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EPSRgui Manual

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EPSRgui Manual

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Contents

1. Introduction

EPSRgui has been created to provide a graphical user interface for the Empirical Potential Structure Refinement (EPSR) routines. For more information on EPSR please refer to the EPSR manual. EPSRgui therefore acts as a 'front-end' for the EPSR routines, thus reducing the need for command prompt/terminal commands but still producing the same result as EPSRshell.

The structure of an EPSRgui project is very similar to that in EPSR. Simulations are set up as project folders, often, although not necessarily, in the EPSR/run directory. For simplicity, the simulation box is automatically named <*project name*>box.ato. If an existing simulation is imported, the simulation box will retain its existing filename.

If a simulation box is particularly large or the component molecule is complex, some of the EPSR processes might take a little longer than usual and EPSRgui will appear non-responsive while the process finishes. Please be patient while this is happening - messages are given at the bottom of the window and also in Settings->Show messages once the process has finished. For longer EPSR processes (fmole and running EPSR) command prompt /terminal windows are opened so EPSRgui can still be used while they are running. Closing these windows before an EPSR process has finished will cause the process to stop immediately and is not recommended. If this does happen, any data might not be saved, and files may become corrupted.

EPSRgui remembers the files associated with the project so that the project can be opened again later and work on the simulation resumed. EPSRgui makes a project file with extension .EPSR.pro where all this information is stored.

Note that EPSRgui is compatible with EPSR version 24 onwards.

2. Installation and setup

2.1.Installing EPSR

Go to the Disord Matt Facebook page for links to download the latest distribution of EPSR (via the Download Gudrun and EPSR link) from Dropbox.

2.1.1. Windows

Unpack the EPSRxxdistribution.zip into a suitable location – either directly on to the C: drive or where programs are usually kept.

Java needs to be installed in order to run a number of the EPSR and EPSRgui routines. Look in Program Files (including x86) for a folder named Java. If it is not there, go to https://java.com/download to download the latest Java software.

In the EPSRXXdistribution\EPSR\startup folder, make sure the system_commands_windows.txt file is appropriate for your computer. Make sure the system_jmol path contains the correct path to the Java executable on your computer e.g.:

```
system_jmol  "C:\Program Files\Java\jre1.8.0_31\bin\java.exe" -jar %EPSRbin%\Jmol.jar
```

2.1.2. Linux

Unpack the EPSRxxdistribution.zip into a suitable location. This should create two folders called EPSR and EPSRfiles in that location. To compile the binaries, first ensure the gfortran compiler is installed and operational. Then open a terminal window and cd to the EPSRfiles folder. Type

```
make -f makefile_xxx clean
```

Then type

```
make -f makefile_xxx
```

This should compile all the EPSR routines and put the binaries in EPSR/bin.

If you need to compile the PGPLOT binaries (map2d, map3d, etc.) then in the *EPSRfiles/src/newsrc* folder are other makefiles that will do this, namely makefile_linux and makefile_mac. (Ignore any other makefiles you find in this folder.) However you will need to edit the line 'PGPLOT_LIB=' in these makefiles to make sure it points to the corresponding files for your system. Then follow the above instructions to compile the routines.

Java needs to be installed and executable in order to run a number of the EPSR and EPSRgui routines. If you want to run MOPAC, then download and install MOPAC, and make sure it has the correct permissions to run.

In the *EPSRXXdistribution/EPSR/startup* folder, make sure the definitions in the system_commands_Linux.txt file are appropriate for your computer. Make sure the system_mopac path is also appropriate.

2.1.3. Mac

Follow instructions for a Linux installation.

2.2.Installing EPSRgui

2.2.1. Windows

Download the EPSRgui installer from ftp://ftp.nd.rl.ac.uk/scratch/EPSRgui/EPSRgui Windows installer and run the executable (for the ftp site: username = anonymous password = *your email address*). Run EPSRgui via the Start menu; a command prompt window will open at the same time as EPSRgui.

2.2.2. Linux

EPSRgui requires the Qt5 libraries (Qt4 is not compatible) so ensure your OS is Qt5 compatible. Qt is often already installed on Linux operating systems; ensure the Qt5 packages *qt5-default*, *qt5-qmake* and *qtdeclarative5* are installed on your system. Also ensure *make* and *g++* are installed. Download the EPSRgui source code from https://github.com/samcallear/EPSRgui. Unzip the EPSRgui folder to an appropriate directory (usually where all other source code/programs are kept) and then open this folder in a terminal window and type

```
qmake -qt5
```

Once qmake has finished type

```
make
```

If there is a problem with the make file, run *make clean* before running *make* again.

To run EPSRgui, open a terminal window and navigate to the EPSRgui folder. Then type

```
./EPSRgui
```

2.2.3. Mac

Download the EPSRgui installer from ftp://ftp.nd.rl.ac.uk/scratch/EPSRgui/EPSRgui Mac installer (for the ftp site: username = anonymous password = *your email address*). Run the installer and then copy the EPSRgui app bundle to Applications. To run EPSRgui double click on the EPSRgui icon in Applications. This will first open a terminal window (which can sometimes be slow) and then EPSRgui.

2.3.Setting up EPSRgui

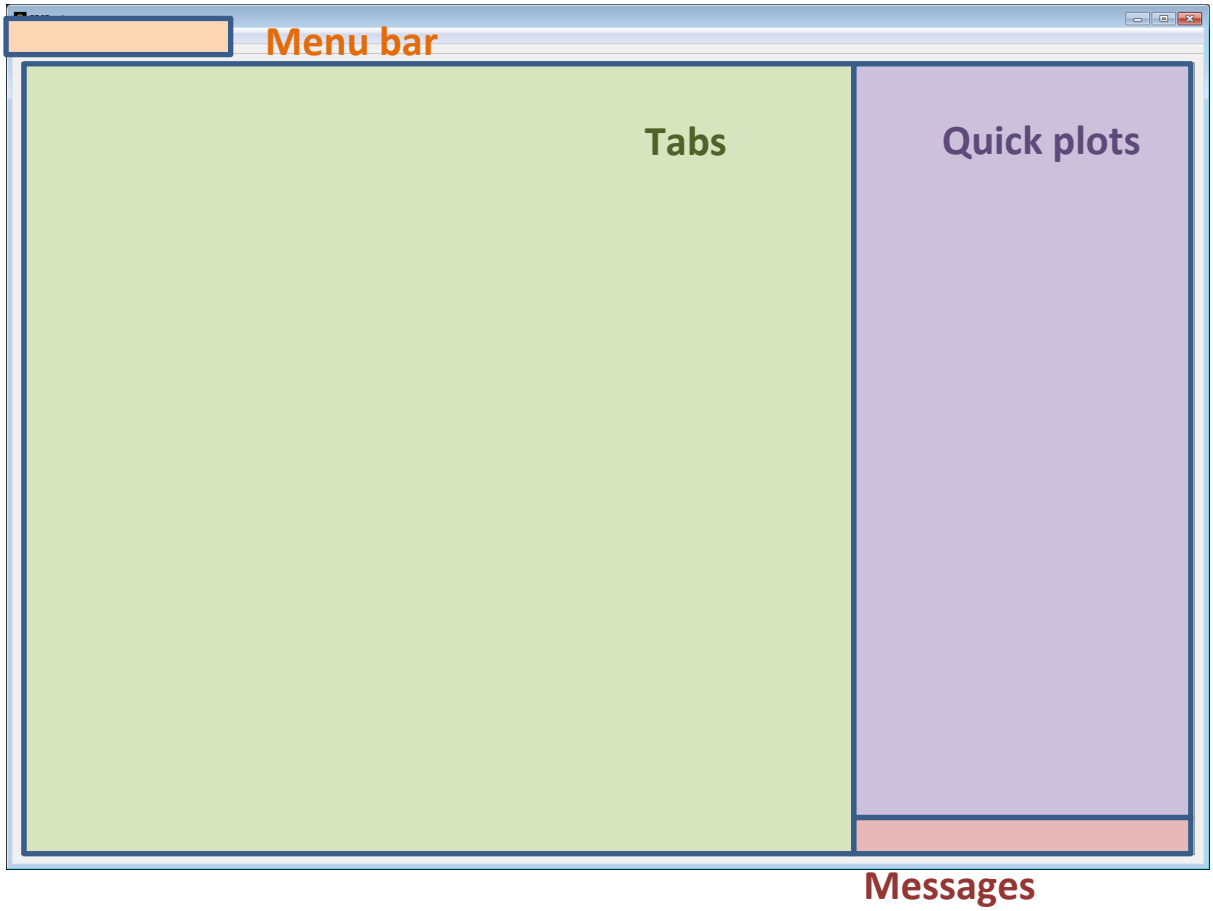
Before EPSRgui can be used, the directory to the EPSR binaries must be defined via the **Settings** menu, **EPSRgui settings** option. In the window that appears, click **Browse** on the *EPSR bin directory* line, navigate to the *EPSR/bin* directory and click **Choose**. The version of EPSR that is specified here

will be used for all projects, including simulations that have been imported and were previously created/run using a different version of EPSR.

To set a default directory for projects to be saved to, e.g. the EPSR run directory, click **Browse** on the *Default project directory* line, navigate to the *EPSR/run* directory and click **Choose**. Click **OK** to save the changes.

These defaults can be edited at any time, but an *EPSR/bin* directory must be specified in order to use EPSRgui. If the EPSR binaries folder is changed, then that setting is saved and the newly specified EPSR binaries folder will be used for all projects from that point forward (or until the setting is changed again).

3. Overview

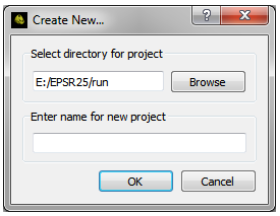


The EPSRgui main window is split into four sections. The Menu bar includes options to start or import a new project, run or stop a simulation, plotting, settings and access to the EPSR and EPSRgui manuals. The Tabs contain all the facilities to build and edit a simulation. The Quick plots enable rapid viewing of the simulation as it progresses. For more detailed plotting with additional options, use the Plot menu. The Messages area shows what is being done/has just been completed by EPSRgui and whether EPSR is running or not (for the current project). A more verbose output from the EPSR routines is given in the messages window accessed via the Settings menu.

4. Menu bar

4.1.File

4.1.1. Create new project

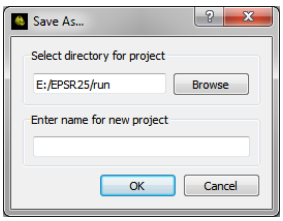


Creating a new project creates a folder that has the same name as the project. The project folder can be created in any directory but it is recommended that no "." are used in the directory name. A project file is also created in the project folder that has the same name as the project and has the extension .EPSR.pro. Key information about the project is automatically saved to this file so as the project can be re-opened later.

4.1.2. Open

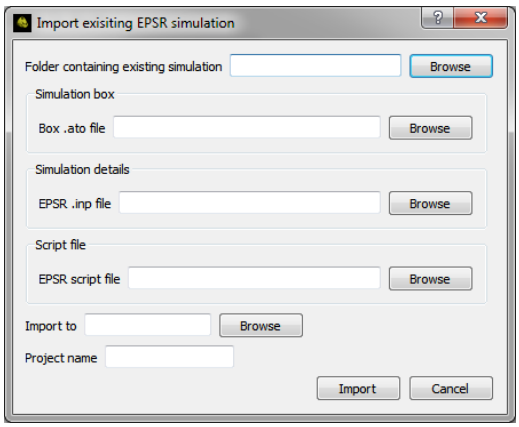
A project can be re-opened where it was last left by opening the .EPSR.pro file.

4.1.3. Save as



Save as enables the entire project to be copied to a new project name. The new project is then opened by EPSRgui.

4.1.4. Import



An existing EPSR simulation can be imported by specifying the folder containing the existing simulation and some key files: the simulation box .ato file, the EPSR input (.inp) file and the EPSR script file.

By default the simulation will be imported as an EPSRgui project in the original folder and keeping its original project name. To create an EPSRgui project of the simulation in a different directory, browse to a different directory in the *Import to* line (the EPSRgui project folder containing the simulation will be placed in this directory). This will leave the original simulation unchanged, but will make a copy of the simulation in a new folder and create an EPSRgui project for it. To change the name of the simulation, change the *Project name* line. This will create an EPSRgui project folder with the new name and containing a copy of all the files from the original simulation.

If an EPSR routine is then called via EPSRgui, the routine being used will be that determined by the *EPSR\bin* folder defined in **EPSRgui Settings** which will not necessarily be the same as that used to run the simulation before it was imported.

4.1.5. Exit

If an EPSR simulation is running, it should be stopped (see Section 4.3.3) and allowed to complete the final iteration before clicking **Exit**. If **Exit** is clicked while EPSR is running a warning message will appear advising this, as premature exit can cause problems on re-opening EPSRgui.

4.2.Edit

4.2.1. Delete simulation box

This will delete the simulation box .ato file, any weights files made and the .EPSR.inp and .pcof files if they have been created. This cannot be undone.

4.2.2. Delete EPSR input file

This will delete the .EPSR.inp and EPSR.pcof files only. This cannot be undone.

4.3.Run…

4.3.1. Run EPSR once

The values in the EPSR Input File tab are saved to the EPSR .inp and .pcof files and then EPSR is run for a single iteration only. Note that most things are not editable while EPSR is running. Once the simulation has been run once, the plotting windows become enabled. Any analysis routines listed in the **Running in EPSR** section of the **Analysis** tab will also be run once.

4.3.2. Run EPSR

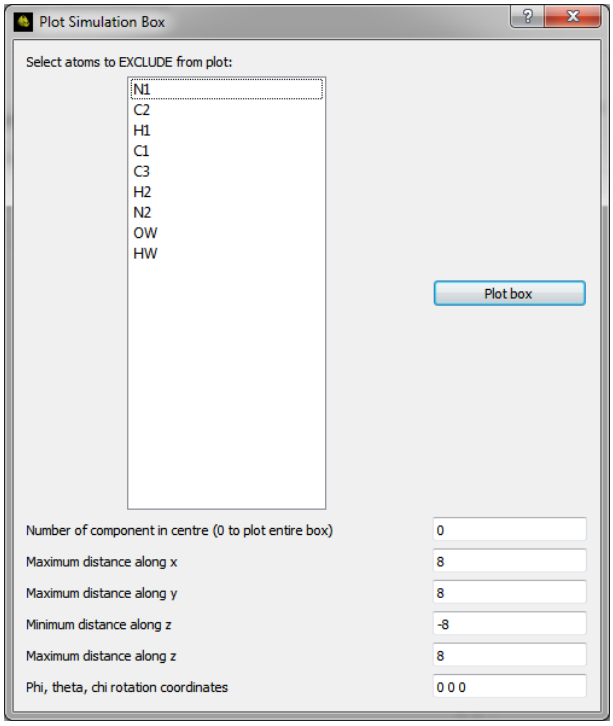
The values in the EPSR Input File tab are saved to the EPSR .inp and .pcof files and then EPSR will run iteratively until **Stop EPSR** is clicked. Note that most things are not editable while EPSR is running. Once the simulation has been run once, the plotting windows become enabled. Any analysis routines listed in the **Running in EPSR** section of the **Analysis** tab will also be run after each iteration of EPSR (unless defined differently in the analysis routine setup).

4.3.3. Stop EPSR

On clicking **Stop EPSR**, EPSR will stop once it has completed the current iteration. The ESPR .inp and .pcof files will be automatically reloaded into EPSRgui at the end of the last iteration.

4.4.Plot

4.4.1. Plot simulation box



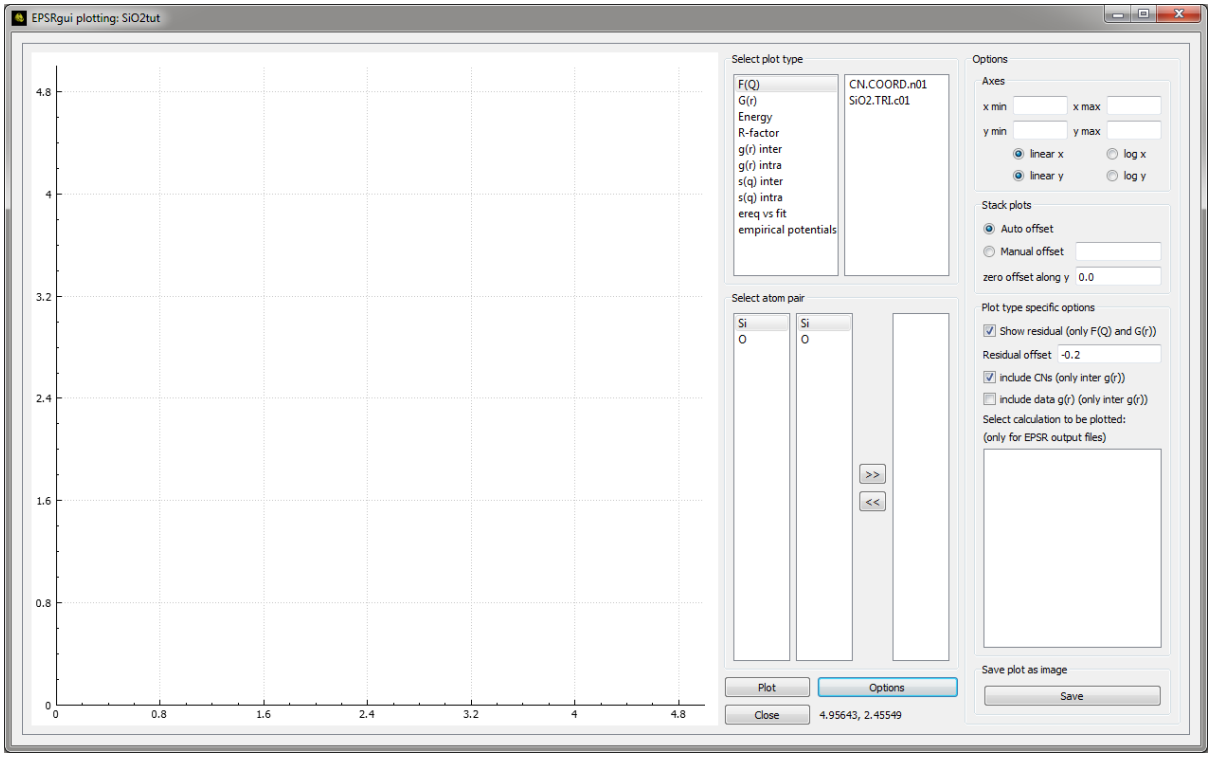
The **Plot Simulation Box** dialog window gives options as to which atoms and how much of the box to plot. The default setting on clicking **Plot box** is to plot the whole box with all of the atoms in it. This shows a snapshot of the current simulation and does not update as the simulation is running. It also creates a .xyz file which can then be opened in a different program.

To plot a subset of the box, click on the atoms to be excluded from the plot (use *Ctrl* to select multiple atoms) and click **Plot box**.

To plot only a part of the box, input the number of the component to be plotted in the middle of the box (this is according to list of components in the simulation box, e.g. if the list contains 40 Si atoms and then 80 O atoms, then the Si components will be 1 – 40 and the O components will be 41 – 120)

and then edit the distances along x, y and z to specify how much of the box is to be plotted. To rotate the box, edit the phi, theta, chi coordinates. Then click **Plot box**.

4.4.2. Plot data



The **EPSRgui plotting** window offers more capabilities than the Quick Plots and enables plotting of data from the simulation. In the **Select plot type** box, the first column enables plotting of the following parameters:

Plot type	*Description*
F(Q)	Experimental data (dots), simulated data (line) and difference (grey line).
G(r)	Fourier transform of experimental data (dots), simulated data (line) and difference (grey line).
Energy	Energy of the simulation in kJ / mol
R-factor	Calculated R-factor for the simulation
g(r) inter	Intermolecular/atomic pair correlation functions; requires atom pairs to be specified. Coordination numbers are included by default but can be removed from the plot in the **Options** menu. The g(r) calculated from the experimental data (depending on the isotopic contrasts, according to the method outlined in the EPSR manual) can be included in the plot using the **Options** menu.

g(r) intra	Intramolecular pair correlation functions; requires atom pairs to be specified.
s(q) inter	Intermolecular/atomic partial structure factors; requires atom pairs to be specified.
s(q) intra	Intramolecular partial structure factors; requires atom pairs to be specified.
ereq vs fit	The energy (amplitude) of the empirical potential plotted against the quality of the fit. This is only available for simulations run using EPSR24 onwards.
empirical potentials	Requires atom pairs to be specified.

To plot anything that requires a pair of atoms to be specified, first select the first atom of the pair from the first column of atoms and then select the second atom from the second column in the **Select atom pair** box. Then click the **>>** button to add the pair to the list of pairs to be plotted. Repeat this until all the pairs you want to plot are listed, then click **Plot**. To remove a pair from the list, click on it and then click **<<**.

In the second column of the **Select plot type** box, the output files for any analysis calculations that have been run are shown. For analysis routines with multiple calculations, the first calculation is plotted by default. To change this, see **Plot type specific options.**

Once the plot type has been selected (and any atom pairs added) click **Plot**. These plots do not automatically update, so click **Plot** again to update them.

To zoom and focus the plotting window:

Action	*Function*
Mouse roller button	Zoom in and out by equal amounts in the x and y axis.
Left click and drag	Drag the plot to a different area for viewing.
Shift + mouse roller button	Zoom in or out along the x axis only.
Ctrl +mouse roller button	Zoom in or out along the y axis only

For additional plotting options, click the **Options** button at the bottom right hand corner of the window. To hide the options menu click the same button again. The menu options are:

Option	*Description*
Axes	To set the axes limits, enter a number into the appropriate axis box – if the box is blank a default value will be used. To change between linear and log axes, click the log or linear buttons.

Stack plots For any multi dataset plots, the offset between the datasets in the stack plot can be automatically chosen (*Auto offset*) or chosen manually selecting *Manual offset* and entering an offset. This offset will be used between each of the datasets.

To shift all the datasets along the y axis (e.g. for use when plotting on a log scale), change the *Zero offset along y*.

Plot type specific options To show/hide the residual or difference curves for the F(Q) and G(r) plots, tick/untick *Show residual*. The offset of the residual with respect to the calculated and experimental datasets can also be specified.

For the intermolecular partial radial distribution functions (g(r) inter) the coordination number can be displayed/removed from the plot by ticking/unticking *Include CNs*.

