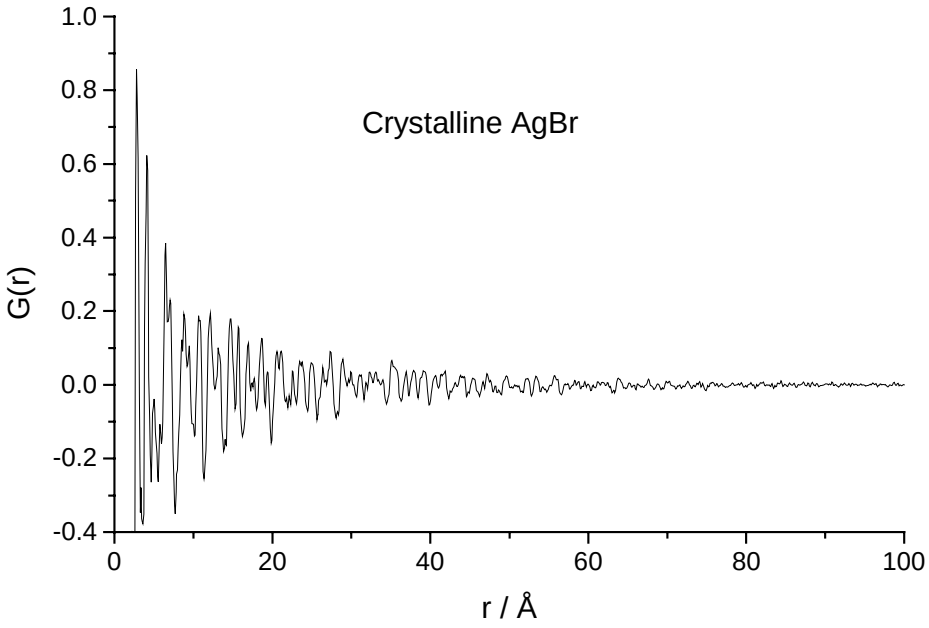
```
 manual (0) or "automatic" (1) ?
0
 Number cells in each direction> 5 5 5
 Unit cell vector a             > 5.78136 0 0
 Unit cell vector b             > 0 5.78136 0
 Unit cell vector c             > 0 0 5.78136
 Number of particle types       > 2
 Number of type  1 in cell      > 4
 Coordinates                    > 0.0 0.0 0.0
 Coordinates                    > 0.0 0.5 0.5
 Coordinates                    > 0.5 0.0 0.5
 Coordinates                    > 0.5 0.5 0.0
 Number of type  2 in cell      > 4
 Coordinates                    > 0.0 0.0 0.5
 Coordinates                    > 0.0 0.5 0.0
 Coordinates                    > 0.5 0.0 0.0
 Coordinates                    > 0.5 0.5 0.5
 Number of Euler angles         > 0
 Output file (no extension, will be .cfg)
agbr_cryst_0
```

4. Look at the file **agbr_cryst_0.cfg**. It contains 1000 atoms 500 Ag and 500 Br, in a cubic box with half box length 14.453 Å. The coordinates of the atoms are given in normalised units (-1 to +1).

