Exercise 1

The RMCProfile working environment

The aim of this exercise is to setup the basic working environment for RMCProfile and to check that the main three programs are working correctly. RMCProfile does not have a GUI at this time so everything is driven from the command line. Windows explorer can be used to set up and move or copy files, and a text editor such as wordpad will be used to edit files where necessary. The commands will then be run from a command prompt window (also known as a DOS window).

1. First, find and launch the X server—this is normal called Exceed and can usual be found at **START** → **ALL PROGRAMS** → **Hummingbird Connectivity** → **Exceed** → **Exceed**. This program runs in the background and will be use to display graphics.
2. Next, find the **rmcprofile** folder—this usually located at **c:****rmcprofile** but you may have placed it somewhere else. Then double click the file **rmcprofile_setup.bat**. This will launch a command prompt window with the correct environment variables set. From here on in this will be referred to as the **rmcprofile** window.
3. Create a working directory on your machine to keep all the RMCProfile files together. This can be done with windows explorer, and something along the lines of **c:****temp****myfolder** is fine.
4. Copy the folder **ex_1** from the **rmcprofile****tutorial** folder to your new working directory.
5. In the **rmcprofile** window change the directory to this new folder; *i.e.* type

   ```
   cd c:\temp\myfolder\ex_1
   ```

   If your working directory is not on the **c:** drive then you will have to type the drive letter and hit return before running the '`cd`' command; *i.e.*

   ```
   H:
   cd h:\myfolder\ex_1
   ```

6. Then type '`dir`' in the **rmcprofile** window. This will list all the files in the directory and it should look similar to the list below:

```
 Directory of C:\temp\pdf_test\ex_1

31/03/2008  13:44    <DIR>          .
31/03/2008  13:44    <DIR>          ..
22/10/2007  22:56            40,495 sf6190k_all_rmc.gr
22/10/2007  22:56               138 rmcsf6_190k.back
22/10/2007  22:56            19,361 rmcsf6_190k.bragg
31/03/2008  13:49            14,089 rmcsf6_190k.cfg
31/03/2008  13:54             1,581 rmcsf6_190k.dat
22/10/2007  22:56             6,809 rmcsf6_190k.fs
22/10/2007  22:56                38 rmcsf6_190k.hkl
22/10/2007  22:56               471 rmcsf6_190k.inst
22/10/2007  22:56                47 rmcsf6_190k.poly
22/10/2007  22:56             2,758 rmcsf6_190k.sf
31/03/2008  13:59            19,704 rmcsf6_190keye.cfg
22/10/2007  22:56            32,104 sf6190k_all_conv8p82.dat
31/03/2008  13:49            30,907 rmcsf6_190k.his
31/03/2008  13:49            33,283 rmcsf6_190k.amp
31/03/2008  13:49           145,767 rmcsf6_190k.out
31/03/2008  13:49            87,320 rmcsf6_190k.braggout
              16 File(s)        434,872 bytes
               2 Dir(s)  13,156,237,312 bytes free
```

7. For now do not worry about what these file are—they are just a set of test files to ensure the programs work correctly on your machine. We will look at them in detail in the next exercise. For now, select the **rmcprofile** window, type

   ```
   rmcprofile rmcsf6_190k
   ```

   and hit return.

   RMCProfile should now start running. It may take a few minutes to initialise, but then it will display various messages explaining what it has been asked to do. It should finish with a set of parameters that indicate how well the data is being fitted. The final part of the output should appear similar to the text below:

```
Peaks calculated
scale  0.210434976038272
Bragg calculations initialised

-------------------------------------------------->
Time used    0.0 ,time limit    0.0 ,Last saved at    0.3

Bragg Chi**2/npts =       0.4830

  10074 moves accepted   89690 generated and   85650 tested
Chi**2/dof 0.8880
Expt  1: Renorm 1.0000  Constant = 0.0000  Chi**2/nq = 2.320
Expt  2: Renorm 1.0000  Constant = 0.0000  Chi**2/nq =0.7584
Restraint energy =  3.465

Total time in loop so far :  4.6876073E-02s
Time per generated move is:   15.6253576278687     ms

Saving configuration and results to disk
*** DO NOT INTERRUPT UNTIL SAVING IS COMPLETED ***
Saving has been completed


Total time taken by program:     10.672
```

8. The next program to check is called **rmcplot**. This program displayes the fits to data obtained with RMCProfile and also the partial structure factors calculated from the RMC configuration. Working again within the **rmcprofile** window, type '`rmcplot.bat rmcsf6_190k`'. A new window should appear, called **PGPLOT Window1**—it may be hidden behind another window. This window is where the graphs will be displayed. In the **rmcprofile** window, enter '`5`' and hit return. The fit to the bragg profile should now be displayed. The fit will not look very good since the model being used to fit it is too small, but for now all that is important is that the fit is displayed at all.