For analysis routines with multiple calculations, the first calculation is plotted by default. To change this, first select the output file in the second column of the *Plot type* box, then select the appropriate calculation in the *Calculation to be plotted* list and click **Plot**.

Save plot as image The plot can be saved as a .jpg/.png/.bmp by clicking **Save**.

4.4.3. Plot using EPSRshell

This opens EPSRshell in a command prompt window which allows plotting using gnuplot. When finished, close the window by typing `q`. See the EPSR manual for more information.

4.4.4. Density plots

Once a density plot calculation has been setup and run (at least one iteration) with EPSR (see Section 9) the results can be plotted from this menu option. Select the plotting routine type from the list and then select the analysis routine name from the file browser in order to plot the density function.

4.5.Settings

4.5.1. EPSRgui settings

The Settings menu contains the EPSRgui settings which determine which version of EPSR is running. This must be set before EPSRgui can be used. Additional options such as a default directory for EPSRgui projects, or an alternative visualiser (that is compatible with EPSR .mol and .ato files) can also be set.

4.5.2. EPSR messages

View all the messages produced by EPSR while running an EPSR routine.

4.5.3. Project notes

Notes about the project can be made and saved along with the project for future reference.

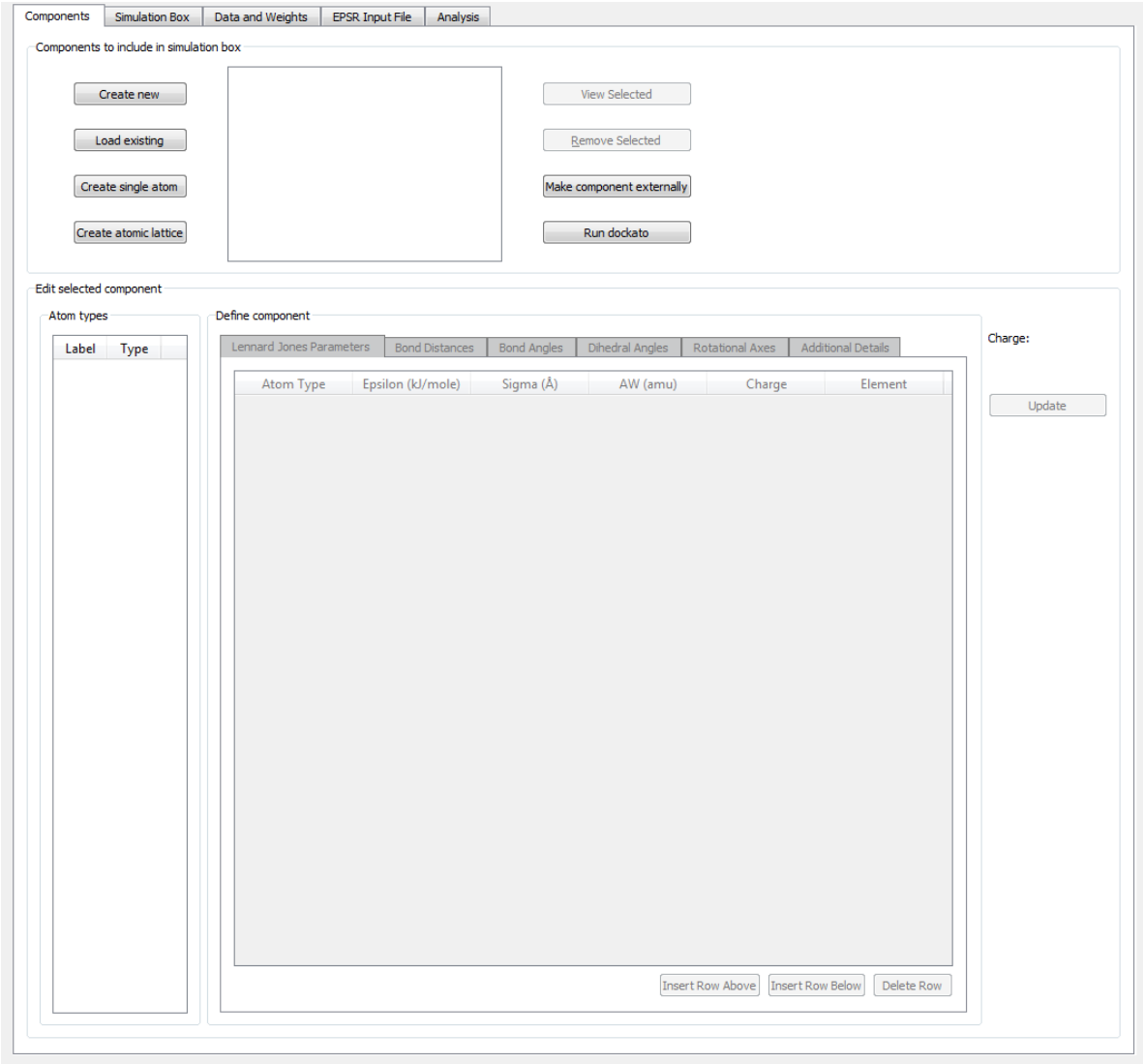
4.6.Help

4.6.1. EPSR manual

The EPSR manual opened is that associated with the binaries set in **EPSRgui Settings**.

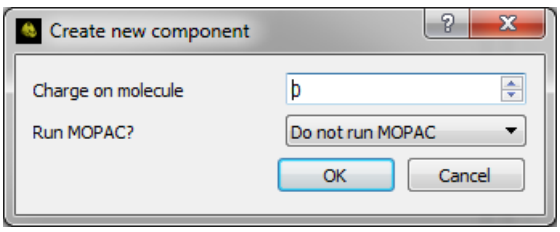
4.6.2. EPSRgui manual

5. Components tab



The **Components** tab is split into two sections – the first to build/load the atomic or molecular components that will be added to the simulation box, and the second to edit these components. Components are defined by an EPSR .mol file (this is a different format to an MDL .mol file which is not compatible with EPSR or EPSRgui) and an .ato file. EPSRgui offers a number of ways to build the components (atoms, molecules and lattices) to go into the simulation box, outlined below.

5.1.Create new



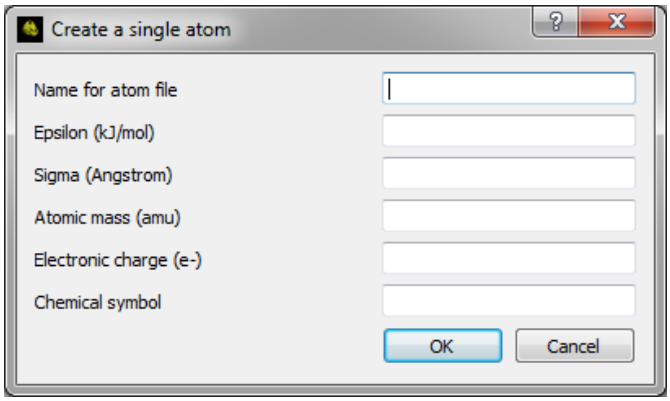
Create a molecule or single atom in Jmol and run MOPAC if desired (for Linux and Mac make sure MOPAC is installed and executable). Once the component has been created in Jmol , save as a .jmol

file. EPSRgui will then create an EPSR .mol and .ato file for the component and it will be added to the list of components. For more details on using Jmol, refer to Tutorial 2 in Section 11. Do not use a '.' within the filename of the new component.

5.2.Load existing

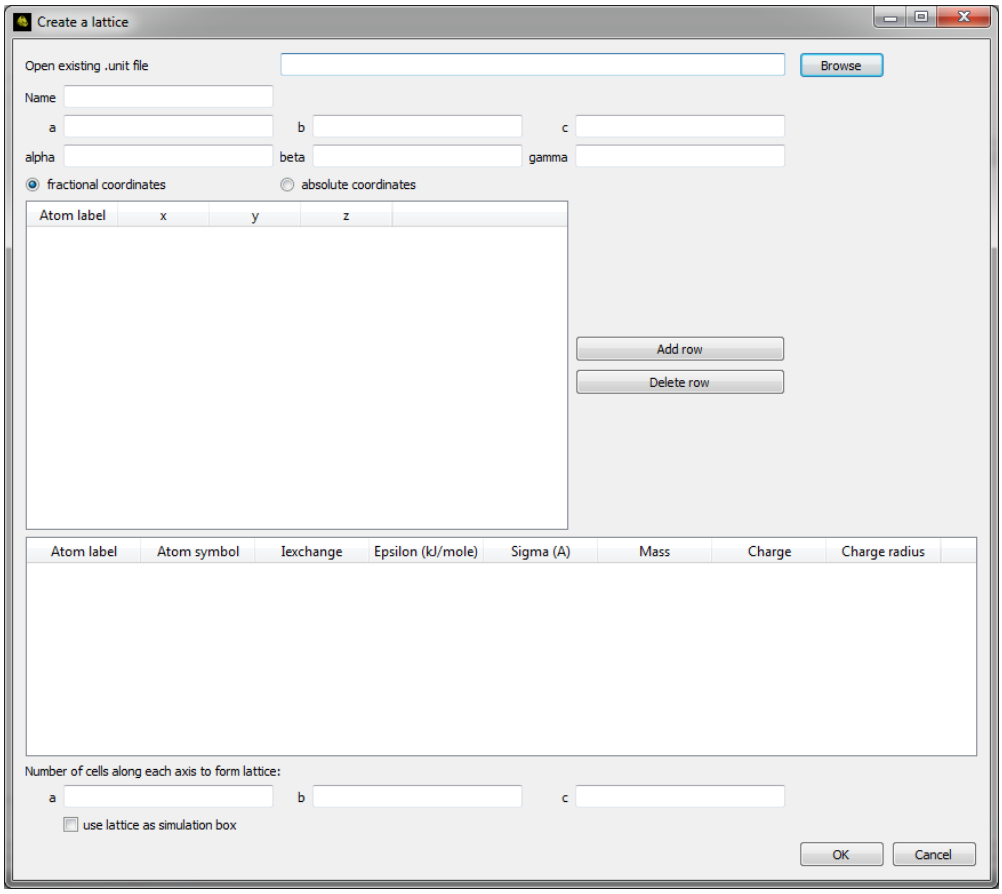
In the file browser that opens, navigate to the component .mol file and load it into the project. A copy of this component will be created in the project directory which is then used with the project. Any missing component .ato files will also be created during this process.

5.3.Create single atom



Complete the fields in the dialog box to create a single atom. Note that EPSRgui does not check feasibility of the values entered so double check them after input.

5.4.Create atomic lattice



An atomic lattice is generated from an existing EPSR .unit file and/or by filling out the fields in the dialog box. The lattice can be used as the simulation box or as a component. If used as a component, note that the component does not have a .mol file, only a .ato file in this instance only.

5.5.Make component externally

This can be used to generate any component within the capabilities of the software specified by the *Alternative visualiser* in **EPSRgui Settings**. Remember to save the component as an EPSR .mol and also an .ato file of the same name as both of these are used in EPSRgui. Once the component has been saved, use **Load existing** to add the component to the project.

5.6.Run dockato

This is currently not implemented.

5.7.View selected

Once a component has been created/loaded into the project it can be viewed by clicking **View selected**. Jmol will be used to view the component unless an *Alternative visualiser* has been set in **EPSRgui Settings**.

5.8.Remove selected

To remove a component from the project click **Remove selected**.

5.9.Edit selected component

Once a component has been loaded into EPSRgui, its Lennard-Jones potential and charge can be edited together with various molecular constraints such as bond distances, angles and rotational groups. It is imperative to click **Update** after making any changes in order for the changes to be saved to the component. If another component is selected from the list before clicking **Update**, any changes made to the previous component will be lost. If the simulation box has already been created, any changes made to the components (via the **Components** tab) must be applied to the simulation box by clicking **Run fmole** in the **Simulation Box** tab (see Section 6). The number of iterations is dependent on the system and the changes made. For more details on fmole refer to the EPSR manual.

For newly created components, the Label column in the *Atom Types* table shows the unique number for each atom in the component which cannot be changed. To check which atom is which within the molecule, click **View Selected** and then show labels. For molecular components, these numbers are used to define the atoms involved in bond distance, bond angle and dihedral angle restraints and rotational axes. They are also used in a number of the Analysis routines (see Section 9). In the *Atom Types* table, each of the atom *Label*s is assigned a *Type* which is the name given to an atom or group of atoms and is used to associate a Lennard-Jones potential with a particular atom or group of atoms. Only atoms in very similar environments should be grouped together. The name can be changed to anything containing letters or numbers between one to three characters long where the first character is a letter and is a capital. When editing the atom *Type*, it is very important to also change the atom *Type* in the *Lennard-Jones potentials* tab (see below). For systems with multiple components, the same atom *Type* cannot be used in more than one component.

For old components the Atom Types table may be blank. If this is the case, the Type for each atom in this component and the number of Lennard-Jones parameters cannot be changed via EPSRgui. The bond distance and bond angle restraints will be defined using the atom Type as the atom name. The dihedral angles and rotational axes will be defined using the numerical label for each atom which can be seen by selecting the component in the list and clicking View Selected and then selecting show labels.

In the Define Component box, there are a number of tabs, all of which can have rows inserted/removed using the **Insert Row Above**/**Insert Row Below**/**Delete Row**/**Delete All** buttons:

Tab Name	*Description*
Lennard-Jones potentials	Each different atom Type defined in the Atom Types table (not for old .mol files, see above) must have an equivalent atom Type in the Lennard-Jones potentials table – this can be appropriate for a single atom or group of atoms in a very similar environment. If the atom Type is renamed in the Atom Types table, it must also be renamed in the atom Type column of the Lennard-Jones potentials table. Additional/superfluous atom Types and

their Lennard-Jones parameters can be added/ removed as needed. The values for the Lennard-Jones potential, atomic weight, charge and element can all be edited. An atomic weight of 2 is generally used for H and D. Click **Update** to save any changes. The overall *Charge* of the component is given above the **Update** button – it is recalculated when **Update** is clicked.

Bond distances Distance between a specified pair of atoms (using the atom *Label* if present, otherwise using the atom *Type*) in Å.

Bond angles Angle between a specified triplet of atoms (using the atom *Label* if present, otherwise using the atom *Type*) in degrees.

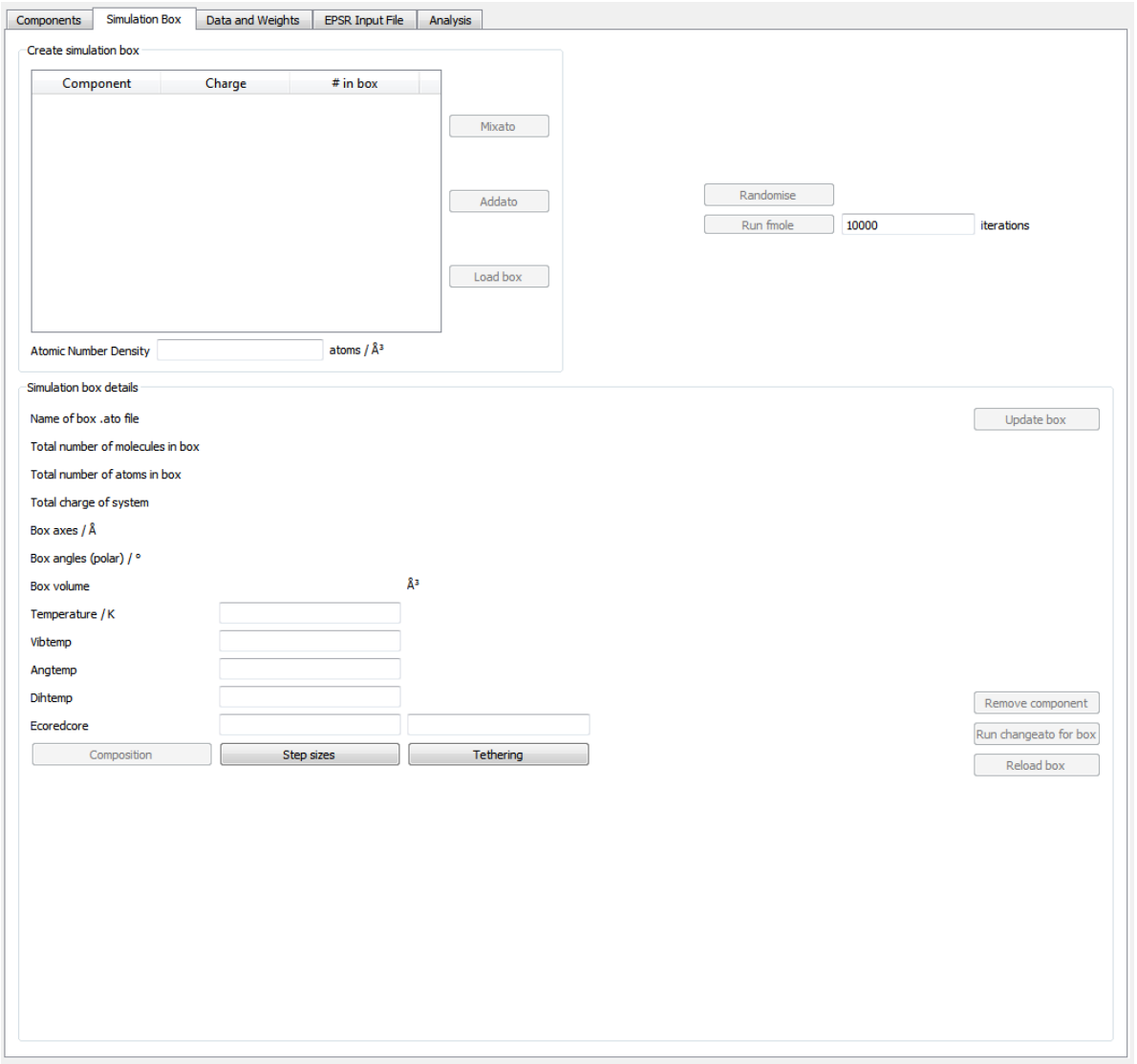
Dihedral angles Angle between two planes defined by two pairs of atoms (always using the numerical atom Label).

Rotational axes Axis about which the component can rotate, defined by a pair of atoms (always using the numerical atom Label).

Additional details if opening an existing component with an old-style .mol file where all the atoms are positioned on 0,0,0 (check this by clicking **View selected** - if you see only one atom when you should see more then it is an old-style .mol file) you will need to click **Run fmole on component**. This implements all the bond and angle etc restraints that are in the .mol file. You can then check the molecule looks as it should by clicking **View Selected** again.

For components that will be the container when using **Addato**, the size of the container can be seen – to change the size and/or shape of this box, click **Run changeato for selected file** – this will run the EPSR routine changeato within a command prompt/terminal window. After changes have been made, type `e` to exit and save. If the component needs to be tethered, tick **Tethered?** and input the number for the tethering atom (use 0 for the centre of mass of the component), the tethering tolerance (a small number is more tightly tethered) and the tethering origin coordinates (use 0.0 0.0 0.0 for the centre of the box). Then click **Update** to implement the changes

6. Simulation Box tab

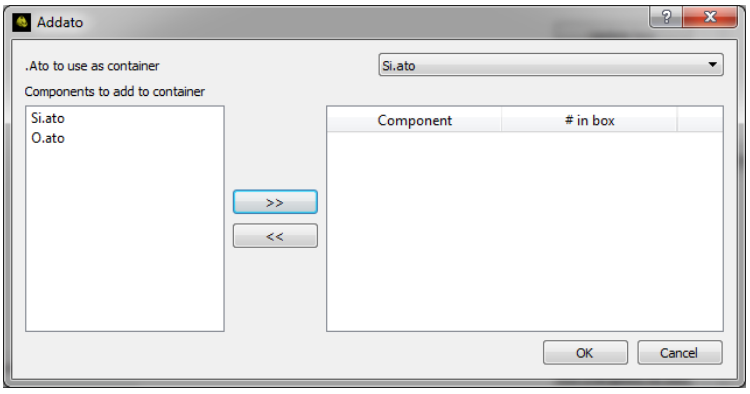


The **Simulation Box** tab is used to create the box, make changes to the box parameters and, after the box has been created, implement any changes made in the **Components** tab to all the components in the box. In the top left hand corner, there is a table of all the specified components and four methods to create/place the components in the simulation box. Remember to make the box size big enough (by adding sufficient components to the box) so as half the length of the box is larger than the largest g(r) to be studied.

6.1.Mixato

This puts the specified number of each component at the centre of a box that is of a size determined from the atomic number density. Note that all the molecules are positioned on top of each other and have their starting conformation therefore it is necessary to click **Randomise** to distribute the components randomly around the box and then click **Run fmole** (e.g. 10,000 iterations). Fmole runs in an external window so the simulation can be prepared further while it is running.

6.2.Addato

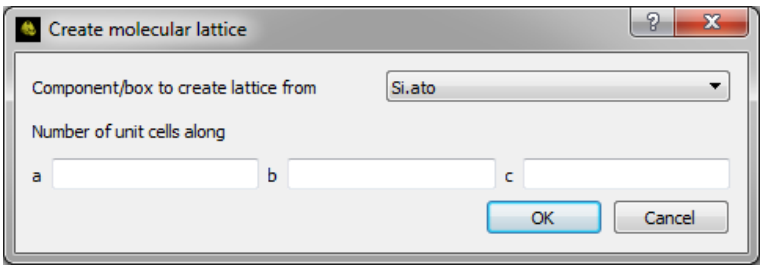


This adds the number of each component specified in the '# in box' column to the container specified in the dropdown list. The size of the container determines the size of the resulting simulation box. The atomic number density is calculated after the box has been built. Note that there can only be 1 component per .ato file in the .ato files to be added to the container. The components are added at random to the container. If a component in the container is tethered, its epsilon and sigma are used together with the epsilon and sigma of the added component(s) to determine the distance at which the nearest components can be added, thus preventing overlap of the tethered container components and the added components. If there is not enough space to add all of the added components, then some will be missed out. The final number of components added will be shown in the composition window which opens when Addato has finished. If Addato is completely unsuccessful and could not find enough space to add any of the components to add, the process is aborted and an error message is shown.

6.3.Load box

Loads a simulation box .ato file made elsewhere. Make sure the names of the .mol files are at the bottom of the box .ato file (in place of moltypeXX) so that changes made to the .mol files are implemented to the box on running fmole. Rename the box .ato file to *<projectname>*box.ato, click **Load box** and select the box .ato file. If the box .ato file is in a different directory it will be copied to the current project directory. Ensure the component files are present in the project directory before starting **Load box** – they will be automatically loaded into the project when **Load box** finishes.