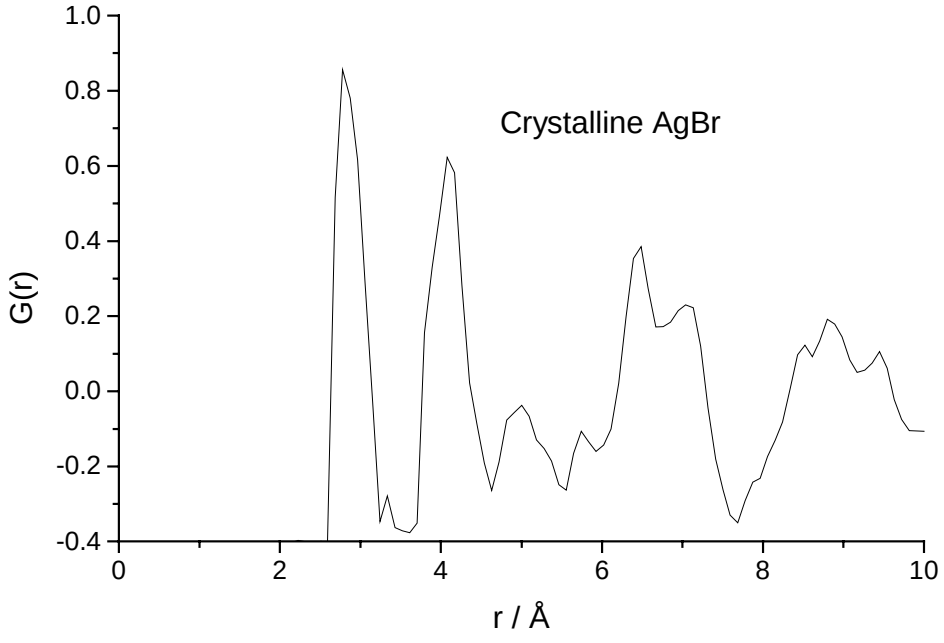
```
 (Version 3 format configuration file)
  Crystal configuration

          0         0         0 moves generated, tried, accepted
          0                     configurations saved

       1000 molecules (of all types)
          2 types of molecule
          1 is the largest number of atoms in a molecule
          0 Euler angles are provided

          F (Box is not truncated octahedral)
            Defining vectors are:
             14.453401    .000000    .000000
               .000000  14.453401    .000000
               .000000    .000000  14.453401

         500 molecules of type  1
           1 atomic sites
                .000000    .000000    .000000

         500 molecules of type  2
           1 atomic sites
                .000000    .000000    .000000

 -1.0000000 -1.0000000 -1.0000000
```

```
 -1.0000000 -1.0000000  -.6000000
 -1.0000000 -1.0000000  -.2000000
 -1.0000000 -1.0000000   .2000000
 -1.0000000 -1.0000000   .6000000
```
etc.

5. Plot the resulting *G(r)* from the MCGR run, **`agbr_mcgr.g`**, with the program **`show`**.



Change the plotting limits to look between 0. and 10. Å. We can see the first peak around 2.9 Å This is the closest Ag-Br distance, the second peak at 4.1 Å comes from the Ag-Ag and Br-Br distances.



6. Check the coordination of Br around Ag from the first peak by integrating from 2.4 to 3.4 Å with the program **coord**:

```
File containing g(r): agbr_mcgr.g
Density: 0.0414
Add constant [0.]: 0.404
Concentration [1.]: 0.5
Coefficient [1.]: 0.2012
Write a file with cumulative coordination (y/n)? n
Select min/max r-value G=Graphically or N=Numerically: n
Minimum r-value [0.]: 2.4
Maximum r-value [Max-r]: 3.4
Coordination=    5.59
```

The result from the example shown is 5.59. This is slightly low (it should be 6) You may have to run for a longer time. Expected $\chi^2 \sim 4$.

7. One way to improve this is to use a coordination constraint on the Ag-Br peak when we run MCGR. Use the control file **agbr_mcgr.dat** and run MCGR again, this time starting from the *G(r)* obtained previously.
agbr_mcgr.dat is shown below:

```
AgBr 300K
.true.          ! rerun
.true.          ! plot
1000
0.0414          ! density
.false.         ! generate partials
1               ! no of partials
1               ! no of zero constraints
1 0 2.2         ! cut-offs
0.1             ! delta
7 100.          ! mr rmax
.false.         ! save
.false.         ! converge only
1               ! no of positivity constraints
1 0 100.1       ! Positivity constraint
1               ! no of coordination constraints
1 2.4 3.4 0.5 0.2012 6. 0.01
.true.          ! smoothing
3
1
0.2 100.1
.false.         ! resolution
200             ! printing
40,5            ! time limits
1 0             ! no of data sets
agbr_slad.fq
1 1000          ! points to fit
0.0             ! const to subtract
0.404           ! coeff.
0.01            ! sigma
.false.         ! renormalise
.true.          ! background
```