   You can use the left mouse click to zoom in on a region. Right-click will then restore the display and pressing '`q`' with the graphics window active will return control to the **rmcprofile** window, from where you can make a new selection or indeed quit. This is a very basic plotting program designed to provide a quick look at the fits. For more comprehensive functionality feel free to use your favourite plotting program, such as excel, sigmaplot, origin, *etc.*

9. The final program to check at this stage is **atomeye**. This can be used to display a ball and stick model of the RMCProfile configuration. It is a quick way to check that the atoms are not in unphysical places and also whether the configuration is physically sensible or not. This program was written by Ju Li at Ohio state university, USA and is not developed by the RMCProfile team; it is just a very useful program, so we use it.

   To check that the program is working, type

   ```
   atomeye.bat rmcsf6_190keye.cfg
   ```

   in the **rmcprofile** window. You will have to quit **rmcplot** if you have not already done so—by entering '`0`'. If **atomeye** is working two new windows should appear: both are called **rmcsf6_190k.cfg**. Don't worry if error messages are displayed in the **rmcprofile** window, so long as the new windows do in fact appear and they remain on the screen. Note that

one or other or perhaps both of the new windows may initially be minimised. If this is the case, click on the new item in the task bar at the bottom of this screen.

The grey text window displays useful information, and is used to enter parameters. The new graphics window displays the image and is the main control window. With this new graphics window active the mouse can be use to move the view. Press '`F1`' to display a list of option in the grey window. To quit the programs press '`q`' with the graphics window active.

10. If everything worked correctly you are now ready to move on to exercise 2.

Exercise 2

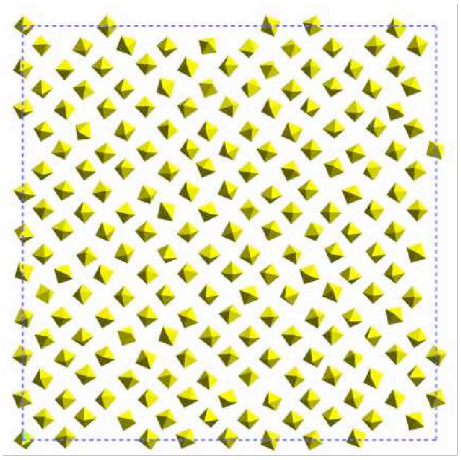
Setting up an RMCProfile refinement

This exercise will guide you through the steps required to set up an RMCProfile refinement from scratch. It is assumed that you already have a GSAS refinement of your data and have produced corrected total scattering data. The **ex_2** folder contains all the data you need, so please copy this to your working area. The **gsas** folder has the GSAS refinement and all data needed to provide bragg profile information for RMCProfile. It also includes a **.cfgcom** file, which contains the information needed to produce an RMC starting configuration using the program **crystal**.

The **data** folder contains time of flight neutron structure factor $F(Q)$ data and the radial distribution $g(r)$. Together with the **gsas** folder, these two folders provide all the information required to run RMCProfile and produce a configuration of the system.

The **rmc** folder contains a completed run together with all the relevant output files—it is included to illustrate what the results will hopefully look like.

The example files supplied are for the molecular crystal SF_6 and the following paragraph gives you some background information to help understand the aim of the RMCProfile refinement.



SF_6 is a disordered molecular crystal made up of SF_6 octahedra arranged over the crystal lattice. Molecular crystals are often the most disordered crystalline systems, giving rise to large amounts of diffuse scattering (this is easily seen in a plot of the example data). The example data and files supplied are taken from neutron scattering experiments carried out at 190 K using the GEM diffractometer at ISIS. At this temperature the crystal structure has body centred cubic symmetry, with one molecule on the corner of the unit cell and one in the centre. However this average structure places the fluorine atoms of neighbouring molecules too close to one another, and so on a local scale the system tries to minimise these contacts by rotating the octahedra in different directions. The system is said to be frustrated, with fluorine–fluorine repulsion driving the motion of the molecules. With the data supplied, you should be able to start with the “ideal” ordered structure and use RMCProfile to model these local deviations from the average bcc arrangement.

The preparation of the files for an RMCProfile refinement can be split into three stages: first, the information from a GSAS refinement is obtained, next the total scattering data is prepared, and finally the control files for RMCProfile are produced. The next three sections take you through each of these stages.

1. As with most RMC modelling, the process actually starts with a GSAS refinement. A GSAS refinement of SF_6 at 190 K is contained in the **gsas** folder and can be used to supply RMCProfile with all the information required to model the Bragg profile. It also contains a **.cfgcom** file with the bcc cell written out in $P1$ symmetry. At the moment I do not have a simple program to go from the GSAS atom positions to this $P1$ cell. However, GSAS supplies all the information required and it is a good exercise to try with your own system: at least it ensures that you start with a good feeling for the long range average structure. To extract the rest of the information needed by RMCProfile, run the program **get_gsas_bragg** on the **.EXP** file and select 'histogram 3' to be extracted for fitting with RMCProfile.