6.4.Create molecular lattice



In the dialog box that opens, select the component or box .ato file to be expanded a specified number of times along each axis. The lattice is then used as the simulation box. Only one component can be made into a lattice; to add additional components to the simulation box, use **Addato**.

6.5.Simulation box details

Once the simulation box has been created, details about it are given in the lower half of the **Simulation Box** tab. Default values are used on creating the box - to make changes to the simulation settings, change the following values and then click **Update box**:

Parameter	*Description*
Temperature	Temperature the data were collected at. Default 300.
Vibtemp	Degree of bond distance restraint; default 65 is usually appropriate. Increase value to increase rigidity (or vice versa). **Run fmole** after **Update box**.
Angtemp	Degree of bond angle restraint; default 1. Linked with Vibtemp therefore an increase in Vibtemp will also increase the rigidity of bond angles. Use a larger value to increase bond angle rigidity without increasing bond distance rigidity (or vice versa). **Run fmole** after **Update box**.
Dihtemp	Degree of dihedral angle restraint; default 10. Linked with Vibtemp therefore an increase in Vibtemp will also increase the rigidity of dihedral angles. Use a smaller value to decrease dihedral angle rigidity without decreasing bond distance rigidity (or vice versa). **Run fmole** after **Update box**.
Ecore	Energy for intramolecular distance restraint; 0 means not used, >0 means the distance specified in dcore will be implemented.
Dcore	Minimum intramolecular distance between atoms in Å; requires a non-zero ecore value to be used.
Step sizes	View and edit the step sizes used to move components during EPSR (Å) by clicking the **Step sizes** button.
Tethering	Any tethered components in the box is tethered are shown on clicking the **Tethering** button. To un-tether a component, type F in the *Tethered?* column and delete the text in the *Tether atom* column. To tether a component, type T in the *Tethered?* column and type 0 (zero) in the *Tether atom* column to use the centre of mass of the component, or the numerical atom label to specify an atom as the point to tether. Type a small number for the *Tethering tolerance* (e.g. 0.1; the smaller the number, the stronger the tethering).

After the simulation box has been created, if any changes are made to the components in the simulation box (via the **Components** tab) it is necessary to **Run fmole** to apply the changes to all the

components throughout the box. The number of iterations is dependent on the system and the changes made. For more details on fmole refer to the EPSR manual.

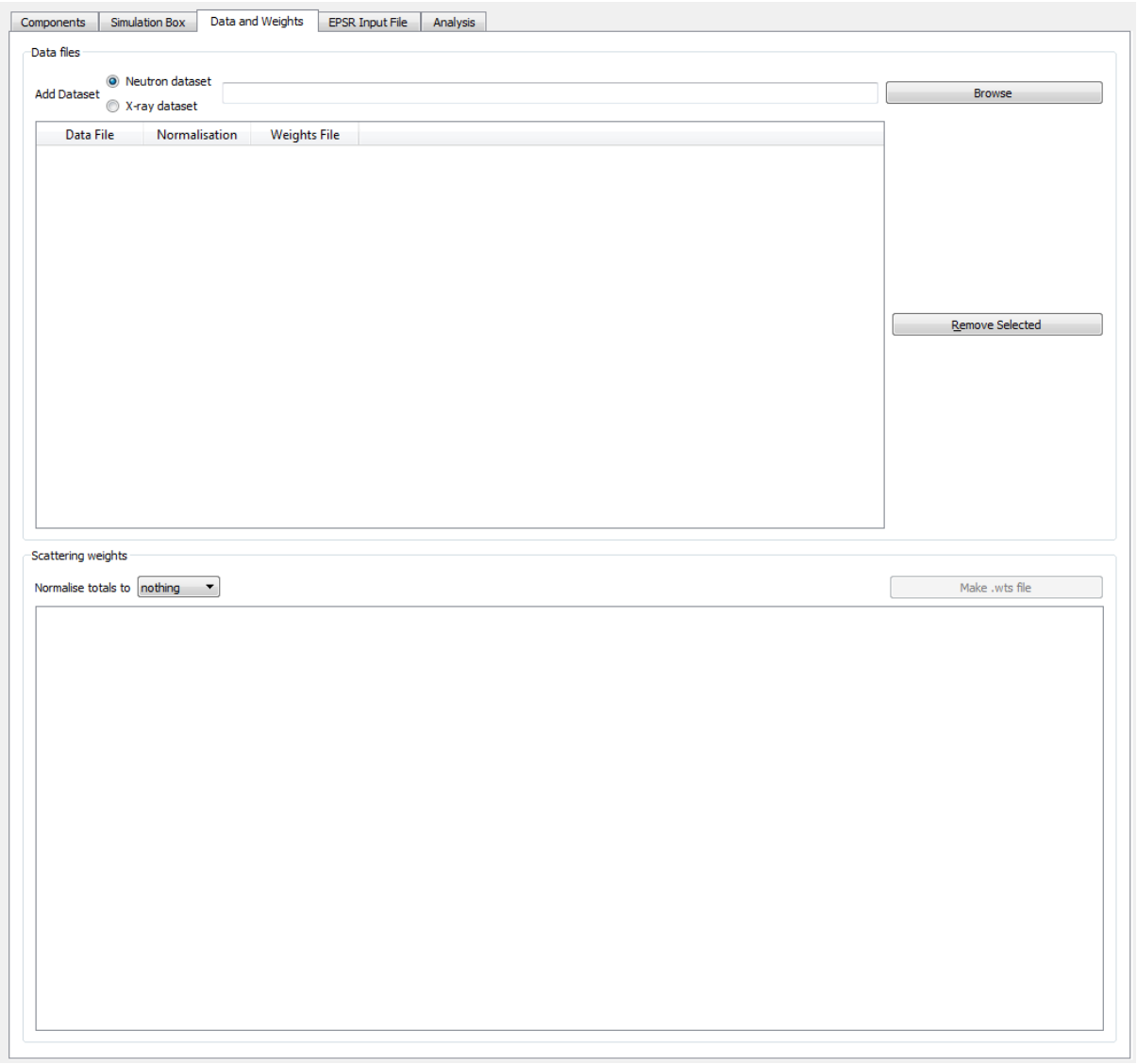
Composition shows the number of each atom type present in the simulation box.

Reload box reads the simulation box file and refreshes the parameters listed in the Simulation box details section; use after **Run changeato for box**.

Remove component removes a single specified component from the simulation box. If weights files already exist for the simulation box and then a component is removed, it is imperative that the scattering weights files are remade (see Section 7) before proceeding with the simulation.

For any additional changes not listed here, click **Run changeato for box** - note that this will run changeato in a command prompt/terminal window.

7. Data and Weights tab



In the **Data and Weights** tab the data files that the simulation box will be refined to are added to the project. Details about the sample that each dataset was collected from are inputted and the associated scattering weights files are prepared in accordance with this information. The weights files are used to calculate the 'theoretical' structure factor equivalent to each dataset for the simulation box.

7.1. Data files

The first section of the **Data and Weights** tab is concerned with adding datasets to the project; the first parameter that needs to be specified is whether the dataset was collected using neutrons or X-rays. On clicking **Browse**, EPSRgui will show the default files produced by GudrunN and GudrunX (.mint01 and .int01 respectively) depending on the radiation selected. For other file types, use the dropdown menu in the **Browse** window to show all file types (*.*). EPSRgui will copy data files into the project folder as necessary; the data file used in the project is the one in the project folder. By default, EPSRgui assumes the data file is in the Gudrun format; if the data file was not produced by

Gudrun, refer to the EPSR manual for each of the file types and then edit the *Edit data files* tab in the **EPSR Input File** tab once the EPSR input file has been created (Section 8.2).

7.2.Scattering weights

In the second section of the **Data and Weights** tab, the scattering weights files are created and edited. For neutron data, Gudrun normalises the data to a standard scatterer by default and then offers additional options to normalise the data further to $\langle b^2 \rangle$ or $\langle b \rangle^2$. Therefore, if standard Gudrun processing for neutron data has been used then select 'nothing' in the *Normalise totals to* drop box. For X-ray data, select the normalisation method used during data correction and processing.

In the *Scattering Weights* table, the *Atom Types* column contains a list of the each atom type present in the simulation box (these atom types are the same as those in the **Components** tab, but are for all of the components in the simulation box). For X-ray data, independent atom form factors are applied automatically so the weights file can be made immediately by clicking **Make .wts file**. For neutron data, further details about the sample that the dataset were collected from need to be inputted. For a sample containing hydrogen atoms, exchangeable hydrogen atoms are specified by typing '1' in the *Exchangeable?* column (use '0' for non-exchangeable). Neutron data also require the isotope of each atom type to be defined. The following table illustrates how this is done for hydrogen atoms:

	Isotope	Abundance	Isotope	Abundance
All natural hydrogen	0	1		
All deuterium	2	1		
50:50 H:D	0	0.5	2	0.5

Atom types that are natural abundance isotopes are always represented by '0' in the first *Isotope* column and '1' in the first *Abundance* column. Once all the details about the sample have been inputted, click **Make .wts file**. This will show the normalisation code in the *Normalisation* column in the *Data Files* table and the name of the weights file in the *Wts File* column. If the *Wts* File column is empty, the weights file has not been created. To make changes to the scattering weights for a particular dataset, click on the dataset, make any changes in *Scattering Weights* table and then click **Make .wts file**. Any changes made are not saved until the **Make .wts file** button is clicked.

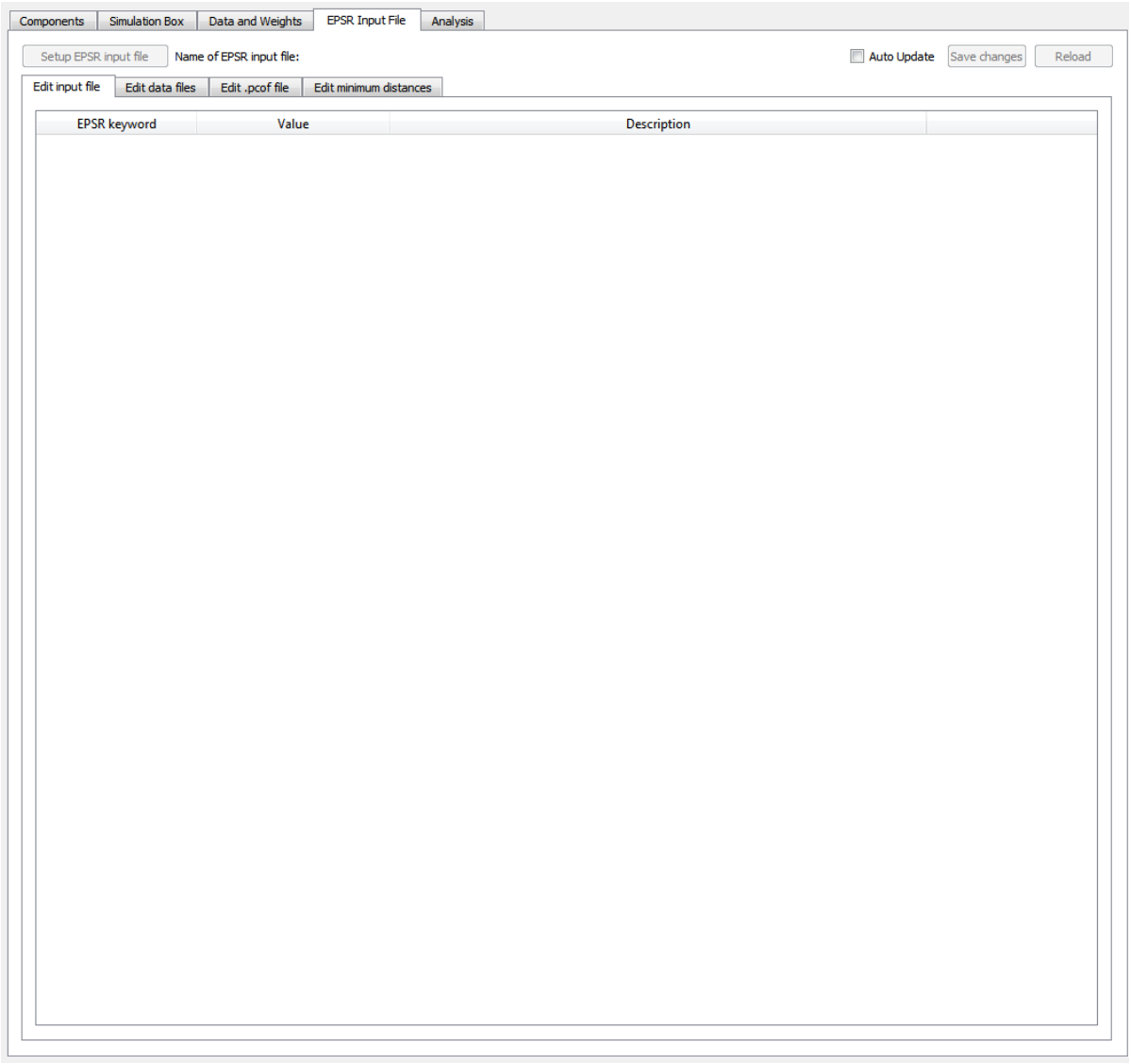
To remove a dataset before the EPSR input file has been created, click **Remove selected**.

If a scattering weights setup file already exists for a dataset that is added, a message will appear asking whether to make a new scattering weights setup file or to overwrite the existing weights setup file. If no changes have been made to the composition of the simulation box, an existing weights setup file can be used, but to be certain that the weights file produced is consistent with the simulation box, it is recommended that a new scattering weights setup file is created.

All of the datasets added to the **Data and Weights** tab will be used when creating the EPSR input file. If a change is made to the weights files after the EPSR input file has been created, use ireset and iinit in the EPSR input file to reset and re-initialise the simulation as the weights files need to be read in

again before continuing. If an additional dataset needs to be added after the EPSR input file has been created, the EPSR input file must first be deleted (Section 4.2.2) before the dataset can be added and the EPSR input file re-created (Section 8). If a dataset needs to be removed after the EPSR input file has been created, either first delete the EPSR input file (Section 4.2.2) or change the EPSR input file to not refine to the dataset (Section 8). This method can also be employed when using a dummy dataset that the simulation box is not refined to, but the structure factor from the simulation box is still calculated.

8. EPSR Input File tab



In the **EPSR Input File** tab, the EPSR input file can be created in accordance with all of the parameters detailed in the previous tabs by clicking **Setup EPSR input file**. Any changes made in this tab are automatically saved on running EPSR, or can be saved manually by clicking **Save Changes**. It is not possible to make changes to this tab while EPSR is running. To see any changes to the EPSR input files while EPSR is running click **Reload**. To automatically show changes to the EPSR input file while EPSR is running tick **Auto update**. Once EPSR has stopped, the latest changes to the EPSR input file are shown automatically.

8.1.Edit input file

The EPSR input file contains information about the simulation as well as parameters used to run different aspects of the simulation. Of particular importance are:

Parameter	*Description*
ireset	'1' by default when starting the simulation. If changes to the weights files are made, change to '2' before restarting the simulation. To use ereqstep, change to '2' for the first iteration.
iinit	'1' by default when starting the simulation. It generally is left at '0' after this unless the simulation is completely reset ('ireset 1').
sizefactor	The first value represents the factor the box size is multiplied by and is used to expand the box if one of the components is particularly bulky or contains a ring. This allows the components to move around the box so as their atoms are not overlapping before the box size is reduced to normal size over successive EPSR iterations.
ereq	The amount of energy given to the empirical potential to overcome the reference potential. '0' means the empirical potential is not refined. A non-zero number means the empirical potential is refined. The size of ereq is dependent on the system being studied and can be changed manually or refined to an optimum value using ereqstep.
ereqstep	'0.0' means ereqstep is not used. To refine ereq to provide the best fit of the simulation box (model) to the data, change ereqstep to '1.0' and change ireset to '2'. Run EPSR. The value of ereq will increase by a step size dependent on the values of sfreq (see below) for an initial assessment before moving on to automatic adjustment of ereq. To stop refining ereq, change ereqstep back to '0.0'.
sfreq	The first value is the number of iterations performed while EPSR performs an initial assessment during which the empirical potential is increased to a number of multiples of kT defined by the second value of sfreq. Increase the second value of sfreq when larger values of ereq are required in order for the empirical potential to have any effect on the simulation. If changing the second value of sfreq after having already started refining the empirical potential, also change iinit to '1' before restarting the simulation. This will use the existing empirical potential as a starting point and will perform the initial assessment followed by automatic adjustment from this point. To reset the empirical potential back to zero and start the initial assessment followed by automatic adjustment from zero, set ireset to '2'.
nsumt	Once the simulation has been improved as much as possible, each frame from each iteration of the simulation can be accumulated to build an average model of the simulation box. '-1' means frames are not being accumulated. Use '0' to start accumulation. The number given in the *Value* column after accumulation has started then shows the number of frames accumulated.

Further information on refining the empirical potential is given in the Tutorials (Section 11) and in the EPSR manual. See Tutorials 5 and 6 (Section 11) for more information on parameters that need to be changed in order to calculate Bragg peaks for samples with long range order.

8.2.Edit data files

The keywords of importance in this tab are:

Parameter	*Description*
nrtype	Default is '5' for data corrected and processed in Gudrun. See EPSR manual for code to use with alternative available formats.
efilereq	Use '1.0' to refine to the dataset, use '0.0' to not refine to the dataset and just calculate the structure factor from the simulation box according to the scattering weights and radiation detailed in the **Data and Weights** tab.
szeros	The minimum Q value for the data; '0.0' means use the first point in the dataset, a non-zero value will be used as the Q_{min}.
rshmin	The minimum r value for background subtraction prior to the fourier transform. Generally, for hydrogen containing systems, 0.7 Å is appropriate as it does not clip the first peak for the X-H bond.

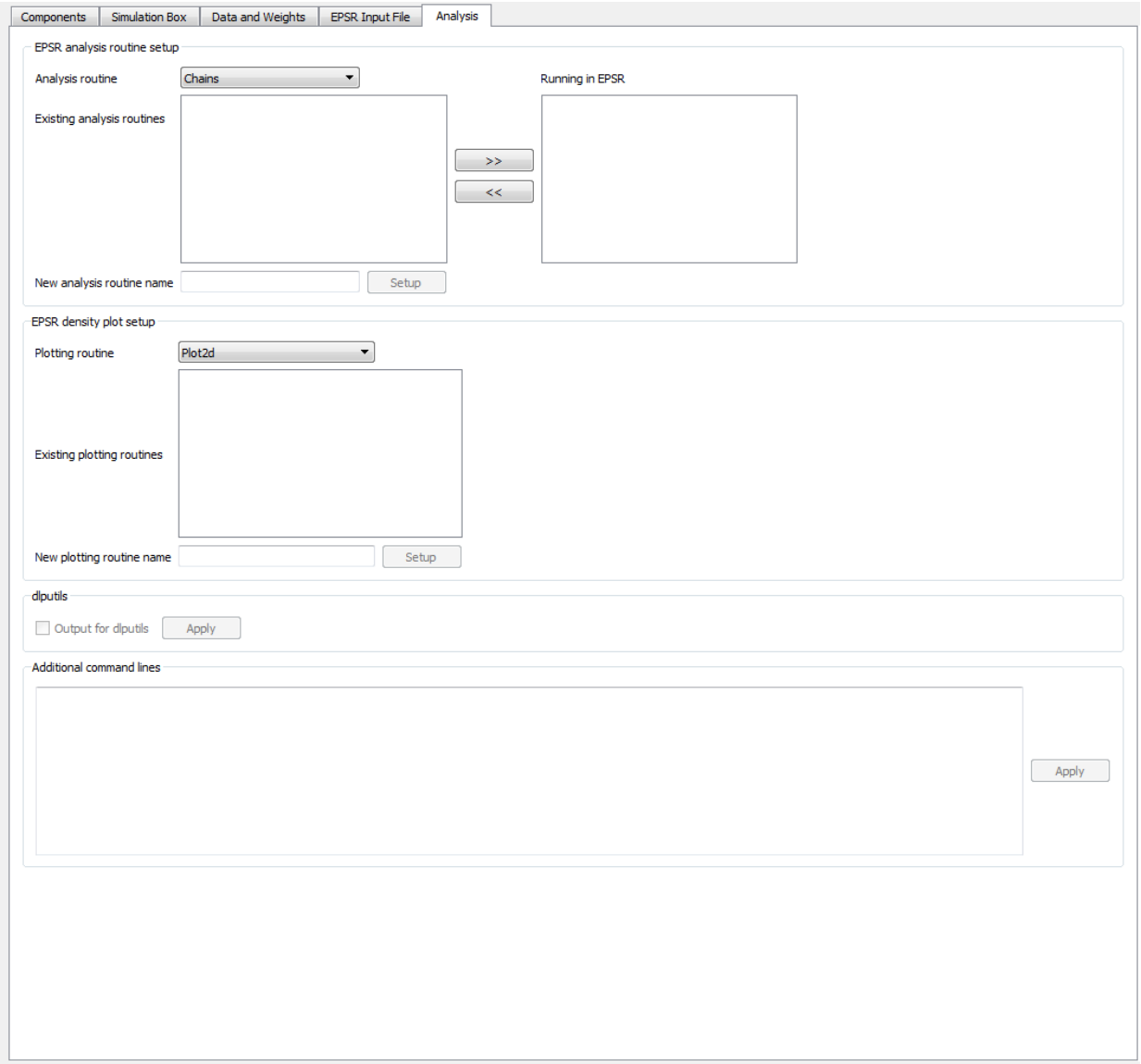
8.3.Edit .pcof file

The pcof file contains information regarding how the reference and empirical potentials are manifested in the simulation and is generally for more advanced settings. See Tutorials 5 and 6 (Section 11) for more information on parameters that need to be changed in order to calculate Bragg peaks for samples with long range order.

8.4.Edit minimum distances

The minimum intermolecular distances between pairs of atom types can be specified in Å. This can be used to prevent atoms from approaching too closely when just using their Lennard-Jones parameters and charges.

9. Analysis tab



The **Analysis** tab enables analysis routines and density function plots to be setup once the simulation is a good fit to the data. To do this, EPSR must first be stopped, analysis routines that are added to the *Running in EPSR list* will then run while EPSR is running.