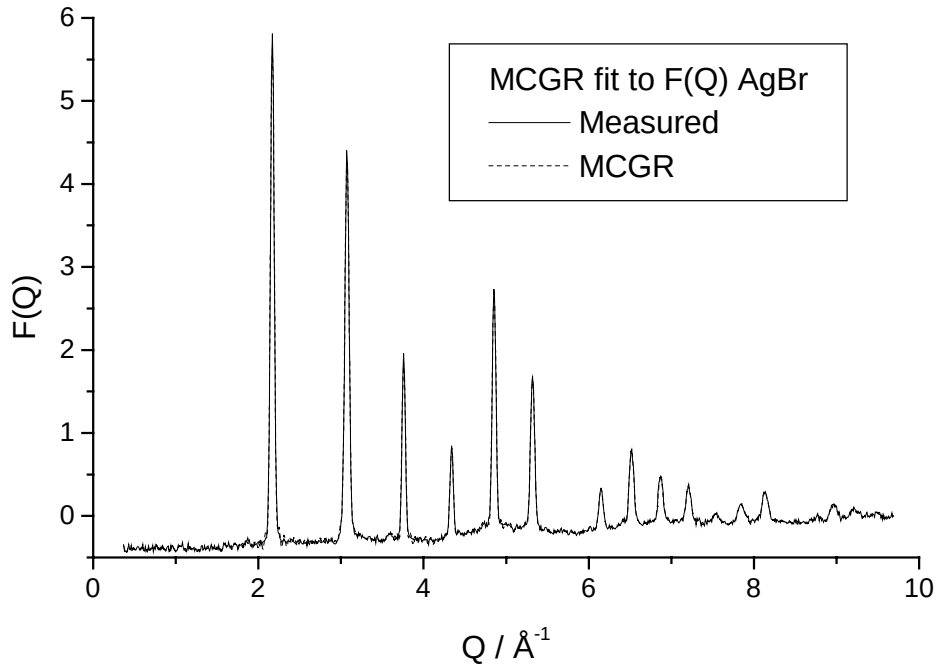
```
1                ! Nparm
.false.          ! magnetic
agbr_mcgr
```

This gives a coordination of 5.93, which is better.

8. Look at the latest MCGR output. You can use the **`rmcplot`** program for this.

```
Graphics device/type (? to see list, default /NULL): /ws
File to plot (or RETURN to exit) > agbr_mcgr.out
Input file contains   2 groups of plots:
  Group   1 contains   1 plots of  3 curves
  Group   2 contains   1 plots of  1 curves
Plot which group (enter 0 to exit) ? 1
```

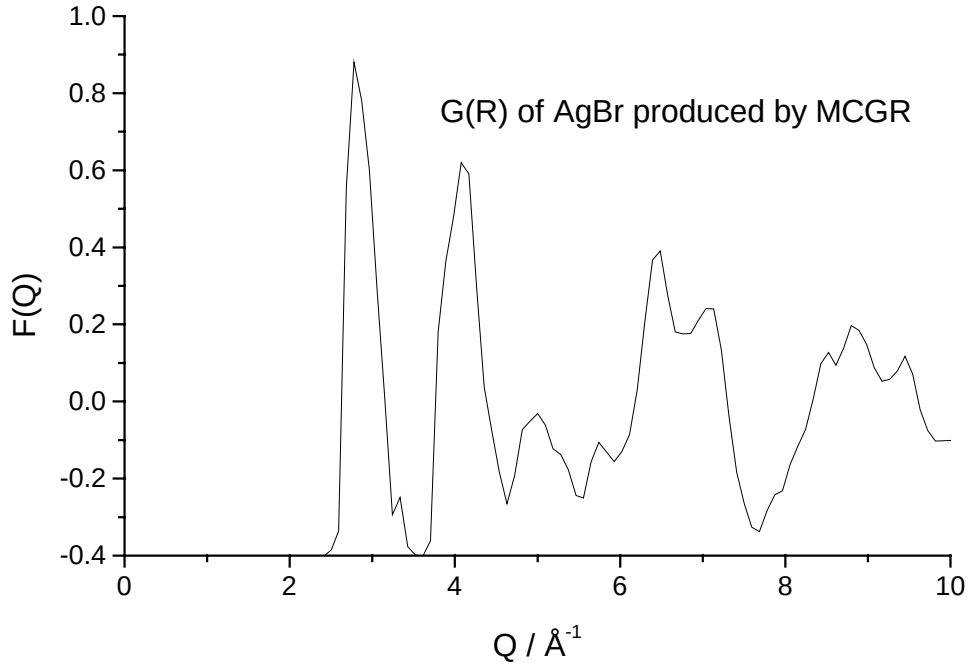
This will plot your original *F(Q)* together with the fitted *F(Q)* and a fitted background. The fit should be quite reasonable. If only a poor fit has been achieved at this stage then either there is something wrong with the parameters used in MCGR or the data contain non-negligible systematic errors. This should be checked very carefully before proceeding. Running RMCA with wrong parameters or poor data is simply a waste of time. The level of fit achieved with MCGR is a measure of the best fit that might be achieved with RMCA. How good the fit is depends on the time it has been run (real time, so a fast PC makes more calculations than a slow one for the same time). You might want to continue the run to improve the fit.