   In the **rmcprofile** window change the directory to the **gsas** folder; *i.e.*

   ```
   cd c:\temp\myfolder\ex_2\gsas
   ```

   Then type '`get_gsas_bragg`' and hit enter. When the program asks for the GSAS filename, enter '`SF6_190k`'. Then enter '`3`' for the histogram required and '`1.0`' for the minimum d-spacing. When asked the minimum, maximum and step for h,k and l, enter

   ```
   -20 20 1
   -20 20 1
   -20 20 1
   ```

   This just sets the maximum hkl value to larger than that allowed by the minimum d-spacing limit. Depending on the particular system, this provides two mechanisms of defining which range of hkl values is fitted in the Bragg profile.

   At this point you should have five files for RMCProfile located in the **gsas** folder: **.bragg**, **.back**, **.inst**, **.hkl** and **.cfgcom**. Copy these files out of the **gsas** folder into the top level of the **ex_2** folder using a common stem name; *e.g.* **sf6_190k.bragg** *etc.* This can be done with windows explorer or using the DOS command '`copy`'.

   In the **rmcprofile** window, move to the top level of the **ex_2** folder by entering '`cd ..`'.

   Now run the **crystal** program, either entering the information contained in the **.cfgcom** file when prompted or using the pipe command

   ```
   crystal < sf6_190k.cfgcom
   ```

   This should produce a 3×3×3 supercell of the bcc structure that will be saved in a file called **sf6_190k.cfg**.

   You have now produced all the files required from the GSAS refinement.

2. The next stage is to prepare the total scattering data for RMCProfile. How to collect and produce total scattering data is beyond the scope of this simple tutorial and so will not be covered here.

The data folder contains an $F(Q)$ file (**sf6190k_all.dat**) produced from three of the detector banks of the GEM diffractometer at ISIS. It is quite common to combine several banks of data into one data set, although RMCProfile can be used to fit many $F(Q)$ data sets simultaneously.

Take a look at the $F(Q)$ file, using excel or any an other plotting program on the PC. A basic alternative, supplied with RMCProfile, is called **genplot.bat**. To use this program to plot the $F(Q)$ data, enter '`genplot.bat sf6190k_all.dat`', followed by

```
2 1 0
1 2 3
```

as answers to the subsequent two questions. This should then bring up a plot of the data file.

The data contained in the $F(Q)$ file are scaled from -1 to 0; these need to be scaled by a factor of 0.27593 (the sum of the neutron partial scattering factors) in order to be suitable for RMCProfile. The data also need to be convolved with the RMCProfile configuration box function to enable a fair comparison. Both of these operations can be performed using the program **convol_norm_new**. For a $3\times3\times3$ supercell, the appropriate truncation distance is 8.82 Å.

In the **rmcprofile** window, move into the **data** folder by entering '`cd data`'. Then type '`convol_norm_new`' and hit enter. Enter '`sf6190k_all.dat`' when asked for an input file name. Then '`8.82`' and '`0`' for the truncation distance and constant to subtract, respectively. For the constant by which to multiply, enter '`0.27593`'. Finally, for the output file name choose something like '`sf6190k_all_conv8p82.dat`'.

Next the $G(r)$ file (`sf6190k_all_gr.dat`) needs to be prepared in a similar way. This file contains the fourier transform of the $F(Q)$ data. Once again the preparation of the $G(r)$ data themselves will not be described here; the data are normally obtained during processing of the total scattering data. Take a look at the file using either a windows plotting program or **genplot.bat**. The $G(r)$ file is scaled from 0 to 1 (as is fairly standard), however RMCProfile requires the data to be rescaled from -0.27593 to 0. This can be performed using the **data_rescale** program.

In the **rmcprofile** window type '`data_rescale`' and then enter. Follow this with '`sf6190k_all_gr`' when asked for the file name; note that the **.dat** extension will be assumed. Then enter '`0.27593`' and '`1.0`' for the constants with which the data are to be multiplied and subtracted. For the output file name choose something like '`sf6190k_all_gr_rmc`' (again the **.dat** extension will be added automatically).

Now copy the new $F(Q)$ and $G(r)$ files into the top level of the **ex_2** folder.

3. The next file to prepare is the main **.dat** control file for RMCProfile. This can be copied from the **rmc** folder to the top level of the **ex_2** folder. You should open this file with a text editor (*e.g.*, wordpad), checking that the names of the data files in the **.dat** file match the names you have chosen. A description of the **.dat** file format and contents is giving in the RMCProfile manual.

   Finally, the file for the polyhedral constraint needs to be prepared. Since the SF_6 molecules form a octahedron, polyhedral restraint '4' can be used and should be set in the **.dat** file. The **.poly** file can be copied from the **rmc** folder or produced with your favourite text editor. Copy the **.poly** file from the **rmc** folder and open it with a text editor. The format is described in the RMCProfile manual and the ideal S–F bond should be set to 1.56.

Next, we need to create two files that describe which atoms are neighbours. These files—in this instance given the extensions **.sf** and **.fs**—can be produced using the **neighbour_list** program. Run this program, and when asked for 'a maximum distance' enter '`1.9`' (since 1.9 Å is larger than the nearest S–F distance but not far enough to include the next nearest neighbours). When producing the **.sf** file the program should report that it has found an octahedron and that the average coordination number is 6. If this is not the case then something is wrong with the **.cfg** file.