9.1.EPSR analysis routine setup

Here, each of the *Analysis routines* outlined in the EPSR manual can be setup. Refer to the EPSR manual for more information regarding what each routine does. After selecting a routine type in the *Analysis routine* dropbox, input a name for a new routine in the *New analysis routine line* and click **Setup**. In the window that appears, fill in the details about the routine. For a routine that can have more than one calculation, use the **Add calculation** button to add more calculations, and the **Remove calculation** button to remove the calculation. Click on the calculation in the list to view and edit its parameters. Once finished, click **Save**. The routine will now be listed in the *Existing routines* list in the *EPSR analysis routine setup* box. To make changes to the routine, select it from the list and click **Setup**. To cancel the changes click **Cancel**. To cancel and delete the routine click **Cancel and**

Delete (this cannot be undone). To add the analysis routine to be run while EPSR is running click the **>>** button (stop the routine from being run using **<<**). Note that if any changes are made to the routine after it has been run in EPSR, then nsumt for the routine should be changed to '0' as otherwise part of the calculation will be done using one set of values and the other part using a different set of values. The results from the analysis routines can be viewed using Plot data in the Plot menu on the Menu bar (see Section 4.4.2).

9.2.EPSR density plot setup

Here, the plotting routines which offer the tools to plot a density function calculated using an analysis routine can be setup (the analysis routine must first have run for at least one iteration before the plotting routine can be setup). After selecting a routine type in the *Plotting routine* dropdown menu, input a name for a new routine in the *New plotting routine* line and click **Setup**. In the window that appears, fill in the details about the routine. Once finished, click **Save**. The routine will now be listed in the *Existing routines* list in the *EPSR plotting routine setup* box. To make changes to the routine, select it from the list and click **Setup**. To cancel the changes click **Cancel**. To cancel and delete the routine click **Cancel and Delete** (this cannot be undone). To run the plotting routine, click Density Plots in the Plot menu on the Menu bar and select the plotting routine type (see Section 4.4.4).

To write an accumulated file of many frames of the simulation for analysis with the dlputils package, tick *Output for dlputils* and click **Apply** to write the .xyz file while also incrementing nsumt in the EPSR input file.

9.3.Output for dlputils

Ticking this box writes an .xyz file (called <*project name*>boxappend.xyz) that contains the atom positions for all of the atoms in the box for every frame of the simulation that is run while the box is ticked. This is a large file that is for use with the *dlputils* package (https://www.projectaten.com/dlputils).

9.4.Additional commands

In the *Additional command lines* box, extra commands can be included that will run after each EPSR iteration. These should be written in the command line format for Windows or the shell terminal format for Linux and Mac. Click **Apply** to include them while running EPSR.

10. Methodologies

The following are some example methods that can be used to create a variety of different systems from simple liquids to porous materials:

- Simple liquid
  - Create/load component
  - Mixato
- Network glass
  - Create/load component
  - Mixato
- Network glass from lattice
  - Makelattice – tick 'use as simulation box'
  - Change 'Tethered?' to 'f' in tethered components table, Simulation box details
- Molecular glass from lattice
  - Create component .mol and .ato and lattice .ato in external software and save to project folder
  - Ensure component is listed at bottom of lattice .ato file
  - Load box
  - If necessary, untether in Simulation box details
- Crystalline porous material
  - Create lattice .mol and .ato in external software
  - Load box
  - Tether lattice in Simulation box details
- Loaded crystalline porous material
  - Create lattice mol and ato in external software
  - Create/load .mol file for added molecule
  - Addato (using lattice as container)
- Amorphous porous material
  - Make a lattice of Q points

  - Create/load components for amorphous material
  - Addato (using Q lattice as container)
- Loaded amorphous porous material
  - Follow above method and refine to data to make the amorphous porous material
  - Create/load components for loaded molecules
  - Addato (using box as container)
- Liquid with nanoparticles present
  - Create lattice .mol and .ato in external software, and increase the box size to produce the correct density of the final system.
  - Create/load the liquid component
  - Addato (using the lattice as the container)

11. Tutorials

In the following pages there are two glass tutorials and two liquid tutorials. It is recommended to work through them in order as the later tutorials are more of a guide than step-by step instructions.

Data for the tutorials are found in the Resources folder in the EPSRgui distribution.

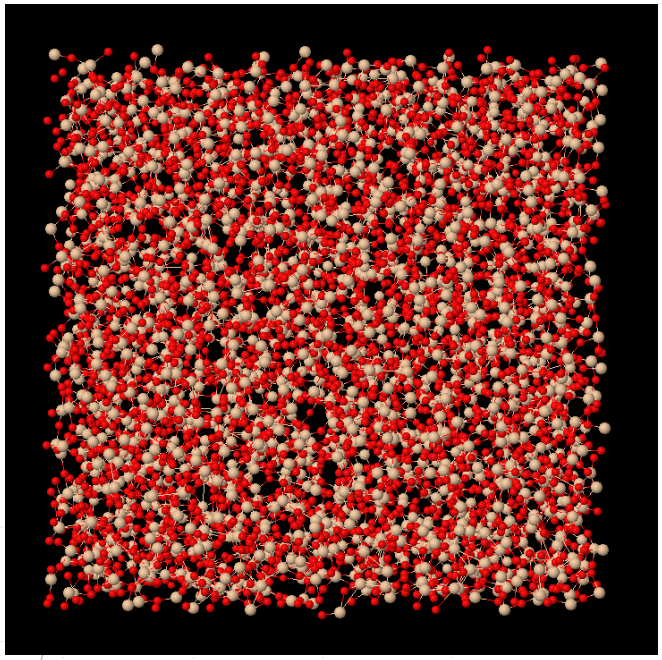
SiO_2

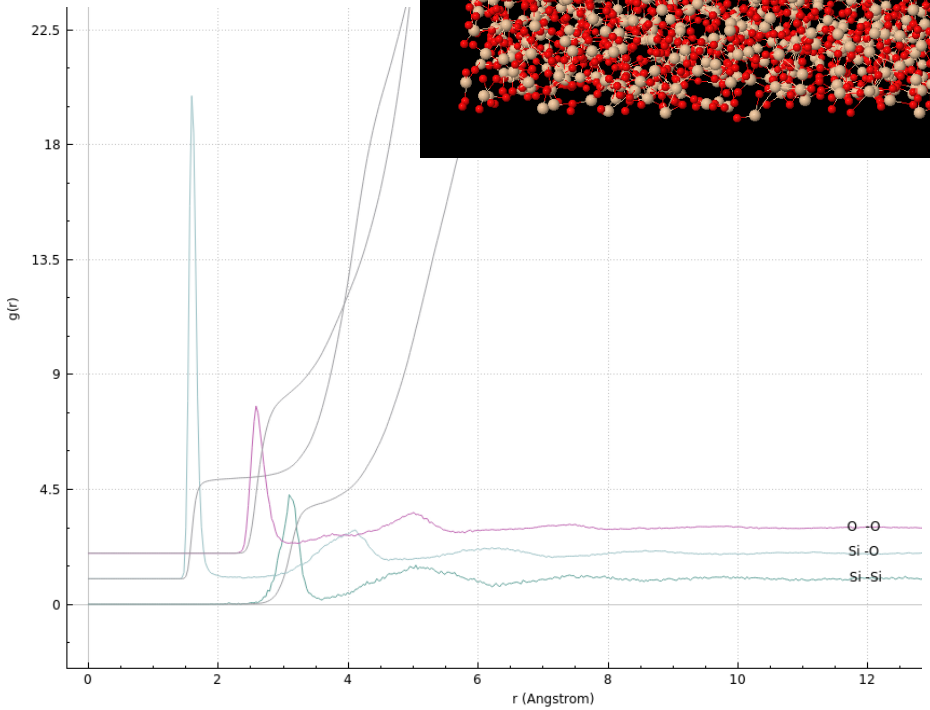
EPSRgui tutorial 1

Purpose of this tutorial

The goal of this tutorial is to build, refine and analyse a model of a simple oxide glass, SiO_2. To achieve this, the tutorial will cover how to:

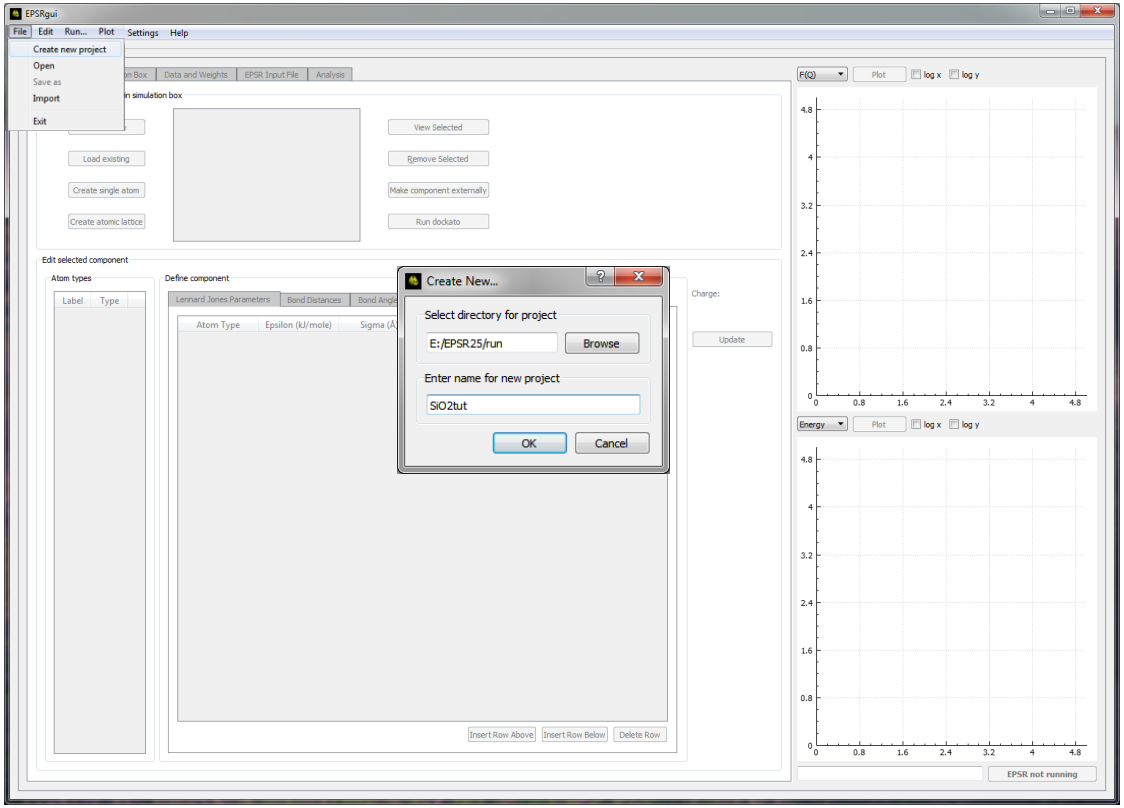
- Create the atomic components and define their Lennard-Jones potentials.
- Create a simulation box containing the components.
- Create scattering weights files for each of the experimental datasets.
- Create a simulation and run it.
- Improve the Lennard-Jones potentials as required.
- Refine the empirical potential.
- Create analysis routines to probe the simulation.
- Run analysis routines and accumulate the distribution functions.
- Plot the results.





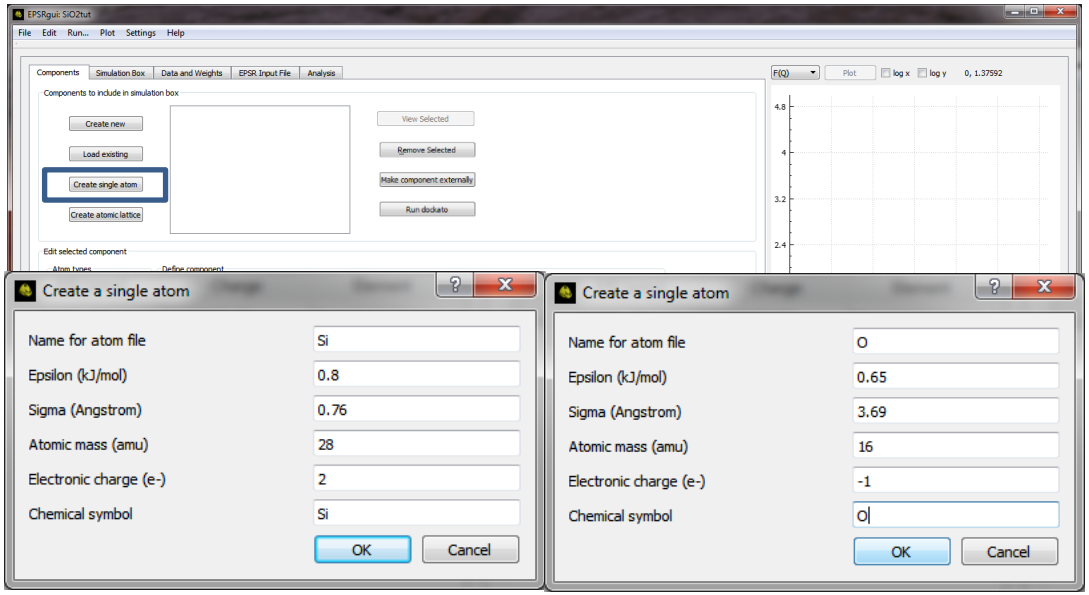
Create a new project

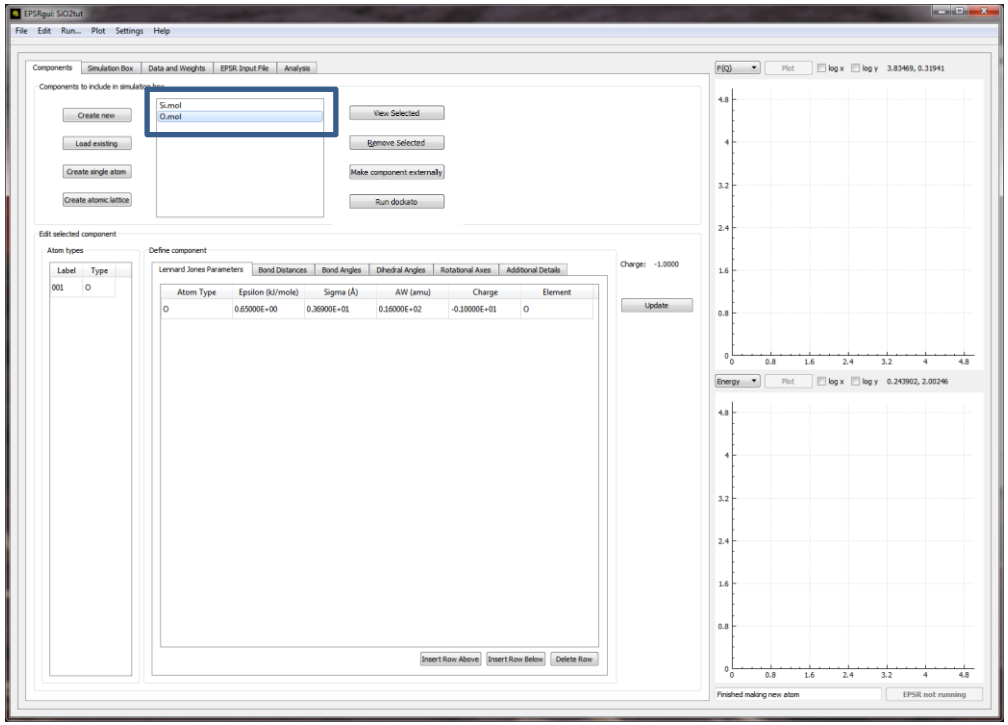
- On the top menu bar, click File -> Create new project…
- The directory for the new project will be in the ESPR run folder (as setup during installation).
- Type the name for the new project, e.g. SiO2tut.
- Click OK.
- If a project already exists with this name an error message will appear as two projects cannot have the same name – use a different name for the new project.
- All files associated with this simulation will be saved to the SiO2tut folder in the run directory.
- The project can be reopened by opening the SiO2tut.EPSR.pro file within EPSRgui.



Create atom components

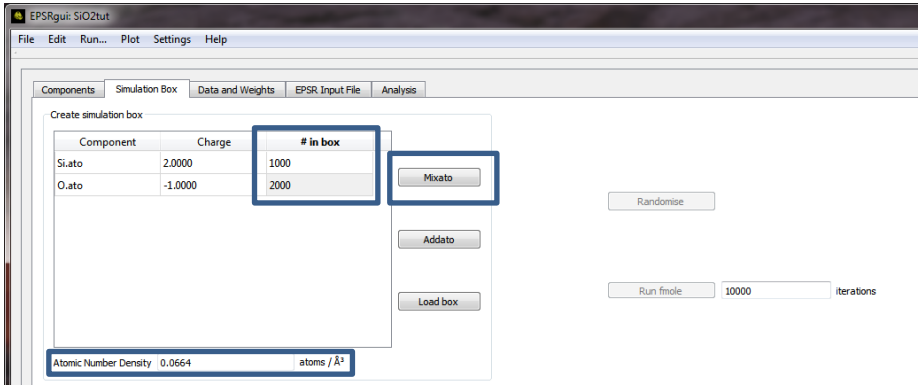
- First the components of the box need to be created. In this case these are the Si and O atoms.
- In the Components tab, click the Create single atom button.
- In the window that appears, enter the values given adjacent for a silicon atom and click OK. As SiO_2 is a covalent glass, partial charges are used to mimic the covalency and expected stoichiometry.
- The details for Si are then shown in the bottom section of the Components tab.
- Click Create Single atom again and fill out the fields this time for an oxygen atom.
- The Components tab now shows Si.mol and O.mol in the list of components to include in the simulation box.
- To view the parameters for each component click on the chosen component in this list.

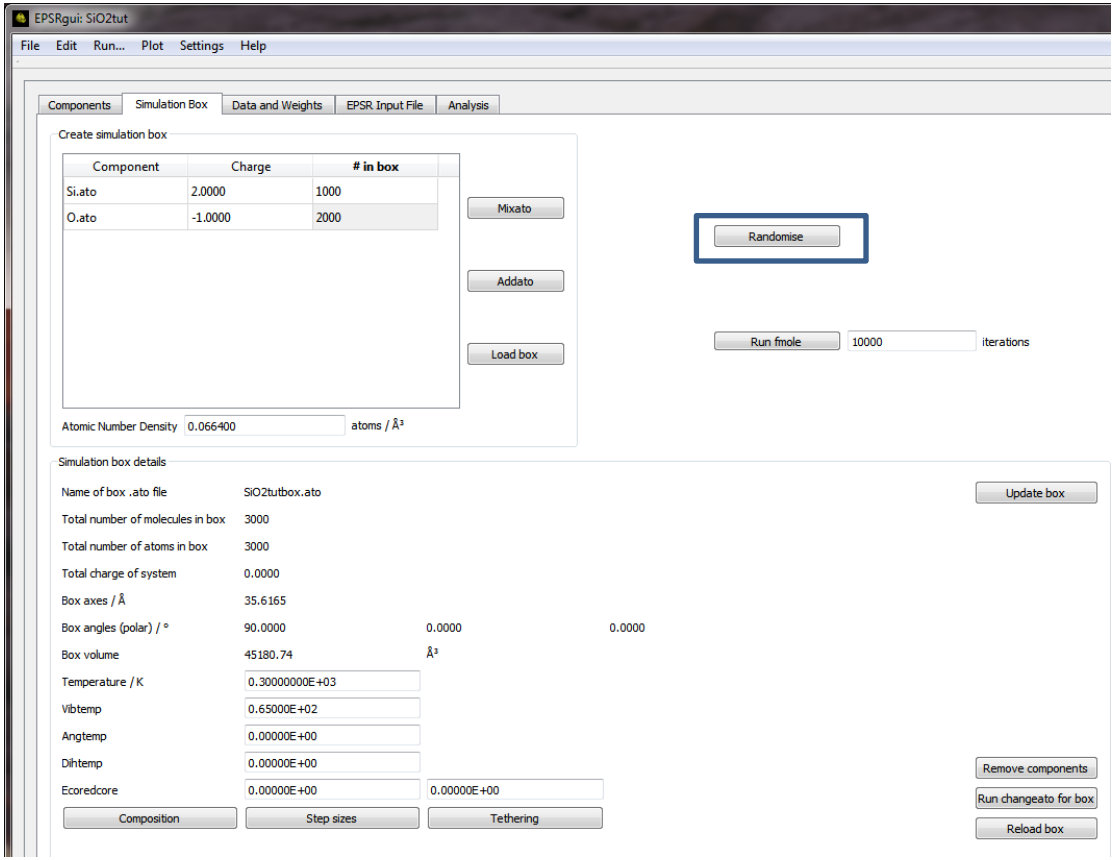




Create the simulation box

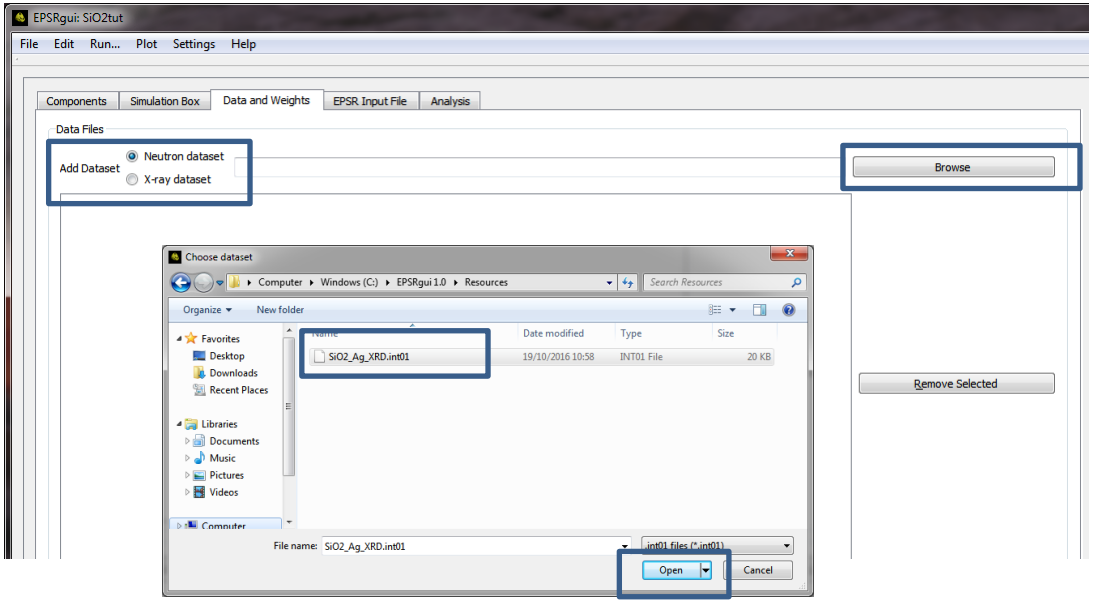
- Click on the Simulation Box tab
- The components and their respective charges are shown in the Create simulation box table.
- Enter the number of each component to be included in the box. In this instance enter 1000 for Si and 2000 for O (double click on the cell to edit it).
- Enter the atomic number density of the system – this is 0.0664 atoms/Å^3.
- Then click Mixato. This creates a cubic simulation box with the given number of each component. The size of the box is determined by the number of atoms and the atomic number density and is given in the Simulation box details at the bottom of the tab. Sufficient components should be added to the box so that half the box length is longer than the longest correlation to be assessed in the simulation.
- The details about the simulation box are shown in the lower part of the window.
- To distribute the components randomly throughout the box, click Randomise.