Now look at *G(r)* by continuing with **`rmcplot`**.

```
Change limits ? (T/F) > f
```

```
Input file contains   2 groups of plots:
  Group   1 contains   1 plots of  3 curves
  Group   2 contains   1 plots of  1 curves
Plot which group (enter 0 to exit) ? 2
hange limits ? (T/F) > t
Data limits are             :
   9.263136E-02             100.041900      -4.040000E-01
7.368294E-01
Current plotting limits are :
   9.263136E-02             100.041900      -4.040000E-01
7.368294E-01
Enter new limits > 0.0 10.0 -.4 1.0
```



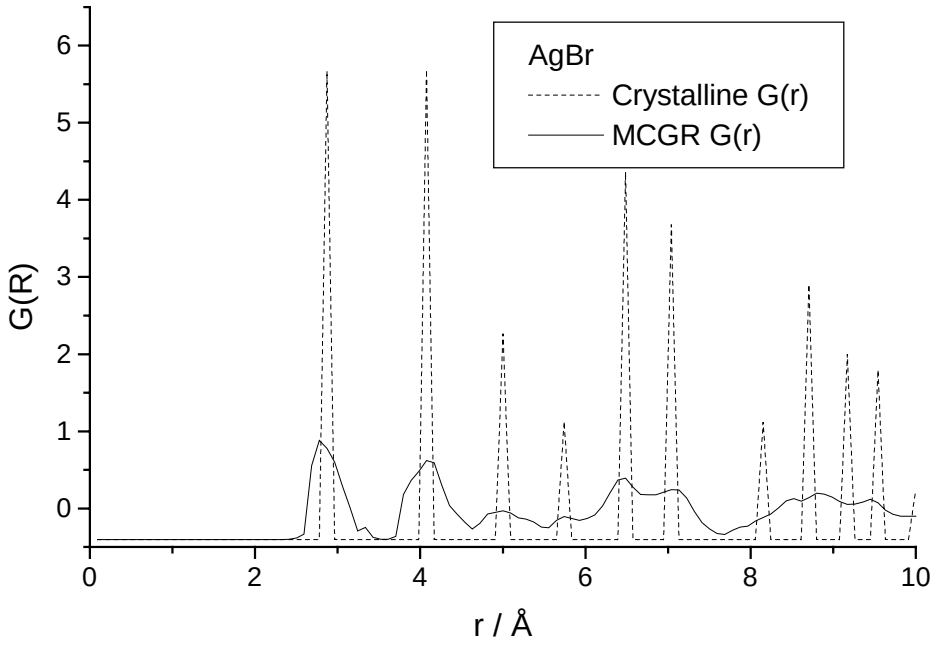
9. Now look at the data file for the RMC model. This is contained in **agbr_cryst_0.dat**.

```
AgBr crystal (Fit to neutron G(r))
0.0414          ! number density
3.3 2.2
    3.3         ! cut offs
0.1 0.1         ! maximum move
9.263136E-02    ! r spacing
.false.         ! whether to use moveout option
0               ! number of configurations to collect
5000            ! step for printing
0 0             ! Time limit, step for saving
1 0 0 0         ! No. of g(r), neutron, X-ray, EXAFS expts
agbr_mcgr.g
1 1000          ! Range of points used
0.              ! Constant
```

```
.087675 .2012
       .11543  ! Coefficients
0.01           ! Standard deviation
.false.            ! whether to renormalise
0              ! no. of coordination constraints
0              ! no. of average coordination constraints
.false.        ! whether to use a potential
```

- The choices of closest approach constraints are taken from *G(r)*. Maximum moves of 0.1 Å are set for each atom
- No coordination constraints are set in this example, but it could be a good idea for well separated peaks in *G(r),* like the first Ag-Br peak.