In the **rmcprofile** window type '`neighbour_list`' and hit enter. Then enter the name of the configuration file; *i.e.* '`sf6_190k.cfg`'. For the following three question answer

```
1
2
1.9
sf6_190k.sf
```

This has produced the list of fluorine atoms connected to sulphur atoms. Next, the list of sulphur atoms connected to fluorine atoms needs to be produced. So answer '`y`' to the question 'Produce another file?' and answer the next few questions with

```
2
1
1.9
sf6_190k.fs
n
```

4. You should now have all the files you need to run RMCProfile on this system. Both the data and the size of configuration (a $3\times3\times3$ supercell) have been chosen to run quickly. A reasonable fit should be achievable within about 10 minutes. However, the configuration is too small to ever give a useful model or fit. Doing so would normally require a large configuration and 10–20 hours of run time. The next exercise will describe how to run RMCProfile on these files.

Exercise 3

Basic RMC refinement

This exercise will guide you through the steps required to run an RMCProfile refinement and perform some basic analysis of the results. There tends to be two stages to the analysis. The first is to check that the minimisation is proceeding usefully, and that model being produce is sensible—this is will be our main aim here. The second type of analysis tends to be sample specific, starting once a finally configuration has been reached and aiming to decide what the model tells us about he systems being studied. Typically this will involve writing custom programs or scripts, and as such the process is very hard to generalise.

1. To start with, copy the **ex_3 directory** into your work area, and make a directory called **start** in it. Then copy the files you created from the top level of you **ex_2** folder into the **start** folder. Next, create a copy of the **start** folder, calling it **initial_fit**. In this folder open the RMCProfile **.dat** file (probably called **sf6_190k.dat**) and change the line

   ```
   10 0.2                        ! Time limit, step for saving
   ```

   to

   ```
   0  0                          ! Time limit, step for saving
   ```

   add save the file. This will tell RMCProfile to initialise and generate initial fit and then stop.

2. In the **rmcprofile** window change the directory to **ex_3****initial_fit**; *i.e.*, enter

   ```
   cd c:\temp\myfolder\ex_3\initial_fit
   ```

   and then '`dir`'. The listing that appears should be similar to the one below:

```
 Directory of C:\temp\pdf_test\ex_3\initial_fit

04/04/2008  12:00    <DIR>          .
04/04/2008  12:00    <DIR>          ..
22/10/2007  22:43            40,495 sf6190k_all_gr_rmc.dat
03/04/2008  21:30               184 SF6_190K.back
03/04/2008  21:30            38,062 SF6_190K.bragg
04/04/2008  11:14           490,797 sf6_190k.cfg
15/09/2006  14:14               558 sf6_190k.cfgcom
04/04/2008  11:24           264,014 sf6_190k.fs
03/04/2008  21:30               158 SF6_190K.hkl
03/04/2008  21:30               746 SF6_190K.inst
04/04/2008  11:15           104,014 sf6_190k.sf
22/10/2007  22:06            32,104 sf6190k_all_conv8p82.dat
22/10/2007  22:56             1,574 rmcsf6_190k.dat
22/10/2007  22:06                47 rmcsf6_190k.poly

              12 File(s)        972,706 bytes
               2 Dir(s)  13,083,623,424 bytes free
```

The input files for RMCProfile should all have a common "stem name', except any data files. So in this example here everything is fine, except that the **.dat** and **.poly** files have the stem name "**rmcsf6_190k**", whereas everything else has a stem name of "**sf6_190k**". So in this case, either set needs to be renamed—it's up to you to choose, but this needs to be done before proceeding.

3. Next type '`rmcprofile [stem name]`' to run RMCProfile; *e.g.*, '`rmcprofile sf6_190k`'. RMCProfile should now run for a little while, and if all seems OK then move on to the next stop. However, if you see an error message such as in the box below:

```
  =================

 Using files: SF6_190K

 Reading configuration file SF6_190K.cfg
 Input density not the same as configuration density
    0.068595    0.068606
Using the configuration density    0.068606
 d/dr,int(d/dr,nr)   1471.69245000000             1471           0
forrtl: severe (29): file not found, unit 4, file
C:\temp\myfolder\ex_3\initial_
fit\sf6190k_all_rmc.gr
Image              PC        Routine            Line        Source
rmcprofile.exe     004A8979  Unknown              Unknown  Unknown
rmcprofile.exe     004A87D7  Unknown              Unknown  Unknown
```

then the name of the $G(r)$ data file in the main **.dat** file is not correct. You would need to edit the **.dat** file and change the name to the correct one, which in this case is **sf6190k_all_rmc.gr**. Once you have saved the new file, rerun RMCProfle as above.