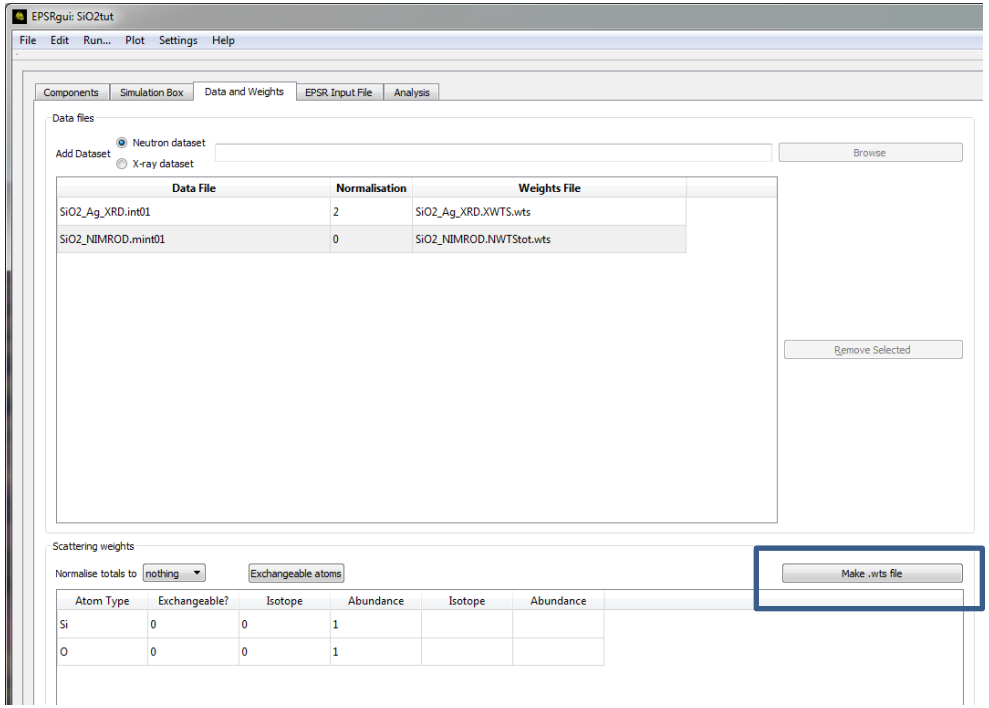




Data and scattering weights

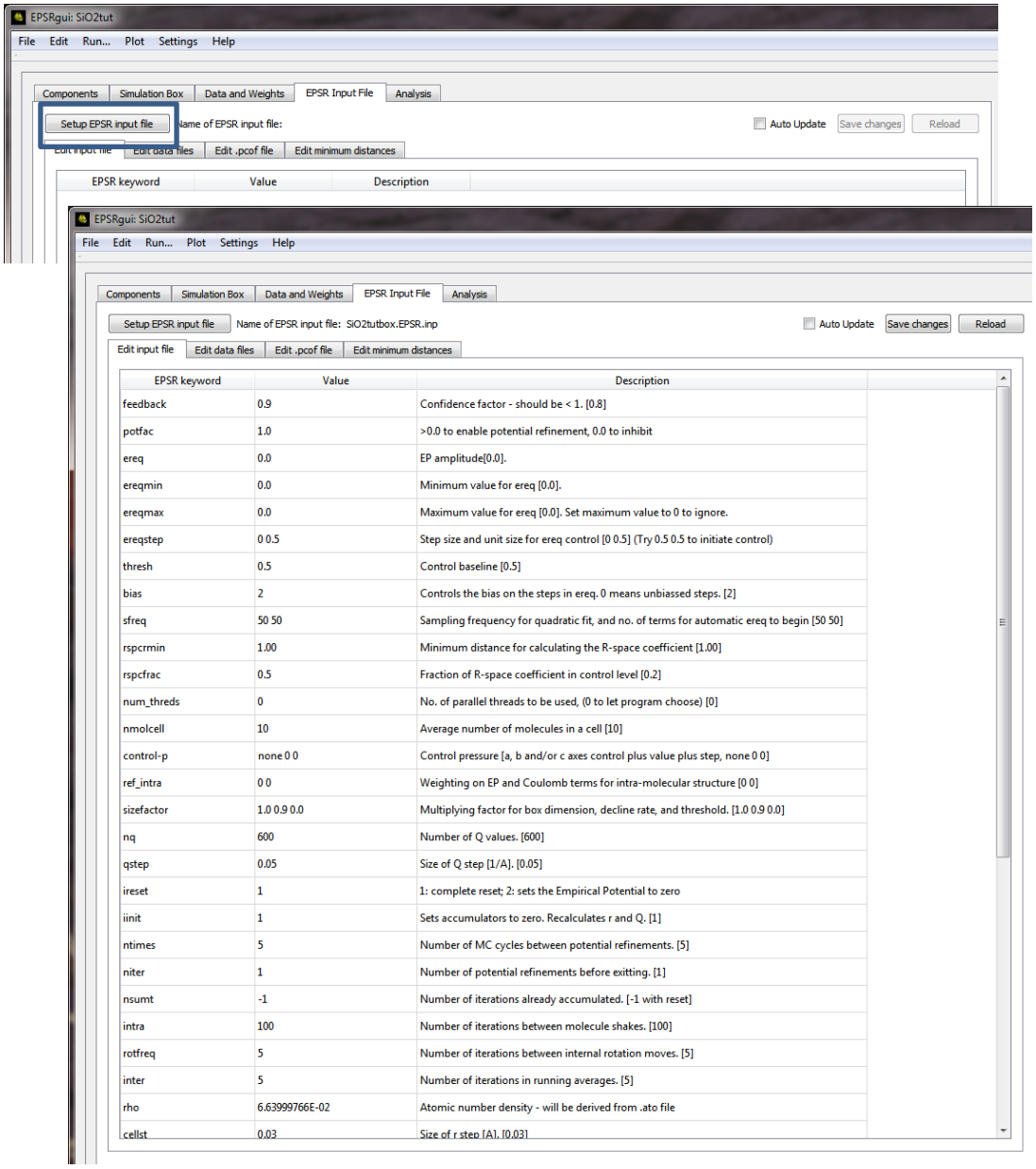
- For EPSR to correctly calculate the structure factor from the simulation box for a given experimental dataset, scattering weights files need to be created that identify whether the experimental data are from neutrons or X-rays, which atoms are isotopically substituted and whether any of the atoms can exchange.
- Click on the Data and Weights tab.
- Select X-ray dataset and click Browse.
- Navigate to the SiO2_Ag_XRD.int01 dataset in the EPSRgui\Resources folder and click Open.
- Click Make .wts file. The .wts file is then shown in the Weights File column of the data file table.
- Now repeat for the neutron dataset.
- Select Neutron dataset and click Browse. Navigate to the SiO2_NIMROD.mint01 dataset in the EPSRgui\Resources folder and click Open.
- Click Make .wts file.





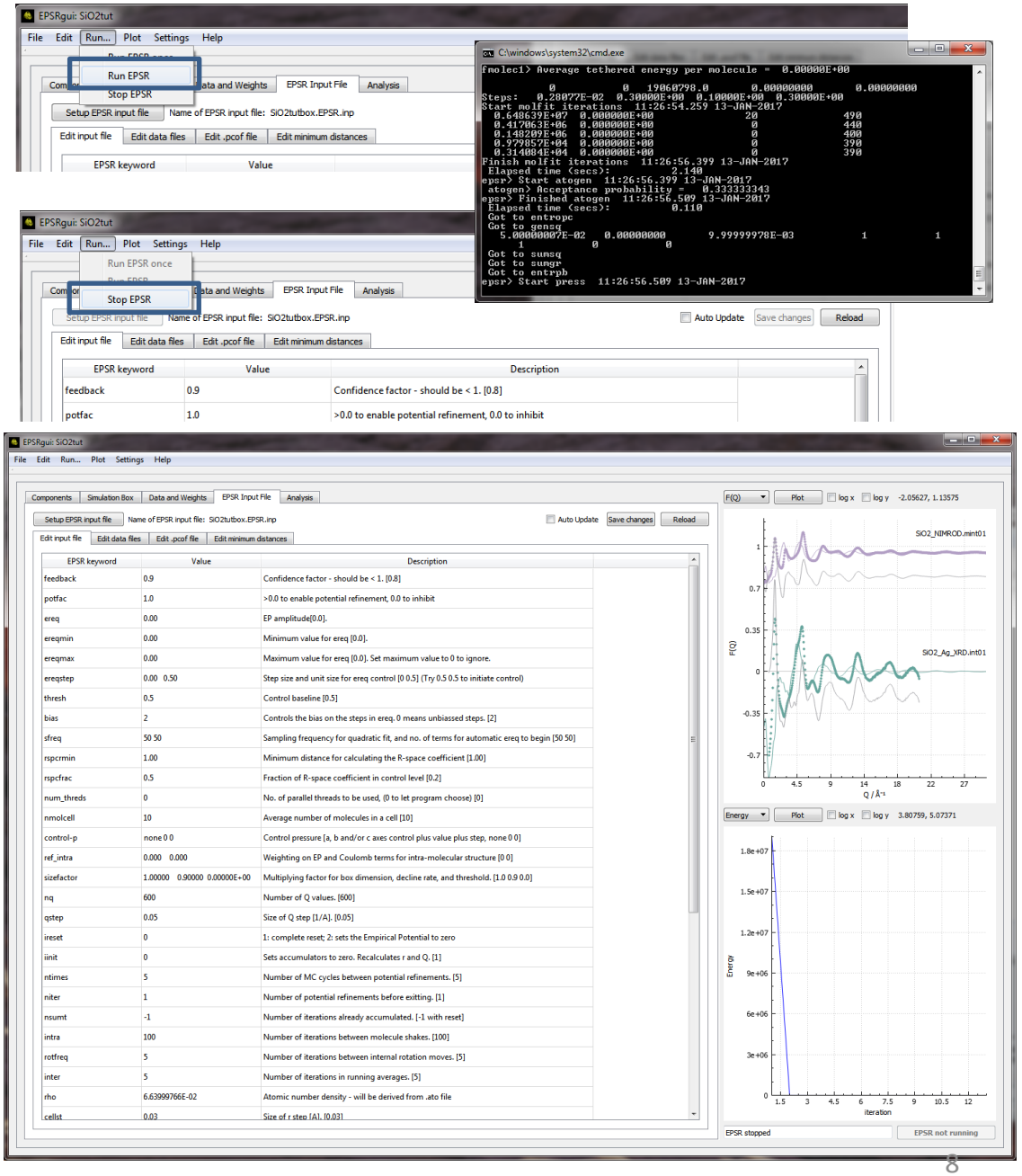
EPSR input file

- The EPSR input file contains the parameters which define the simulation settings.
- Click on the EPSR input file tab and click Setup EPSR input file.
- This creates an input file with the default settings. It is created using the components, simulation box, data files and weights files created in the last steps.
- The details contained in the input file are listed in the tabs. For this tutorial, the default settings are fine to get the simulation started so nothing needs to be edited.



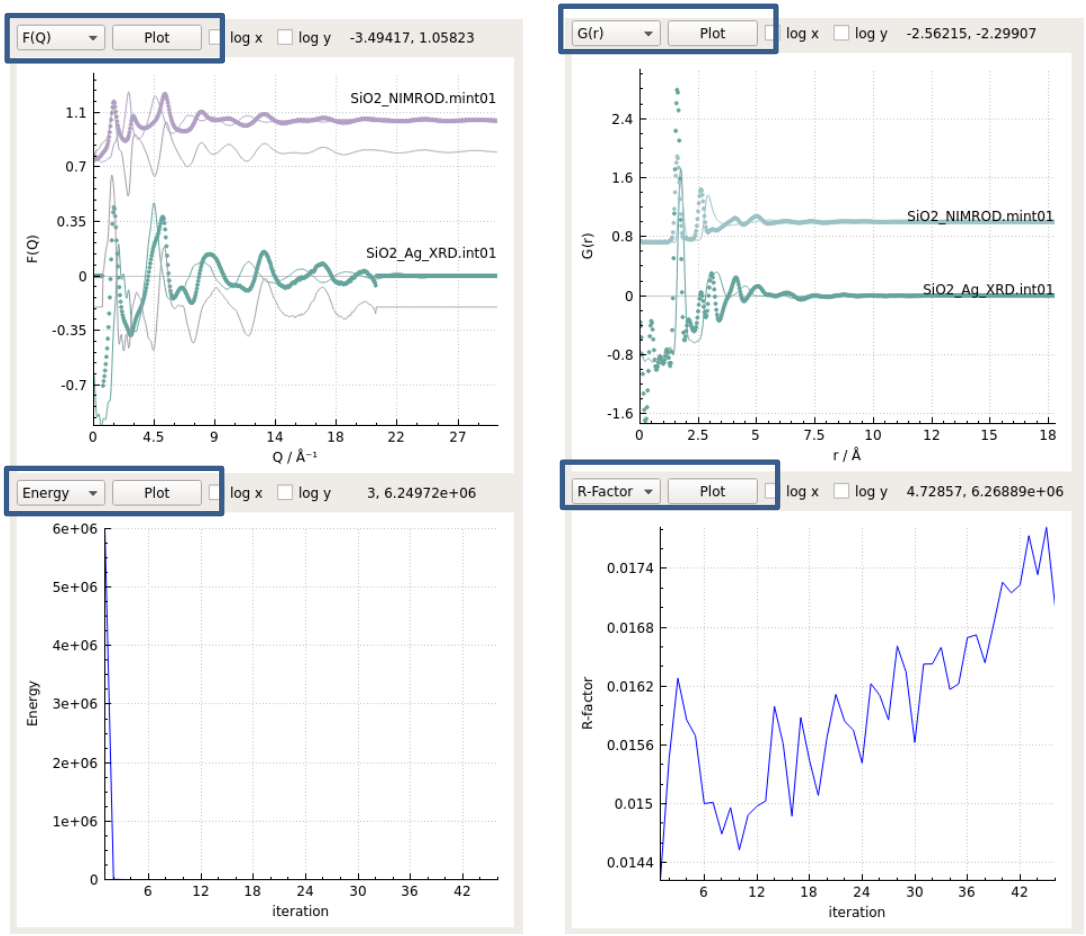
Running EPSR

- It is now time to run EPSR: on the top menu bar click Run…-> Run EPSR.
- On the bottom right hand corner an ‘EPSR running’ sign is shown, and in the command prompt/terminal window various messages are shown while EPSR runs.
- While EPSR is running the simulation cannot be edited.
- Wait about 30s and then stop EPSR: on the top menu bar click Run…->Stop EPSR.
- EPSR will stop once it has finished the current iteration - once finished the sign in the bottom right hand corner will turn grey and say ‘EPSR not running’.
- In the Messages window (Settings->Show messages) the results of the final iteration are shown.
- The EPSR input file will be automatically reloaded with the values from the last iteration and the plots on the right hand side of the screen will also update.



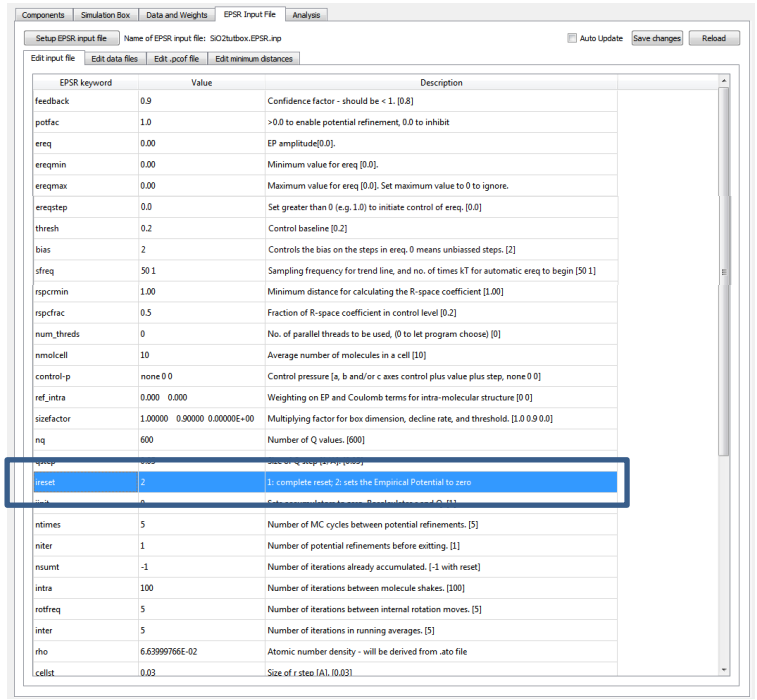
Examining the simulation

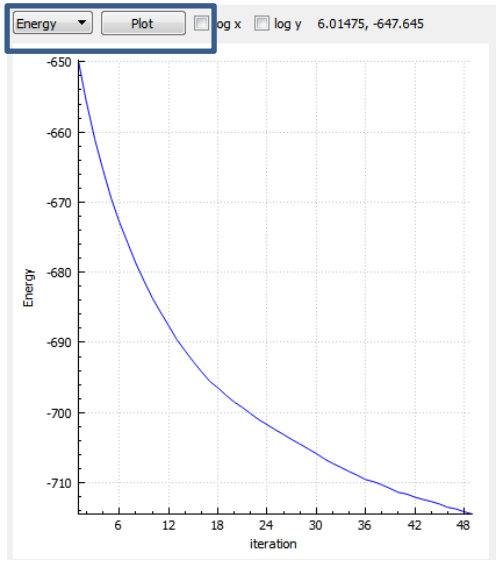
- Once the simulation has performed one iteration several aspects of the simulation can be viewed.
- On the right hand side of the screen, there are two plots which show the data and calculated structure factor for the model (F(Q)). As the simulation has only just started, the fit will be quite poor but the calculated values from the model should bear some resemblance to the data.
- To view the radial distribution function for the model and the data click on the drop down menu, choose G(r) and then click Plot.
- Other aspects of the simulation such as Energy or R-factor can also be plotted by selecting from the drop down menu and clicking Plot.

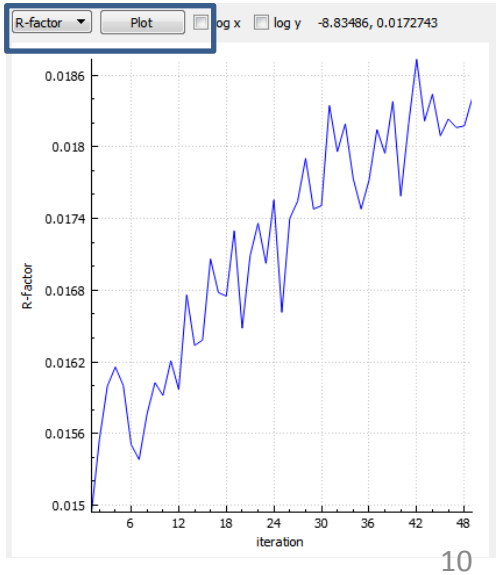


Proceeding with the simulation

- The Energy plot shows that the energy has reduced to such a small value that it is barely visible on the plot. This is because the components were initially placed randomly in the box but have now been moved to more appropriate positions owing to the reference potential defined by the Lennard-Jones parameters.
- To use this configuration as the new starting point, in the EPSR input file tab, change the value of ireset to 2.
- Then run EPSR again by clicking Run…->Run EPSR. Any changes made to the input file are automatically saved on running EPSR.
- Choose Energy in one of the plot drop down menus and click Plot.
- You can now see that the energy is negative and (after ~50 iterations) following a downward trend. However, the R-factor plot is not improving…
- To refresh the graph click Plot again.