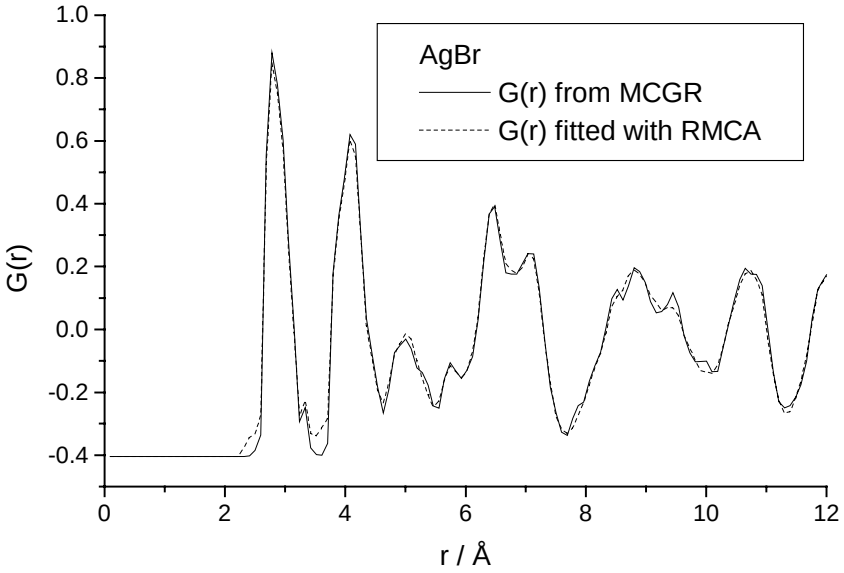
Copy the crystalline configuration **agbr_cryst_0.cfg** to **agbr_cryst.cfg**. Now run RMCA for zero time by giving file **agbr_cryst_0** as input. This will write the (not yet fitted) *G(r)* from the crystal configuration to file **agbr_cryst_0.out**. Look at it with **rmcplot** and you get a plot like:



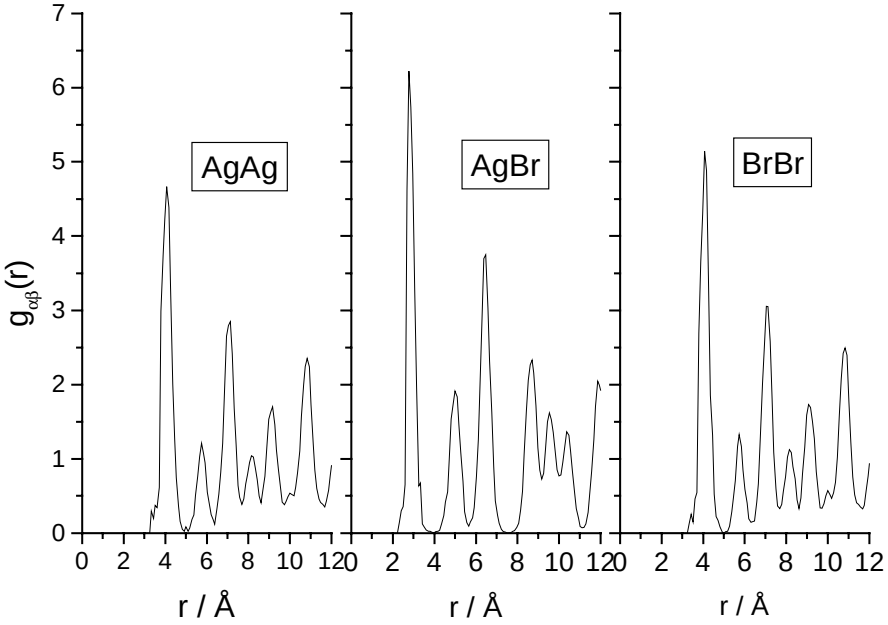
The crystal peaks are sharp while the *G(r)* from MCGR has wider peaks. The point of this is to check that the peaks have the correct positions before a proper run is made. If not, there is something wrong and there is no point in continuing.

10. Now we are ready to start RMC modelling. The RMCA data file has been discussed earlier. Run **rmca** and give as input file **agbr_cryst** (no extension). This will take 60 minutes (It probably takes longer to get a good fit). When χ^2 starts to oscillate around some value the fit is finished. Expected $\chi^2/nq \sim 4.5$.

11. When the RMCA job has finished you can plot its output (RMC fit and the partial $g_{\alpha\beta}(r)$) with **rmcplot**.



Plot the partial $g_{\alpha\beta}(r)$.