4. After a short while (being nice and vague as it depends on the PC being used), RMCProfile should finish initialising and then display the level of the current fit, as in the box below.

```
 scale  0.200816278534226
Bragg calculations initialised

-------------------------------------------------->
Time used    0.0 ,time limit    0.0 ,Last saved at    0.2

Bragg Chi**2/npts =    2388.2426

      0 moves accepted       1 generated and       0 tested
Chi**2/dof  2733.
Expt  1: Renorm 1.0000  Constant = 0.0000  Chi**2/nq =0.1070E+05
Expt  2: Renorm 1.0000  Constant = 0.0000  Chi**2/nq = 116.9
Restraint energy = 0.5785

Total time in loop so far :  1.5624762E-02s
Time per generated move is:   5.20825386047363     ms

Saving configuration and results to disk
*** DO NOT INTERRUPT UNTIL SAVING IS COMPLETED ***
Saving has been completed


Total time taken by program:      7.141
```

In the **rmcprofile** window, type '`dir`' and hit enter to produce a list of the files in the directory. You should seen that several new files have been produced. The **.his** and **.amp** files are just history files for restarting a run. The results of the refinement are contained in the **.cfg** file (note the original will have been replaced), the **.out** file and also the **.braggout**. These last two files contain the fits to the data, together with other useful information such as the partial radial distribution functions. They can be plotted using the **rmcplot.bat** program.

Now type '`rmcplot.bat [stem name]`'—*e.g.*, '`rmcplot.bat sf6_190k`'—and select '`1`' from the menu when it appears. A plot of the partial $g(r)$ functions should appear in the graphics window (you may need to find it if it is hidden). In this case, the plot should be a series of delta functions, since all the atoms are on the ideal positions given by the average structure. Press '`q`' (with the graphics window selected) to return control to the menu.

Next, select '`5`' from the menu, and a plot of the Bragg profile fit should appear. The position of the peaks in the RMC fit should be correct, as should the peak shape and background, since these all come directly from the GSAS data. The only aspect that will be wrong is the intensity of the peaks. Again, this is because all the atoms are on their "ideal" positions, and hence there is no thermal motion or static disorder in the configuration. Consequently, the first thing RMCProfile will do is to displace the atoms in order to reduce the intensity of these peaks. The polyhedral constraint will help maintain the SF_6 octahedral connectivity during this process, and the total $G(r)$ will define the final local structure of these polyhedra. Again, press '`q`' with the graphics window selected inorder to return control to the menu.

Finally, select '`3`' from the menu, and a plot of the fit to the total $G(r)$ will be displayed. As with the partial $g(r)$ functions, the total $G(r)$ function consists of a series of delta functions. The actual data (the red curve) is lurking somewhere at the bottom of these. Use the left-click of the mouse to zoom in on the low-r region and produce a plot that spans roughly from 0 to 3.5 in x and -0.5 to 6 in y. You should now be able to see the data more clearly

and it will be easier to see that—unlike the Bragg profile fit—the positions of the peaks are not correct. This tells us straight away that the real local structure of the SF_6 octahedra and their local environment is not the same as that derived from the ideal average structure. We can say this even though we havent yet refined anything. Press '`q`' to return to the menu and select '`0`' to exit.

To finish our look at the initial model we will now produce a 3D model of the starting configuration in **atomeye**. Type '`rmc_to_atomeye`' in the **rmcprofile** window and enter the following line in answer to the questions (note that you may have to modify the answer accordingly if you are using a different stem name to me):

```
sf6_190k.cfg
S 32.0
F 19.0
```

This will create an **atomeye** file called **sf6_190keye.cfg**. To plot this file, type '`atomeye.bat sf6_190keye.cfg`' in the **rmcprofile** window. With the atomeye graphics window active, pressing '`tab`' will toggle use of the perepective view. If you then press '`page down`' the atom spheres will shrink. Next, press '`b`', and the S–F bonds will be displayed; this will make it easier to visualise the SF_6 octahedra. This configuration should look like a bcc array of octahedra, as defined by the average structure. Examine the structure and the **atomeye** function for a while, then when you are happy to move on, press '`q`' whilst the graphics window is active.

5. The next step is to use RMCProfile to refine this model. Make a copy of the initial fit directory called **first_run**. Open this directory and edit the **[stem name].dat** file (*e.g.*, **sf6_190k.dat**), changing the line

   ```
   0 0                        ! Time limit, step for saving
   ```

   to

   ```
   10 0.2                        ! Time limit, step for saving
   ```

   add save the file. This will tell RMCProfile to refine the structure for 10 minutes. The small configuration used here will not produce a very good fit but it should illustrate the minimisation process.

   In the **rmcprofile** window, change to the **first_run** directory and type '`rmcprofile.bat [stem name]`' (*e.g.*, '`rmcprofile.bat sf6_190k`'; normally you would only need to type '`rmcprofile [stem name]`' but here the **.bat** stops RMCProfile from taking all of the CPU power). A new window will appear, called **RMCProfile running**, and the progress of the refinement will be displayed here. The run will take 10 minutes and during this time you can also follow the progress of the fits in the rmcprofile window using **rmcplot.bat**. Every time you choose a different plot, **rmcplot** reloads the file, so in this way you can follow the progress by re-plotting the various fits. RMCProfile will save the current fits every 0.2 minutes.