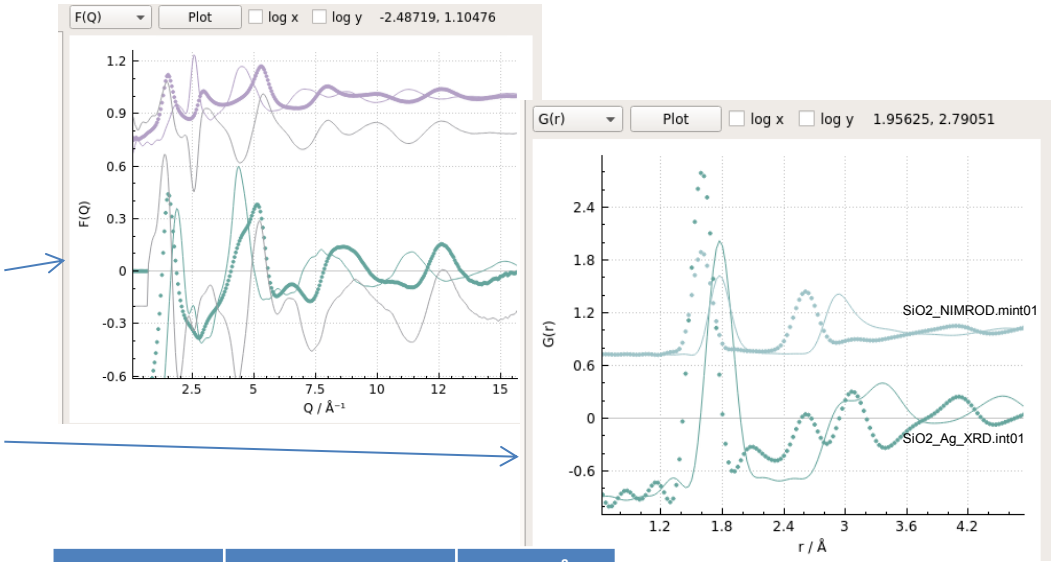




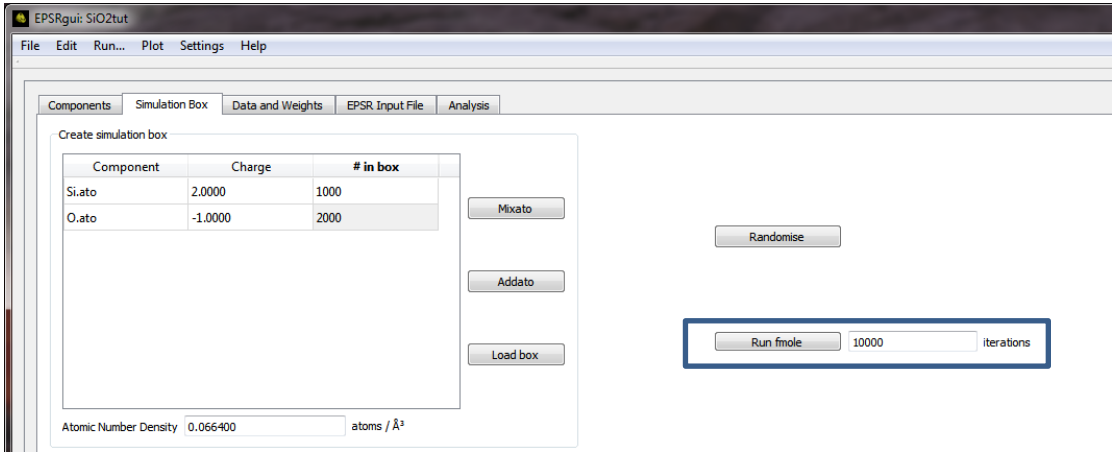


Improving the simulation – the reference potential

- On examining the simulation, it can be seen that the peaks for the model F(Q) are not fitting the data as they are shifted to the left or right. In r-space it can be seen that the Si-O bond distance is too short in the model compared to the data (1.6 Å) as the peak is shifted to the left. This suggests that the Lennard-Jones parameters of the components are not appropriate as they are not allowing the atoms to approach in a manner that fits the data.
- Now try using the optimised Lennard-Jones potentials given in the adjacent table - first stop EPSR (if necessary) and then, in the Components tab, edit the epsilon and sigma values for the silicon and click Update. Repeat this for the oxygen and click Update.
- In the Simulation Box tab Run fmole 10000 times to apply the changes to the simulation box.
- Run EPSR again – see how the new values influence the peak positions and if the fit has improved.
- Equilibrate the box by running the simulation until the r-factor and energy plateau.

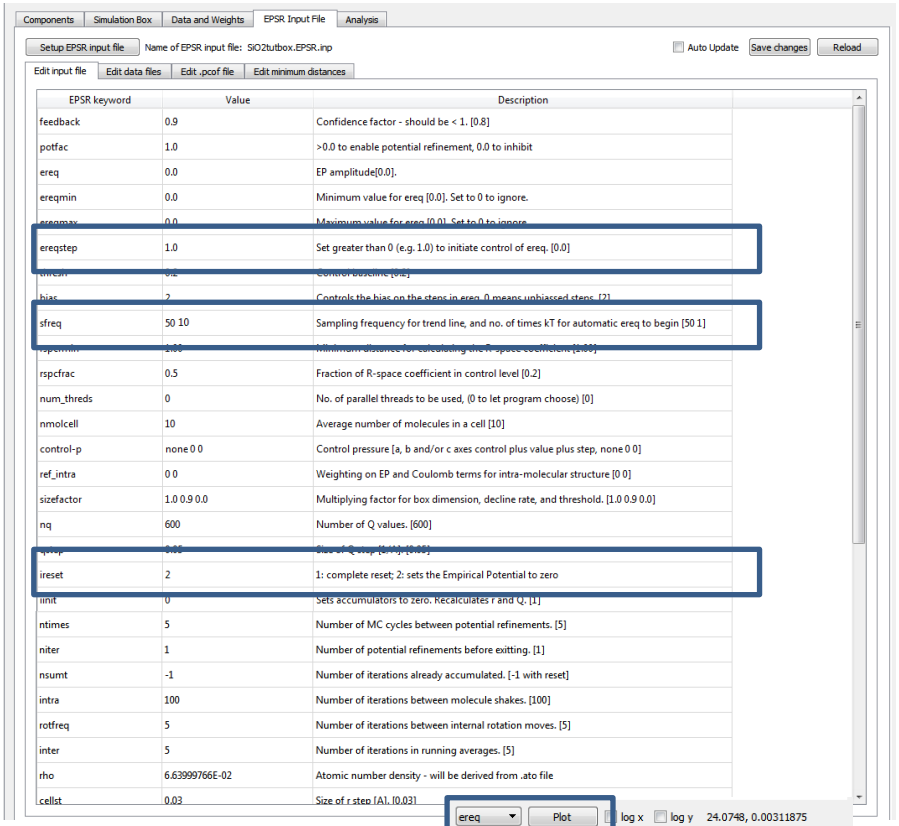


Atom Type	Epsilon (kJ/mole)	Sigma (Å)
Si	0.175	1.03
O	0.165	3.5



Improving the simulation – the empirical potential

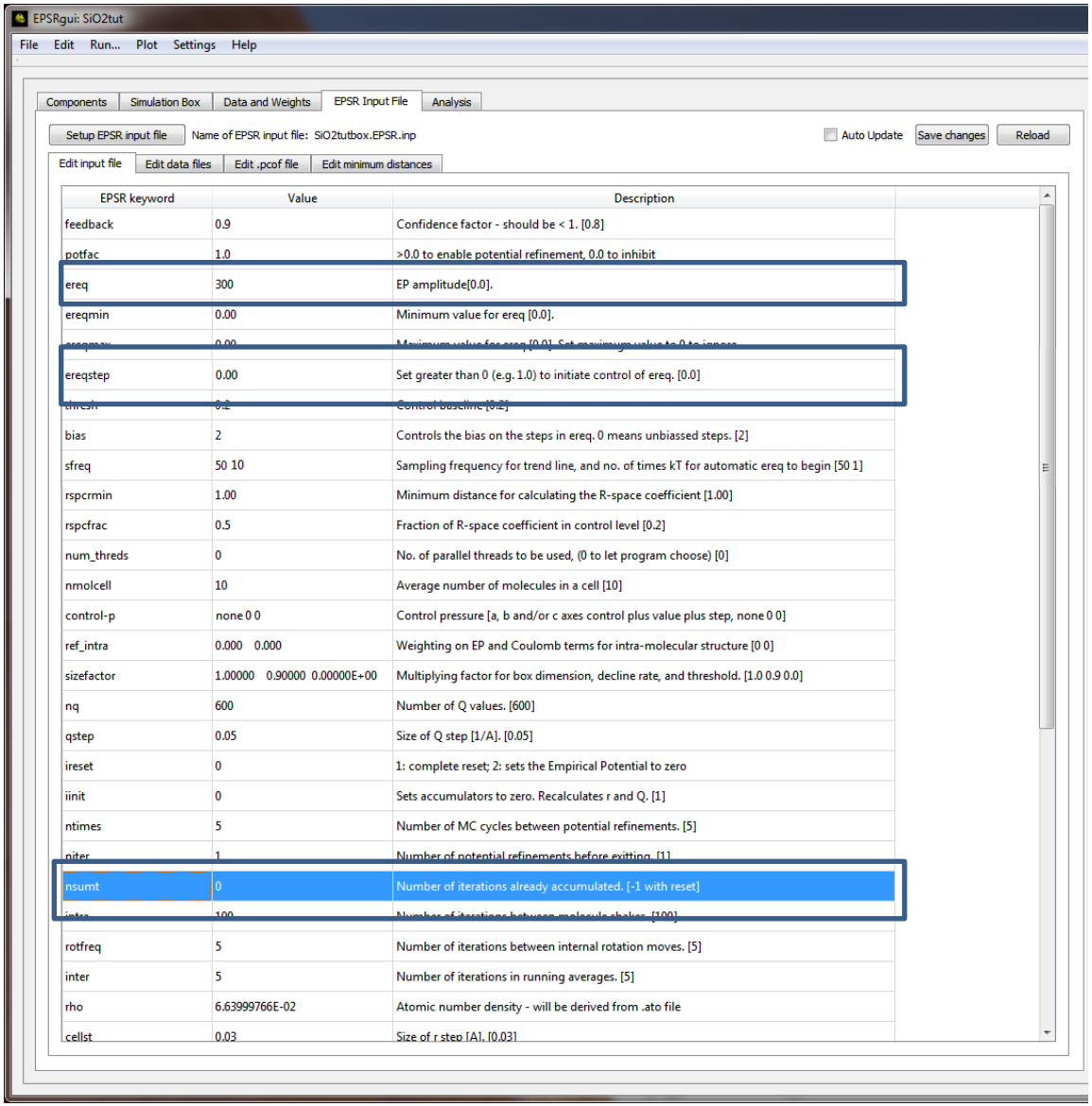
- Once the fit is as good as can be obtained from the reference potential alone, it is time to start refining the empirical potential.
- First, stop EPSR.
- In the EPSR input file tab, change the ereqstep value to be 1 and the sfreq value to be 50 10. Also, change the ireset value to be 2.
- Run EPSR again.
- EPSR will now be refining the empirical potential so as to allow the atoms to move in such a way as to get a better fit to the data. The amount of energy EPSR uses to achieve this is decided by EPSR by assessing what the recent improvement to the fit has been for a certain energy value. This can be plotted by selecting ereq from the plot drop down menu and clicking Plot.
- Make a note of the value of the ereq energy at which the quality of fit is best.



Read off an approximate lowest energy value that provides the best fit (in this case, ~300).

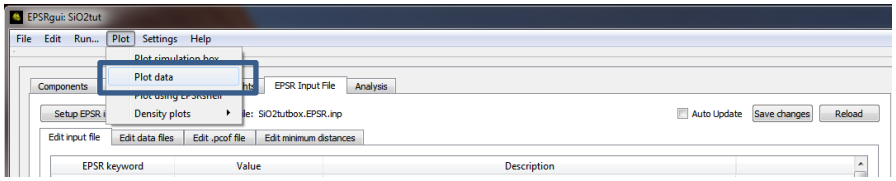
Accumulating the refined simulation box

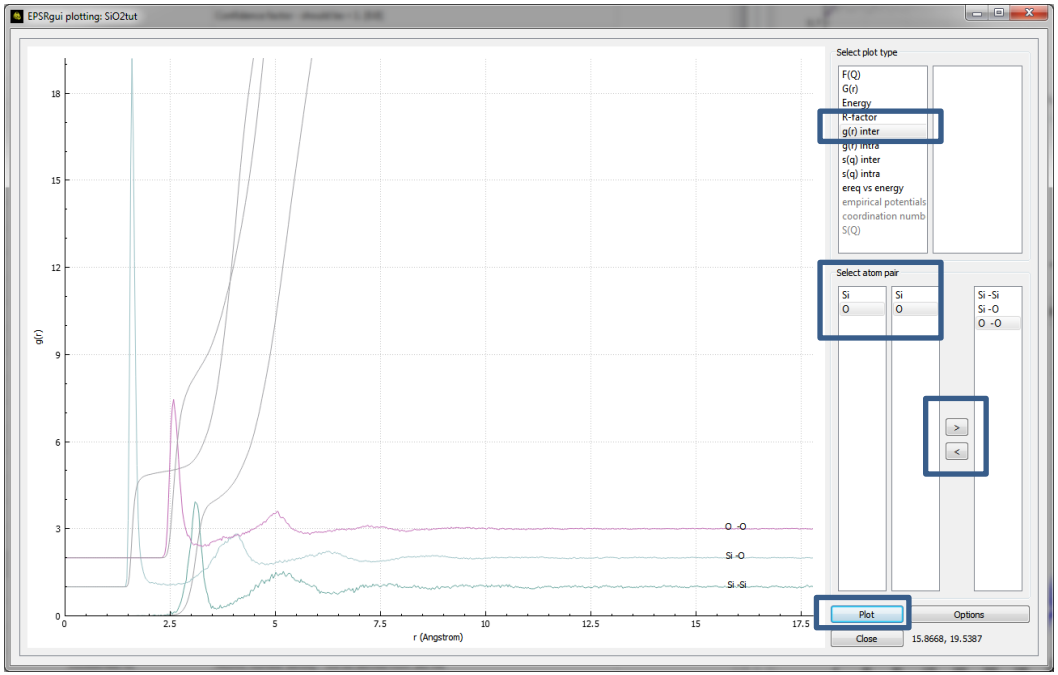
- Once the simulation has been improved as far as possible, and a good value for ereq has been identified, stop EPSR.
- In the EPSR input file tab, change ereq to the best value identified from the ereq plot. Also change ereqstep to be 0.0.
- To start accumulating the positions of the atoms over a number of frames of the simulation (in order to improve statistics for the pair correlation functions etc), change the value of nsumt to be 0.
- We also want to set up analysis routines so that they will be performed on each frame of the simulation while EPSR is running. Before we know what to setup we need to take a look at the simulation so far…



Analysing the refined simulation box – g(r)

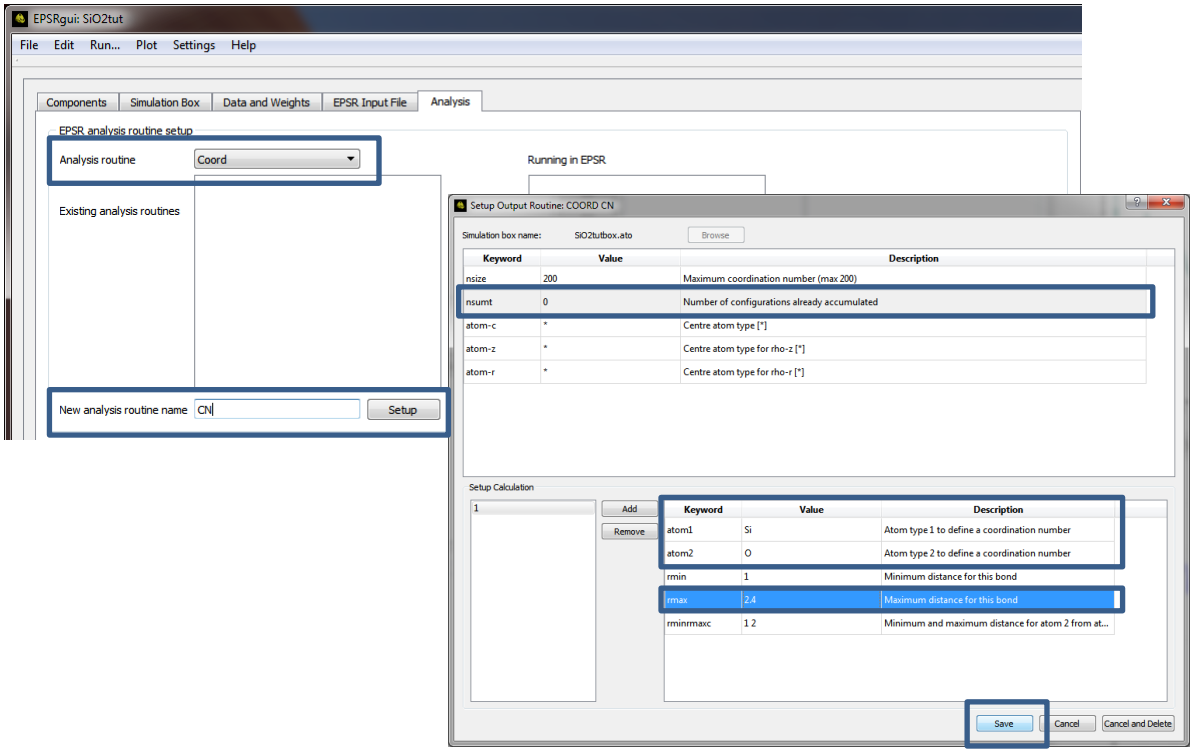
- On the top menu bar, click Plot->Plot data.
- In the plotting window that opens, click g(r) inter to plot the intermolecular pair correlation functions for selected atom pairs.
- Click on each atom in a pair and click the > button to add the pair to the list of pair correlation functions to be plotted. Repeat this for each atom pair to be plotted. To remove an atom pair, click on it and then click the < button.
- Then click Plot.
- This plots the intermolecular g(r) together with the coordination number (in grey).
- To re-position the plot, right click and drag. To zoom in and out use the mouse roller wheel. To zoom in and out along the vertical axis only, hold down Ctrl while using the mouse roller wheel. To zoom in and out along the horizontal axis only, hold down Shift while using the mouse roller wheel.
- The most commonly occurring nearest neighbour distance can be read off from the first peak maximum. Make a note of the maximum r value which could still be considered the nearest neighbour for each g(r) (usually the end of the 1st peak or the 1st minimum).

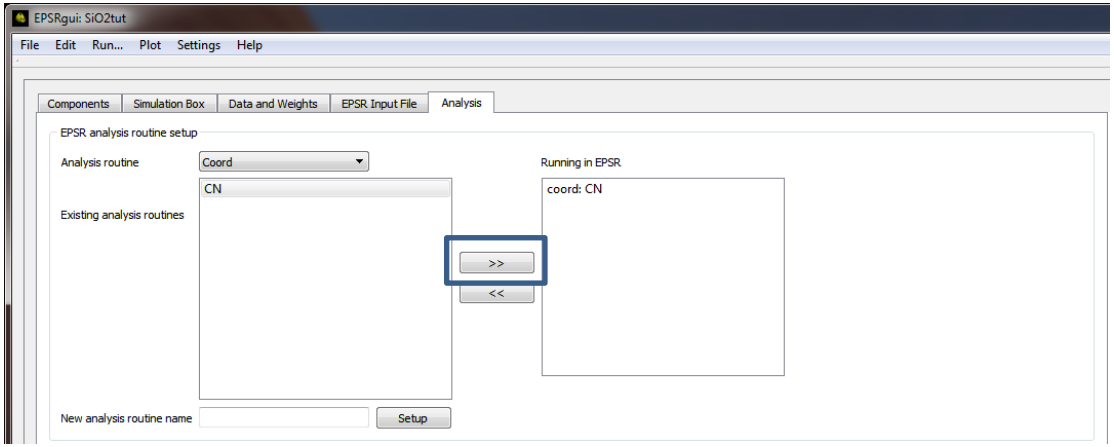




Calculations from the refined simulation box – coord

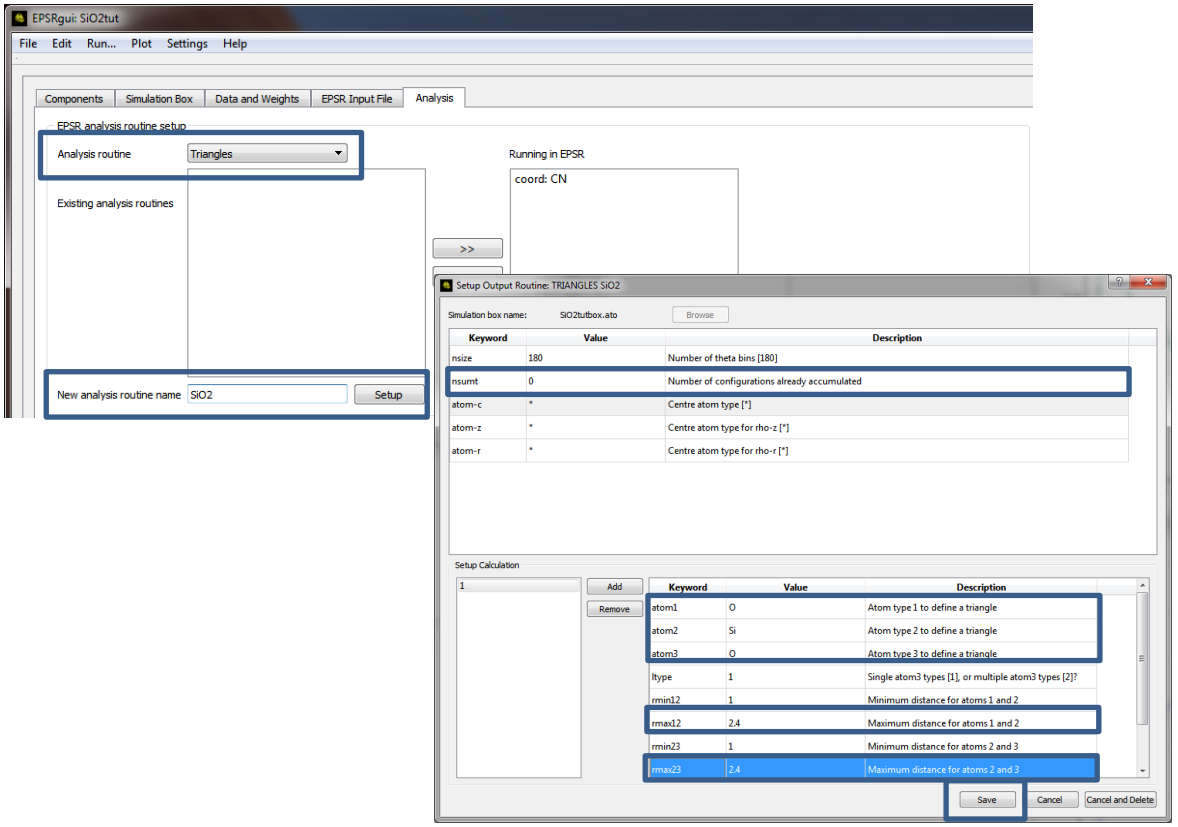
- Click on the Analysis tab.
- In the Analysis routine drop down menu, select Coord.
- In the New analysis routine name type CN and click Setup.
- In the dialog window that appears change the following values
  - nsumt: 0
  - atom1: Si
  - atom2: O
  - rmax: <read off from g(r) plot>
- Press Save.
- The analysis routine file CN will now appear in the Existing analysis routines box. Click the >> button to add it to be run when EPSR runs.