12. Ball and stick pictures of the different configurations can also be produced with the program **confplot.exe**. See the manual for this program for instructions how to use it. Here are some examples:

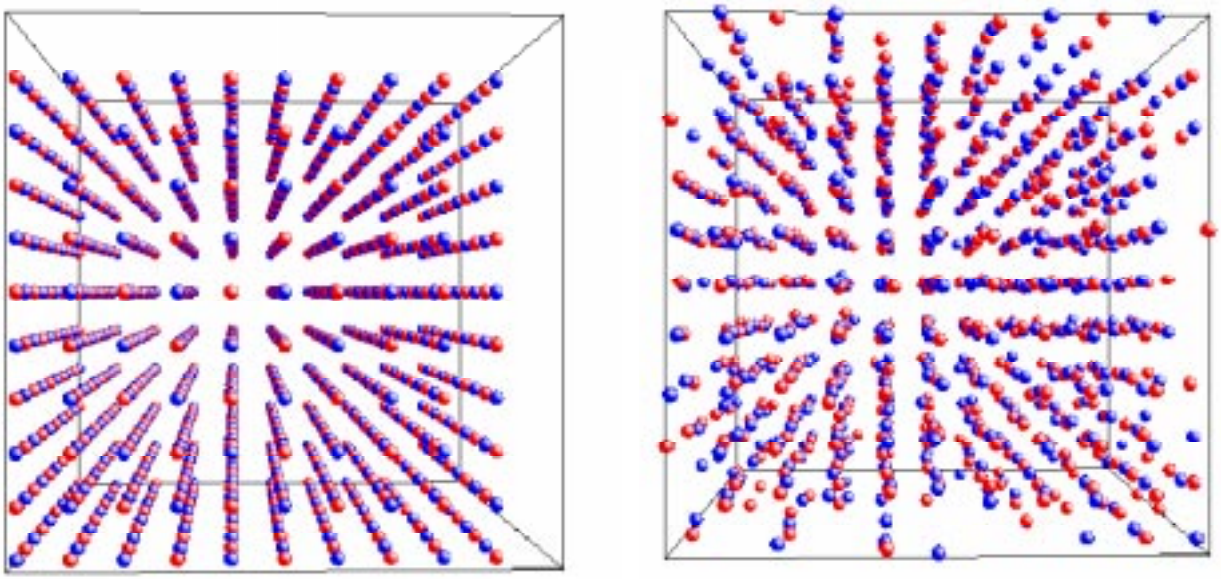


Figure to the left show the original configuration of AgBr before RMC calculation. The right figure shows a "snapshot" of the configuration after RMC calculation.

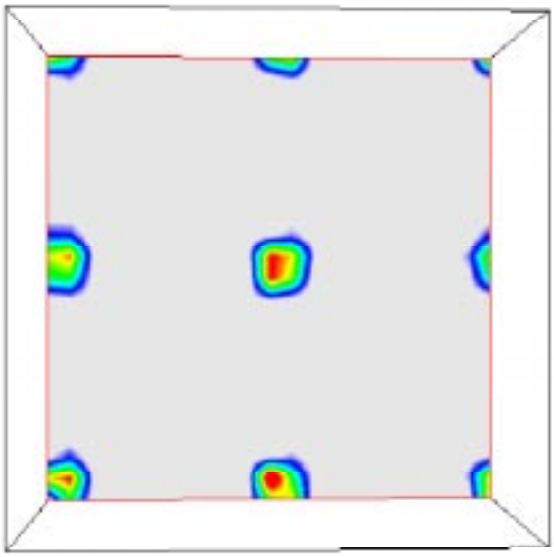


Figure showing a contour plot of the atomic density in AgBr from RMC calculation in the (100) plane.

13. It is also possible to run RMC by fitting to *F(Q)* instead of *G(r)*. Because of the limited size of the configuration however, we need to convolute the measured *F(Q)* in *r* space by a step function. This can be done with the program **convol** and the truncation distance to be used is the (minimum) half box length. This length can be found in the beginning of the configuration file. Run **convol**:

```
Input file          > agbr_slad.fq
Truncation distance > 14.453401
Output file         > agbr_slad.cfq
```

The convoluted structure factor is now in **agbr_slad.cfq**. Copy the configuration **agbr_cryst_0.cfg** to **agbr_cryst_fq.cfg** and use the control file **agbr_cryst_fq.dat** for a new run of **rmca**.Expected χ^2/nq ~ 30.
Check the result as described above.