   Initially the Bragg profile and other data fit improves at the expense of the restraint energy and so, as predicted, the octahedra are pulled apart to reduce the Bragg intensities. Eventually the fit to the data get close enough that the restraint energy starts to dominate and RMCProfile starts to minimise it again and rebuild the octahedra. As the restraint energy

starts to reduce, the fit to the $T(r)$ (Expt. 1) improves as well. As the refinement progresses the general trend is for all the χ^2 to reduce; however, if you look closely you will notice that some will increase at various times. This shows that the weighting of the data is correct and that local minima are being avoided.

Once the refinement has finished, examine the fitting parameters in the **RMCProfile running** window and then type '`exit`' and hit enter to close this window.

If you havent done so already, take a look at the final fits using **rmcplot.bat**. The fits to the Bragg profile and $S(Q)$ should look reasonable, although there are extra peaks in the Bragg profile due to the small configuration size. The fit to the $T(r)$ should also be fairly reasonable although the fit may not quite have finished its minimsation process, and hence the noise is caused by the limited number of atoms in the configuration.

If you would like to see the fits produced by a quick-ish run with a $10\times10\times10$ supercell then take a look at the files in the **ex_3\sf6** folder. Here the Bragg profile fit is probably as good as it can be. The $T(r)$ fit is better, but still not perfect. Note that in this run the $S(Q)$ data was refined as three separate banks—hence there are three fits to plot.

Exercise 4

Refinement of magnetic structures

Introduction

This exercise focusses on the use of RMCProfile to refine magnetic structure in magnetic materials. Just as RMC can be used to refine the crystal structure of a material in terms of the positions of atoms in a large supercell, we can refine magnetic structures in terms of the orientations of spins in similar atomistic configurations. One of the advantages of an RMC approach to magnetic structure refinement is that it is often possible to solve the magnetic structure even when starting from a completely random ensemble of spin orientations.

The example we will work through concerns the magnetic structure of the well-known antiferromagnet MnO. At temperatures below 120 K the $S = \frac{5}{2}$ magnetic moments of the Mn^{2+} ions align ferromagnetically within (111) planes of the rocksalt crystal lattice. The magnetisation direction within planes then reverses from one plane to the next, giving the overall antiferromagnetic structure shown in Fig. 4.1. In fact there is also a slight deviation from cubic lattice symmetry associated with this magnetic transition, but here we will ignore this effect.

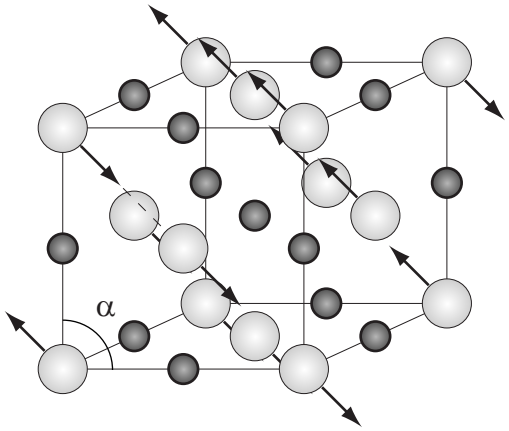


Figure 4.1: The antiferromagnetic structure of MnO: Mn and O atoms are shown as large light-grey and small dark-grey spheres, respectively.

The MnO atom and spin RMC configurations

We are going to refine the spin orientations in a $4\times4\times4$ supercell of the unit cell shown in Fig. 4.1. The file **mno.cfg** contains the positions of 512 atoms—256 Mn and 256 O atoms. The positions of these atoms have been displaced slightly from their average positions. A version of this configuration file in the format readable by **atomeye** is given as **mnoeye.cfg**. It is worth taking a look at the structure in **atomeye** at this stage, just to familiarise yourself with the atom positions. A picture of the configuration is shown in Fig. 4.2.

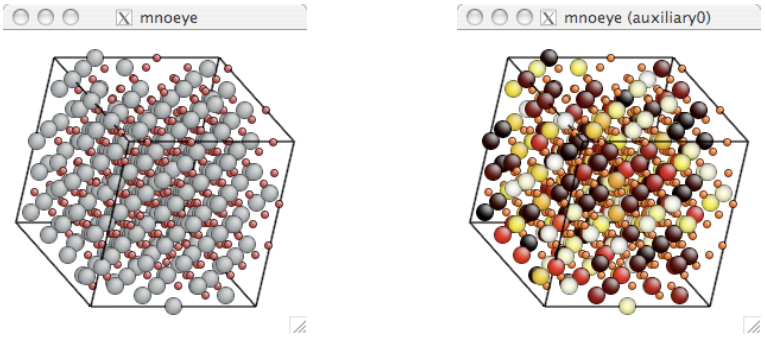


Figure 4.2: The RMC starting configuration as seen in **atomeye**, using default colouring (left) and with Mn atoms coloured by the initial spin directions (right).