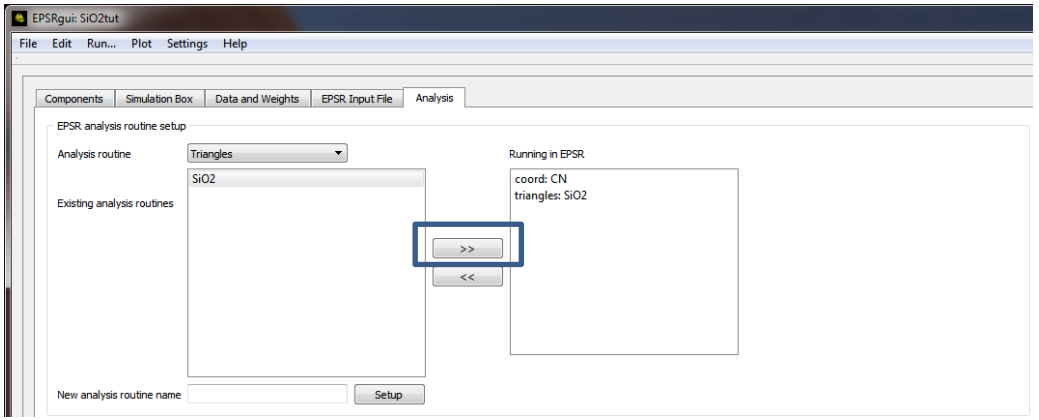




Calculations from the refined simulation box – triangles

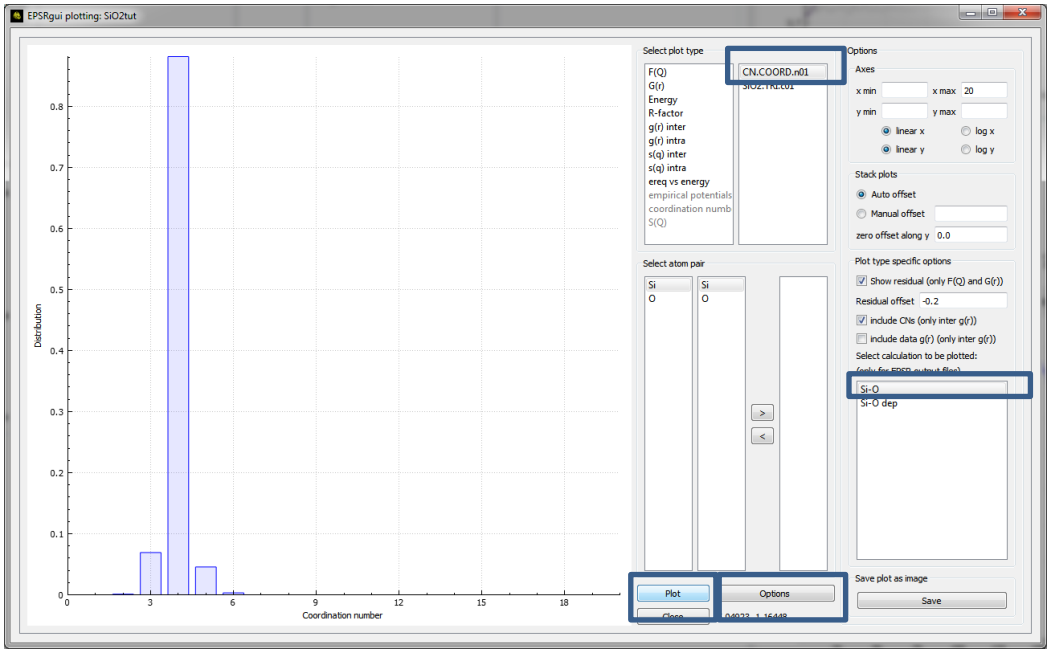
- Click on the Analysis tab.
- In the Analysis routine drop down menu, select Triangles.
- In the New analysis routine name type SiO2 and click Setup.
- In the dialog window that appears change the following values
  - nsumt: 0
  - atom1: O
  - atom2: Si
  - atom3: O
  - rmax12: <read off from g(r) plot>
  - rmax23: <read off from g(r) plot>
- Press Save.
- The analysis routine file SiO2 will now appear in the Existing analysis routines box. Click the >> button to add it to be run when EPSR runs.

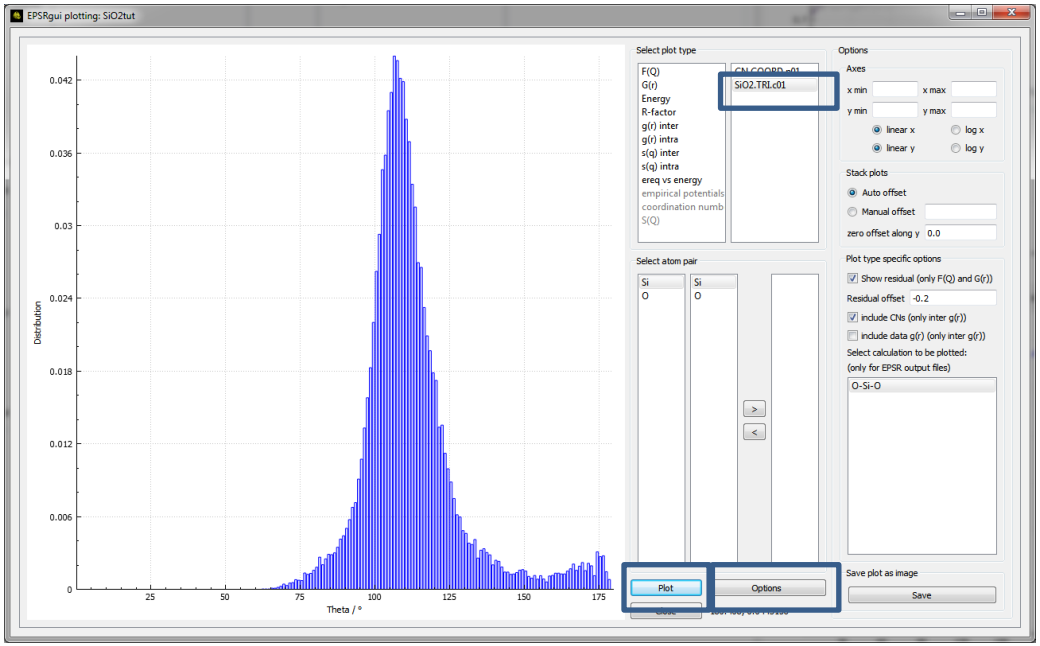




Performing analysis routines

- Once all the analysis routines have been set up, run EPSR.
- Even while EPSR is running, the outputs from the analyses can be viewed by clicking Plot->Plot data.
- In the top right hand corner, the analysis routines that have been running are listed.
- Click on the CN.COORD calculation and click Options on the bottom right hand corner. This opens additional plotting options.
- Select the atom pair you want to see the coordination number for in the list in the Plot type specific options box and then click Plot.
- This shows a histogram of the normalised number of instances that each coordination number is observed in the accumulated frames of the simulation (as defined during setting up the routine).
- Repeat this for the triangles (TRI) calculation.
- This shows a histogram of the normalise number of instances that each angle is observed in the accumulated frames of the simulation (as defined during setting up the routine).





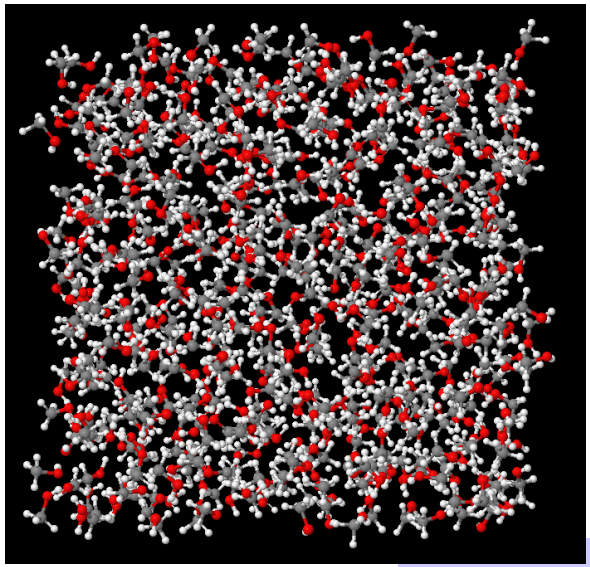
Methanol

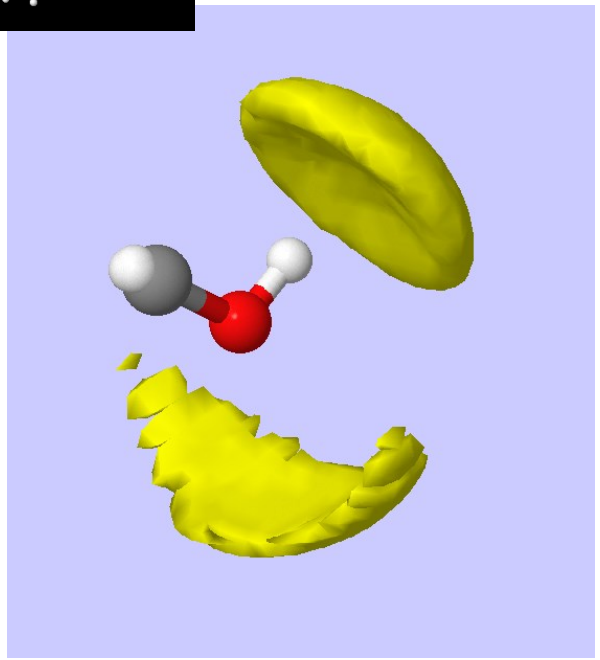
EPSRgui tutorial 2

Purpose of this tutorial

The goal of this tutorial is to build, refine and analyse a model of a simple liquid, CH_3OH. To achieve this, the tutorial will cover how to:

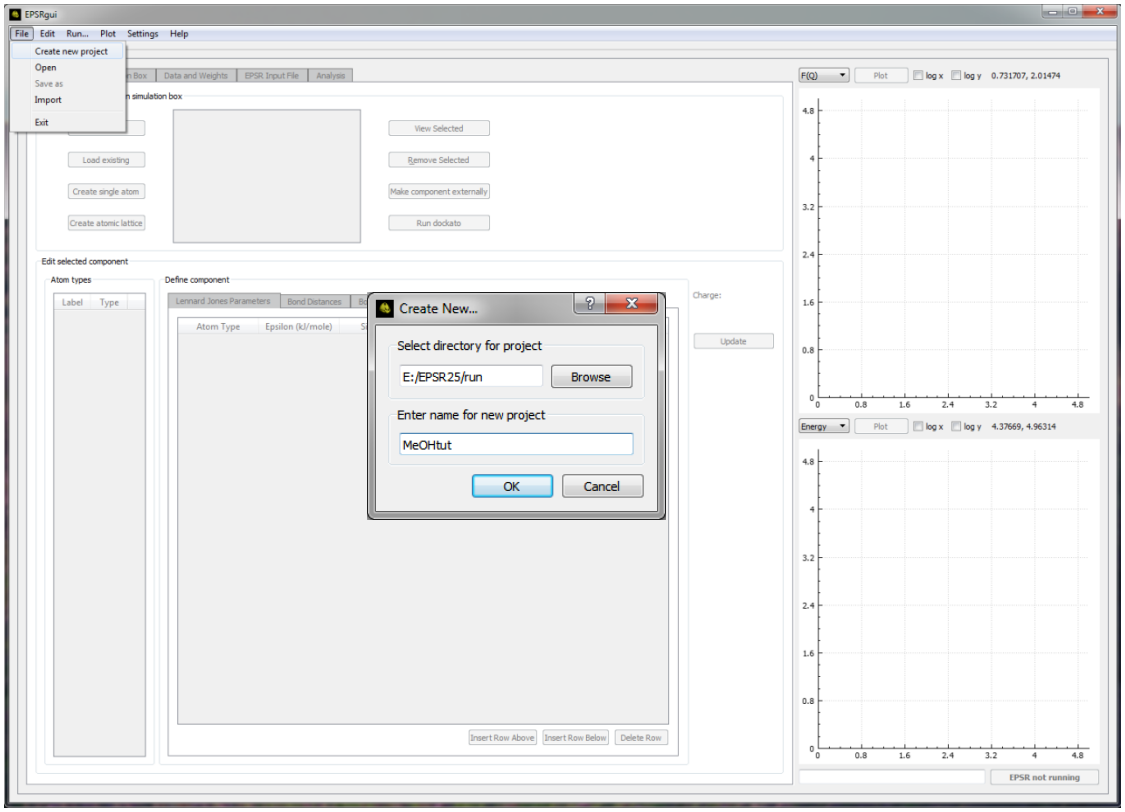
- Create the molecular component and define the Lennard-Jones potentials for each atom type.
- Create a simulation box containing the component.
- Create scattering weights files for each of the experimental datasets.
- Create a simulation and run it.
- Refine the empirical potential.
- Create analysis routines to probe the simulation.
- Run analysis routines and accumulate distribution functions.
- Plot the results.





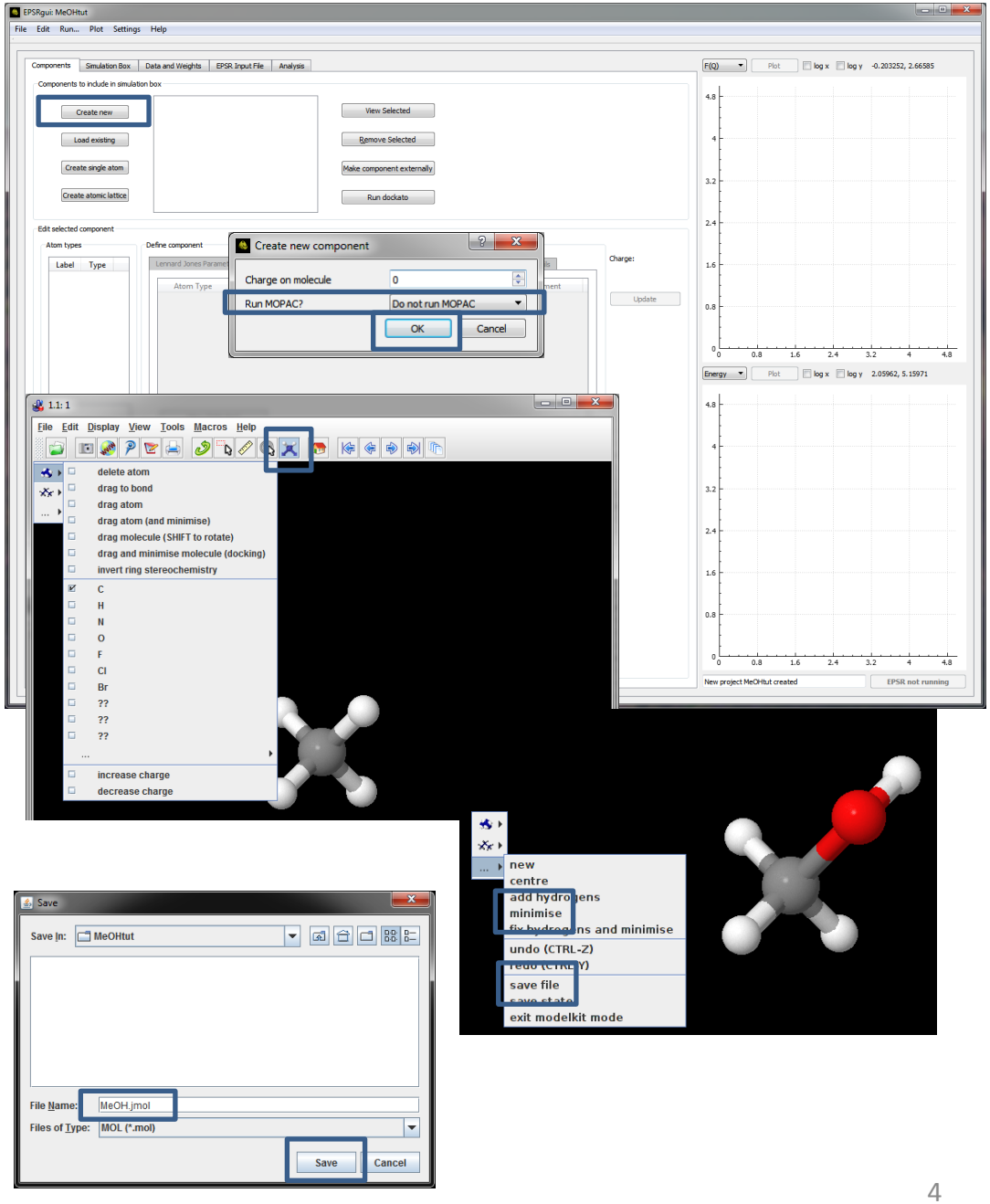
Create a new project

- On the top menu bar, click File -> Create new project…
- The directory for the new project will be in the ESPR run folder (as setup during installation).
- Type the name for the new project, e.g. MeOHtut.
- Click OK.
- If a project already exists with this name an error message will appear as two projects cannot have the same name – use a different name for the new project.
- All files associated with this simulation will be saved to the MeOHtut folder in the run directory.
- The project can be reopened by opening the MeOHtut.EPSR.pro file within EPSRgui.



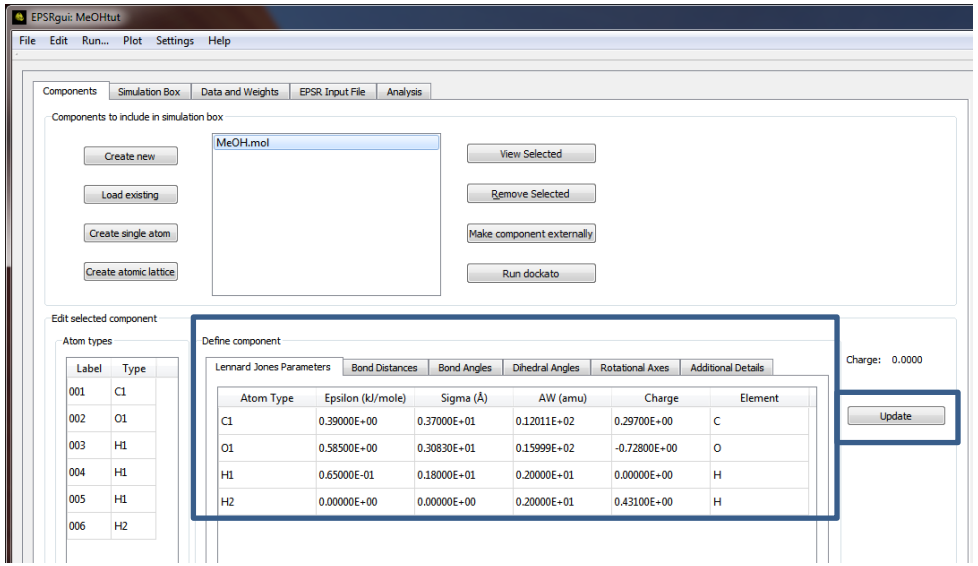
Create the molecular components

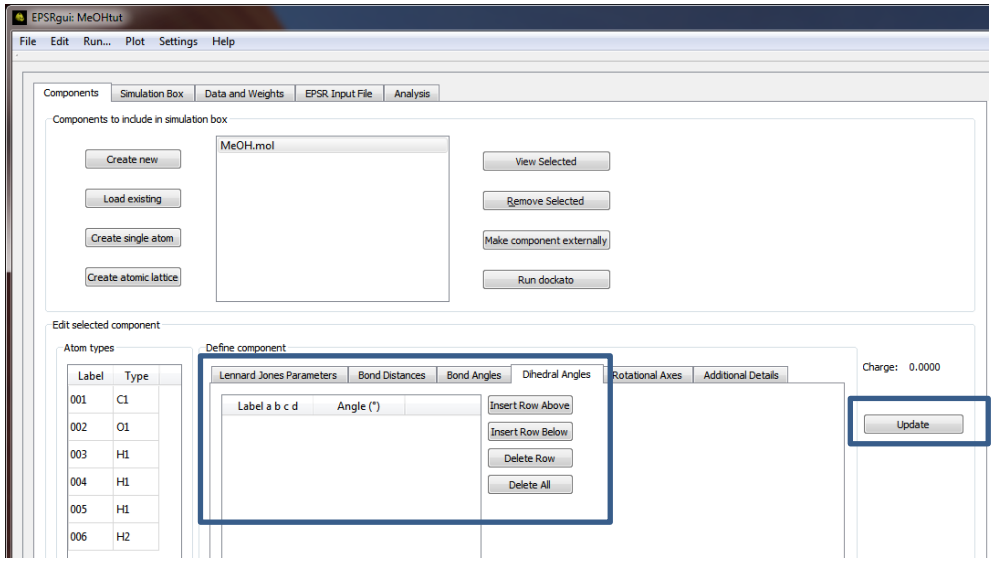
- First, the methanol molecule needs to be constructed.
- In the Components tab, click Create new.
- In the window that appears, MOPAC can be used (provided it is installed) to optimise the molecular geometry once the component has been created. To opt to do this, choose a MOPAC option (AM1 or PM3 are recommended) and then click OK.
- In the Jmol window that appears click on the atom icon and a carbon atom with 4 hydrogens attached to it will appear.
- Right click on the black background and on the atom menu tick O.
- Left click on one of the hydrogen atoms to change it to a hydroxyl group.
- Right click on the black background and in the … menu click minimise. Repeat this a couple of times.
- Right click on the black background and in the … menu click save file.
- In the Save dialog, save the file as a MeOH.jmol. It is very important to save this as a **.jmol**, DO NOT SAVE IT AS A .mol file.
- Click Save.
- Close the Jmol window.
- If MOPAC has been run, check the calculation has been successful by checking the output given at the bottom of Settings->EPSR messages.