A set of 256 random spin orientations are given in the file **mno_spin.cfg**. One method of visualising these orientations is to colour the Mn atoms in our **atomeye** configuration according to the individual spin directions. There is a program **auxprep** provided that helps prepare the relevant files. If we run the command

```
auxprep < auxprep.in
```

then a new file, **mnoeye.aux** is produced, which can be used to tell **atomeye** how to colour each atom. Relaunching **atomeye** via

```
atomeye.bat mnoeye.cfg
```

shows the same configuration as we saw previously. Now press '`F11`', and **atomeye** will ask whether you want to "load auxiliary properties from (mnoeye.aux)"; hit enter at this point. The Mn atoms will now be coloured according to the spin orientations in **mno_spin.cfg**. Different colour palettes can be loaded by turning "caps lock" on, then while holding down the "ctrl" key, press "=" (there are about ten or so different palettes). A typical view is shown in Fig. 4.2. The main point is that things look quite random!

It is instructive to see what the diffraction pattern looks like when calculated from this combination of atomistic and spin configurations, and how it differs from the experimental data. The RMCProfile parameter file **mno.dat** is set up ready to be used for this magnetic refinement. The experimental data are stored within the file **mno_10k_sq.dat**, and we are using a Q range of approximately $0 < Q < 25\,\text{Å}^{-1}$. These data have already been convoluted with a box function of width $8.88\,\text{Å}^{-1}$, which is half the box size of our configuration. Running the program using the command

```
rmcprofile mno
```

we obtain the output file **mno.out**, which includes the fit-to-data shown in Fig. 4.3. There is reasonable agreement over most values of Q, except between $0 < Q < 3\,\text{Å}^{-1}$, where the key magnetic structure reflection is not modelled well at all.

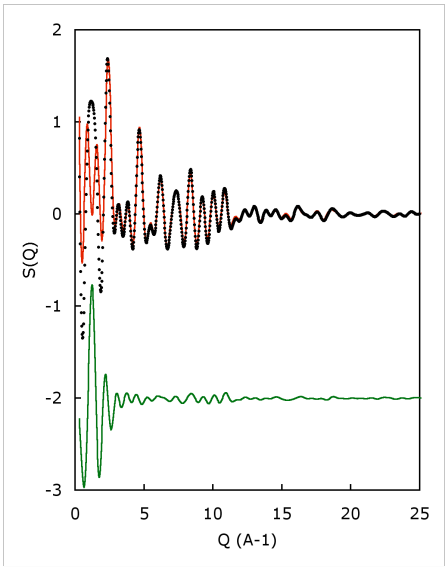


Figure 4.3: Initial RMC fit to neutron scattering data for MnO. Data are shown as solid points, the RMC fit as a red line, and the difference (data−fit) shown as a green line, shifted by 2 units.

RMC refinement

In order to proceed with a refinement of the magnetic structure, we must edit the **mno.dat** file to tell RMCProfile how long to run the refinement, and also how often to save. The relevant line in the parameter file is

```
0 0                          ! Time limit, step for saving
```

which we change to

```
5 1                          ! Time limit, step for saving
```

It so happens that five minutes is sufficient in this simple case to arrive at a reasonable fit to the magnetic structure. More complicated structures will take longer! We run the program as before, using the command

```
rmcprofile mno
```

The fit should have converged within five minutes with a goodness-of-fit reducing from its initial value $\chi^2 = 395.9$ to $\chi^2 \simeq 12$. If the value of χ^2 is significantly larger than this value, it might be worth running RMCProfile once more.

Analysis

First, we can take a look at the new fit-to-data, once again by plotting the values given in **mno.dat**; a representative plot is given in Fig. 4.4. The key difference with the previous fit is that the (111) magnetic peak is now well modelled. Note that our refinement only involved moving the magnetic moments (all the atom positions remain the same), so it really is the magnetic structure that accounts for this peak.

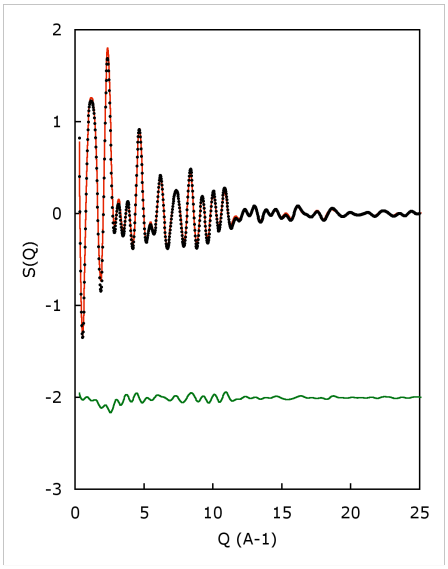


Figure 4.4: A typical equilibrium RMC fit to neutron scattering data for MnO.

Before looking at the actual spin configuration, we are going to set up RMCProfile to produce a series of equilibrium configurations. This will help us produce smoother distribution functions by increasing sample size. Again, we need to amend the **mno.dat** file, this time changing

```
.false.                 ! number of configurations to collect
500                     ! step for printing
5 1                     ! Time limit, step for saving
```

to

```
.true.                  ! number of configurations to collect
500                     ! step for printing
10 5                    ! Time limit, step for saving
```

Again, we run RMCProfile using the command

```
rmcprofile mno
```

but this time it will save a copy of the configuration file after every 500 generated moves, numbering the files sequentially. In order to generate 50 new configurations, we will need to leave the program to run for approximately 10 minutes.

Meanwhile, what we really want to do is to see what the newly-refined magnetic structure looks like. We will use **atomeye** for this purpose, so we need to run the command

```
auxprep < auxprep.in
```

which will produce a new **mnoeye.aux** file from the equilibrium spin configuration. Launching **atomeye** with

```
atomeye.bat mnoeye.cfg
```

will now show the new structure. Again, load in the **.aux** file using '`F11`', which will represent the spin directions on each Mn atom. Because there are four different symmetry-equivalent [111] axes, the actual direction of the magnetic ordering will differ from run to run. Nevertheless a typical configuration is shown in Fig. 4.5. What should be clear, after some playing with the orientation, is that the magnetic structure is now composed of ferromagnetic layers, as described in the introduction.

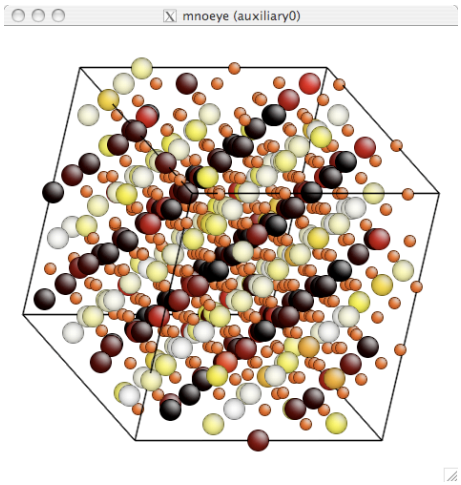


Figure 4.5: A typical RMC equilibrium configuration as seen in **atomeye**.

Finally, we return to the series of equilibrium configurations produced by RMCProfile. If fewer than 50 configurations have been prepared in the 10 minutes, then run the program once again (it will automatically resume its sequential numbering from the correct point), until sufficiently many have been saved. We are going to use these configurations to look at the actual distribution of spin orientations (rather than the broad ordering pattern, which we observed with **atomeye**). To do so, we extract a distribution histogram using the command

```
spindist < spindist.in
```

which produces a new file, namely **mno_spins.out**. The numbers in this file correspond to a logarithmic probability of observing a spin pointing in a specific direction.

An intuitive method of viewing these distributions is a projection onto the surface of a sphere. There is a program provided that converts **mno_spins.out** into a sphere projection; we execute it with the command

```
spinplot < spinplot.in
```

This produces a picture in the **.ppm** format, which we convert using

```
convert mno_spins.ppm mno_spins.bmp
```

A typical distribution is shown in Fig. 4.6, which in this case shows that the spins are aligned parallel and antiparallel to an axis very close to $[112]$.

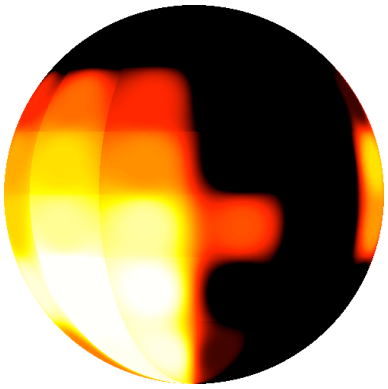


Figure 4.6: A typical spherical spin distribution (black = low probability; white = high probability). The view is taken looking down $[100]$ with the $[010]$ axis to the right hand side, and the $[001]$ axis towards the top of the figure. In this particular case, alignment appears to be approximately parallel (and antiparallel) to $[112]$.

We can use the same program to look at this distribution from arbitrary angles, and even produce an animated **.gif**. We will do this quickly here, by editing the file **spinplot.in**, changing the last entry from '`F`' to '`T`'. This part of the file is a flag that instructs the program to prepare a series of views that can be assembled to form an animation. Re-running the command

```
spinplot < spinplot.in
```

will now give a series of 24 files numbered **01_mno_spins.ppm** to **24_mno_spins.ppm**. Finally, we combine these into a single animated **.gif** with

```
convert -delay 20 -loop 0 *_mno_spins.ppm mno_spins.gif
```

The animation **mno_spins.gif** can then be viewed in a web browser.

Further notes

Other methods of analysing the RMC output include the generation of spin-spin correlation functions, which measure the the degree of correlation between spin orientations as a function of distance. Also we can extract some information about the spin excitations—*i.e.*, the magnons—from the sharpness of the peaks in these correlation functions.