Define the Lennard-Jones potentials

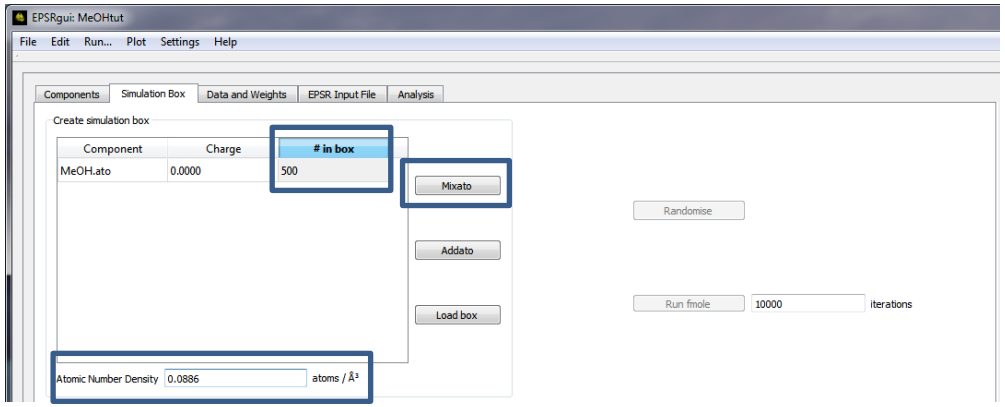
- The .jmol file just saved has now been converted into an EPSR .mol file and is shown as a component to be included in the simulation box.
- In the Atom types table, the Label gives the number of each atom in the molecule – this number is unique to each atom. In the adjacent column is the atom Type – this is usually a letter and a number and is not necessarily unique. In this example, the methyl hydrogen atoms all have the same type which means they will all have the same reference potential. As they have the same environment, this is fine for this simulation.
- Default Lennard-Jones potentials for each atom type are given in the Define component box.
- Edit the Lennard-Jones potentials and charges to be consistent with the potentials and charges given by Jorgensen *et al.* and click Update.
- Check that the charge shows the molecule is neutral.
- Bond distances, bond angles, dihedral angles and rotational axes can also be defined.
- As the methyl group can rotate freely and the hydroxyl group can rotate freely, make sure there are no dihedral angles. Click on the Dihedral Angles tab and if anything is listed in the table, click Delete All. Then click Update.

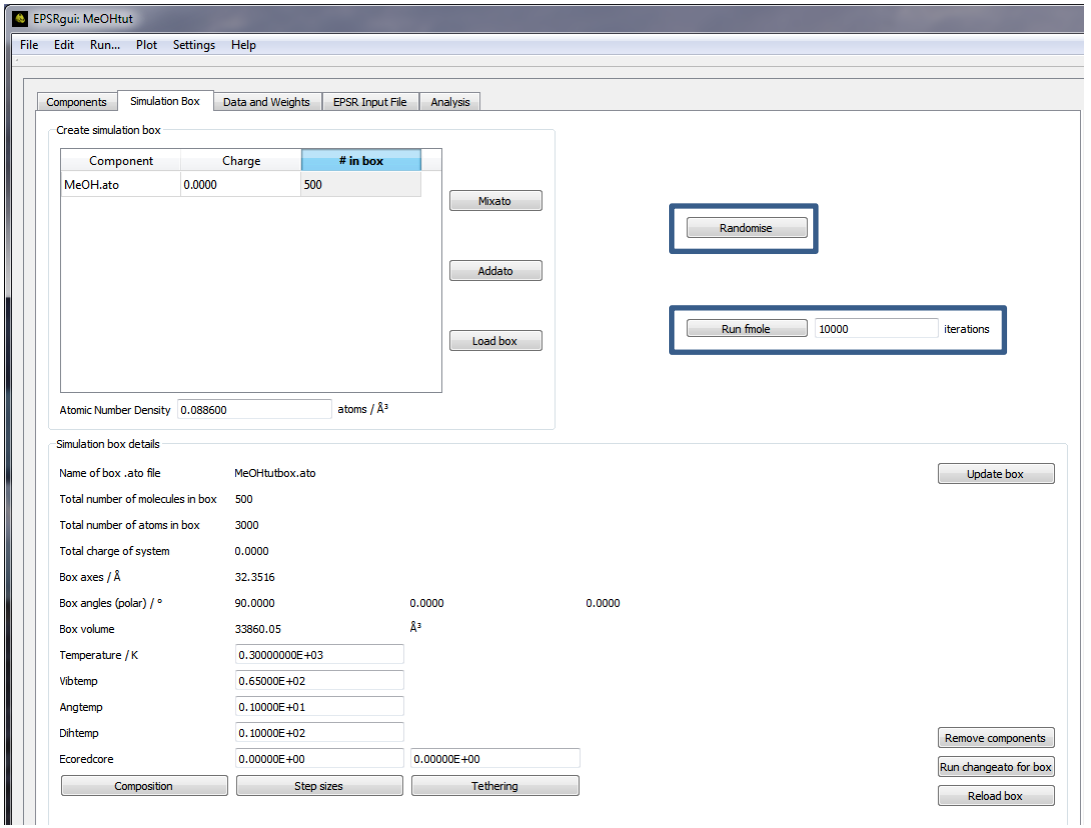




Create the simulation box

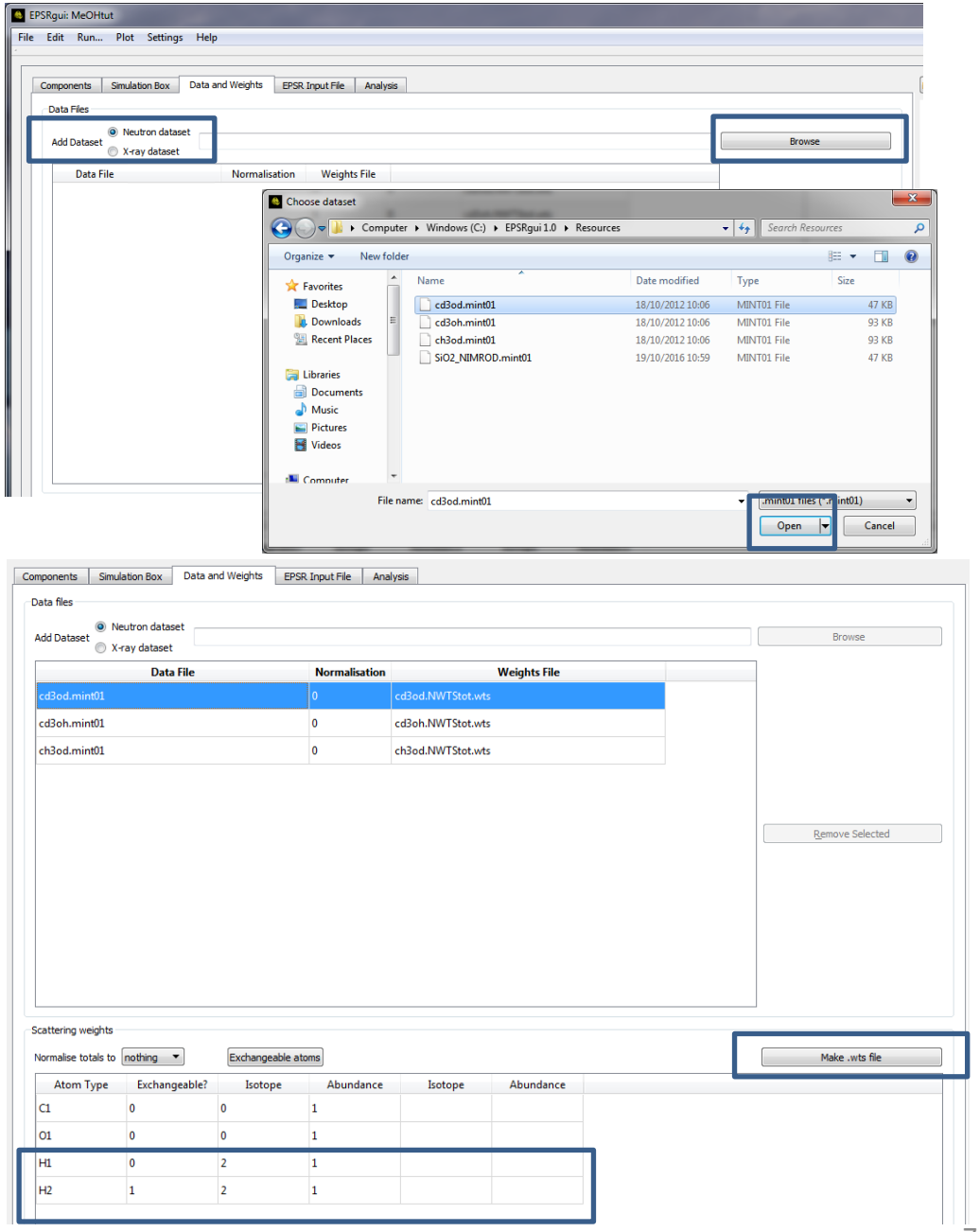
- Click on the Simulation box tab.
- Enter the number of methanol molecules to be included in the box. In this instance enter 500.
- Enter the atomic number density of the system – this is 0.0886 atoms/Å^3.
- Then click Mixato. This creates a cubic simulation box with the given number of each component. The size of the box is determined by the number of atoms and the atomic number density and is given in the Simulation box details at the bottom of the tab. Sufficient components should be added to the box so that half the box length is longer than the longest correlation to be assessed in the simulation.
- To distribute the components randomly throughout the box, click Randomise.
- To add some disorder to the molecule to represent the thermal motion of the atoms, click Run fmole (10,000 iterations are recommended). The amount of disorder is controlled by Vibtemp (see manual) – 65 is generally appropriate, but if vibtemp or any other parameters in the Simulation box details are changed, Run fmole in order for the change to be applied throughout the simulation box.



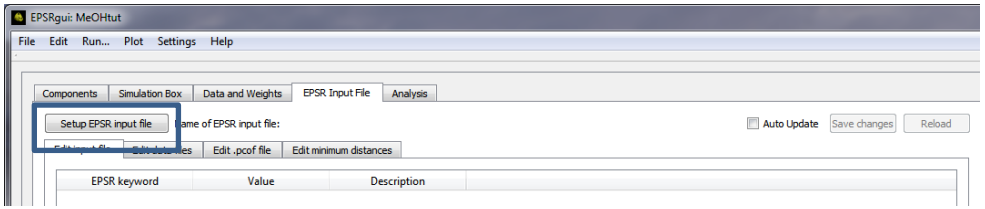


Data and scattering weights

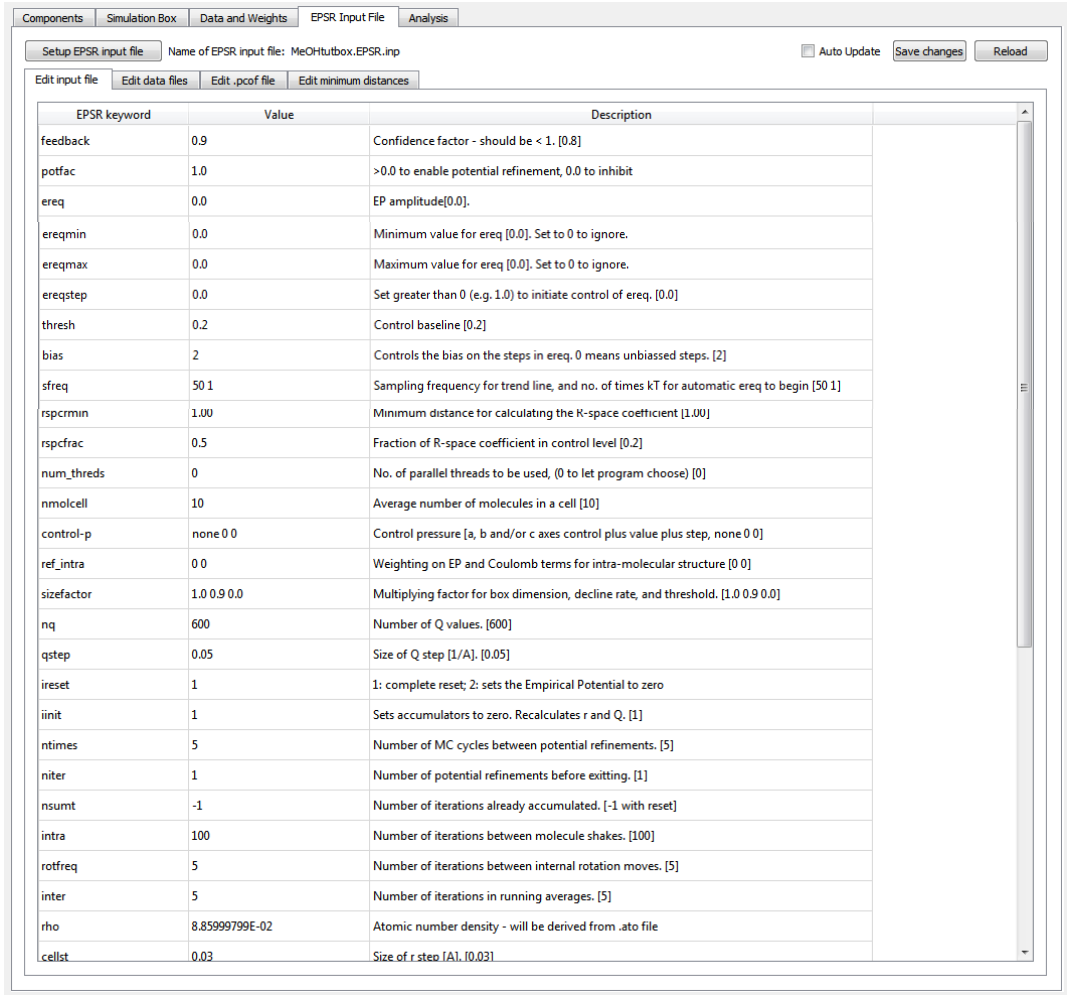
- For EPSR to correctly calculate the structure factor from the simulation box for a given experimental dataset, scattering weights files need to be created that identify whether the experimental data are from neutrons or X-rays, which atoms are isotopically substituted and whether any of the atoms can exchange.
- Click on the Data and Weights tab.
- Select Neutron dataset and click Browse.
- Navigate to the cd3od.mint01 dataset and click Open.
- As this is a fully deuterated sample, change the methyl hydrogens, H1, to 2 in the isotope column. The abundance is 1 as all of the H1 atoms are deuterated.
- As the hydroxyl hydrogen can exchange, change H2 to 1 in the exchangeable column, and as it is deuterated, change the isotope to 2 (again this is fully deuterated so the abundance is 1)
- Click Make .wts file.
- Repeat this for the cd3oh.mint01 and ch3od.mint01 datasets, but using the appropriate isotopes for dataset. For a 50:50 H:D sample the first isotope is 0 as it is natural hydrogen and the abundance is 0.5, the second isotope is 2 as it is deuterium and the abundance is 0.5.



EPSR input file



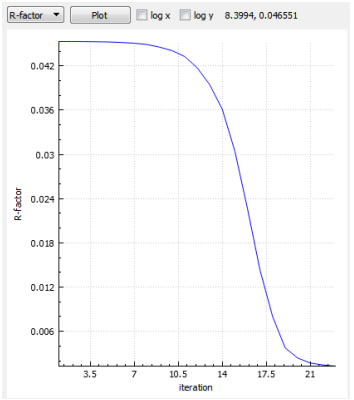
- The EPSR input file contains the parameters which define the simulation settings.
- Click on the EPSR input file tab and click Setup EPSR input file.
- This creates an input file with the default settings. It is created using the components, simulation box, data files and weights files created in the last steps.
- The details contained in the input file are listed in the tabs. If this molecule contained rings, e.g. a phenyl ring, it would be recommended to change size factor to 5.0 0.9 0.0 so as to temporarily expand the box to prevent the rings interlocking. However, for methanol, the current settings are fine.

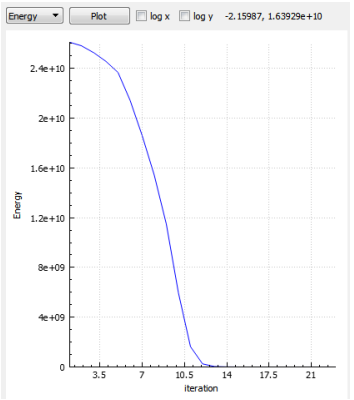


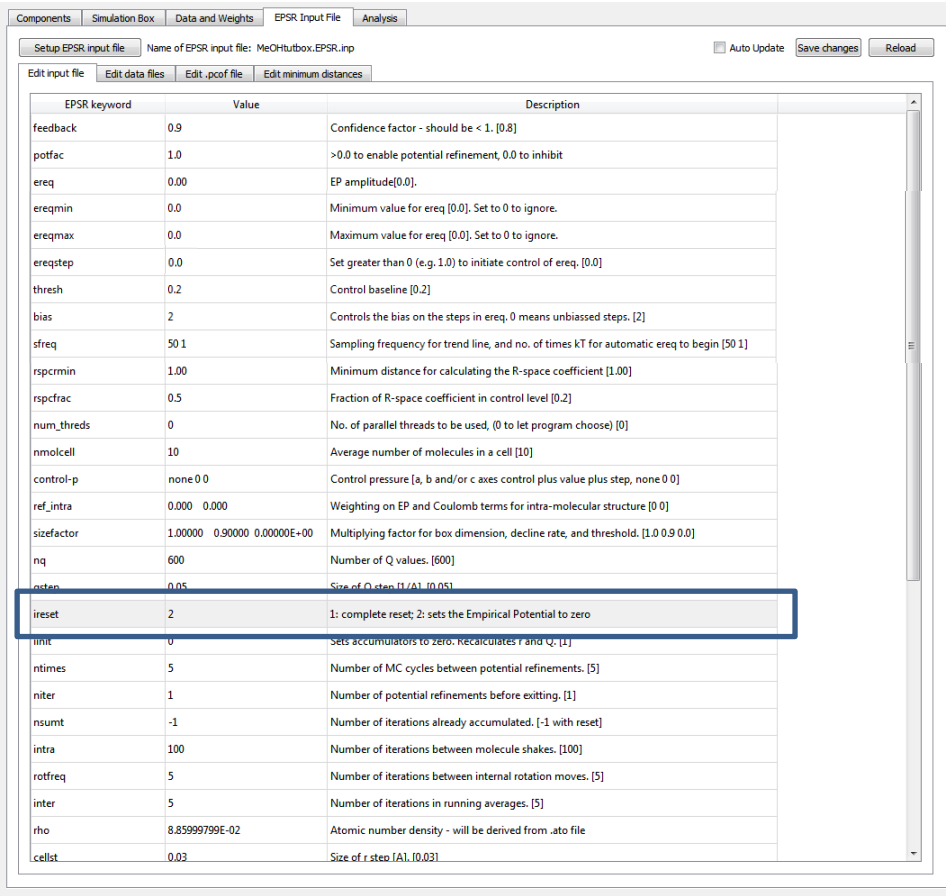
EPSR keyword	Value	Description
feedback	0.9	Confidence factor - should be < 1. [0.8]
potfac	1.0	>0.0 to enable potential refinement, 0.0 to inhibit
ereq	0.0	EP amplitude[0.0].
ereqmin	0.0	Minimum value for ereq [0.0]. Set to 0 to ignore.
ereqmax	0.0	Maximum value for ereq [0.0]. Set to 0 to ignore.
ereqstep	0.0	Set greater than 0 (e.g. 1.0) to initiate control of ereq. [0.0]
thresh	0.2	Control baseline [0.2]
bias	2	Controls the bias on the steps in ereq. 0 means unbiassed steps. [2]
sfreq	50 1	Sampling frequency for trend line, and no. of times kT for automatic ereq to begin [50 1]
rspcrmin	1.00	Minimum distance for calculating the R-space coefficient [1.00]
rspcfrac	0.5	Fraction of R-space coefficient in control level [0.2]
num_threds	0	No. of parallel threads to be used, (0 to let program choose) [0]
nmolcell	10	Average number of molecules in a cell [10]
control-p	none 0 0	Control pressure [a, b and/or c axes control plus value plus step, none 0 0]
ref_intra	0 0	Weighting on EP and Coulomb terms for intra-molecular structure [0 0]
sizefactor	1.0 0.9 0.0	Multiplying factor for box dimension, decline rate, and threshold. [1.0 0.9 0.0]
nq	600	Number of Q values. [600]
qstep	0.05	Size of Q step [1/A]. [0.05]
ireset	1	1: complete reset; 2: sets the Empirical Potential to zero
iinit	1	Sets accumulators to zero. Recalculates r and Q. [1]
ntimes	5	Number of MC cycles between potential refinements. [5]
niter	1	Number of potential refinements before exitting. [1]
nsumt	-1	Number of iterations already accumulated. [-1 with reset]
intra	100	Number of iterations between molecule shakes. [100]
rotfreq	5	Number of iterations between internal rotation moves. [5]
inter	5	Number of iterations in running averages. [5]
rho	8.85999799E-02	Atomic number density - will be derived from .ato file
cellst	0.03	Size of r step [A]. [0.03]

Running EPSR

- It is now time to run EPSR: on the top menu bar click Run…-> Run EPSR.
- After a few seconds, plot the data in reciprocal space and real space and examine the decrease in energy and r-factor using the plots on the right hand side of the window.
- Wait about 30s and then stop EPSR: on the top menu bar click Run…->Stop EPSR.
- Once EPSR has finished the last iteration and stopped, change ireset to 2 and run EPSR again.
- Replot the energy to see if it is negative and still decreasing - to refresh the graph click Plot again.
- Continue running EPSR until the Energy and R-factor plots plateau (they do not need to be smooth).

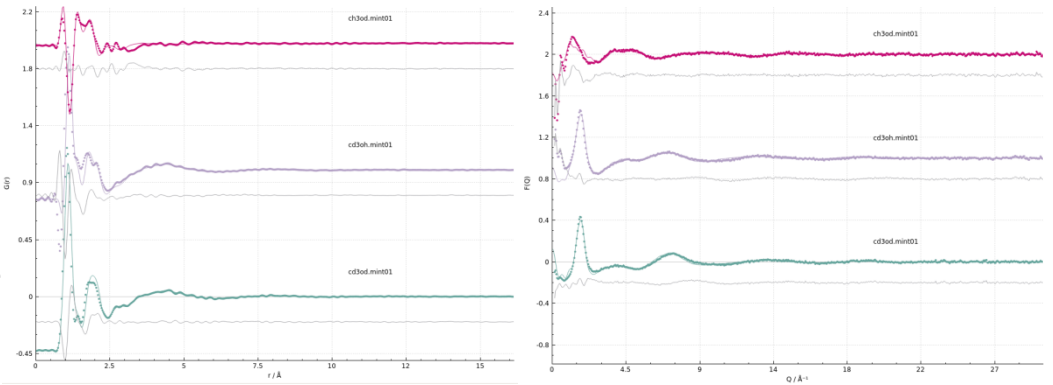


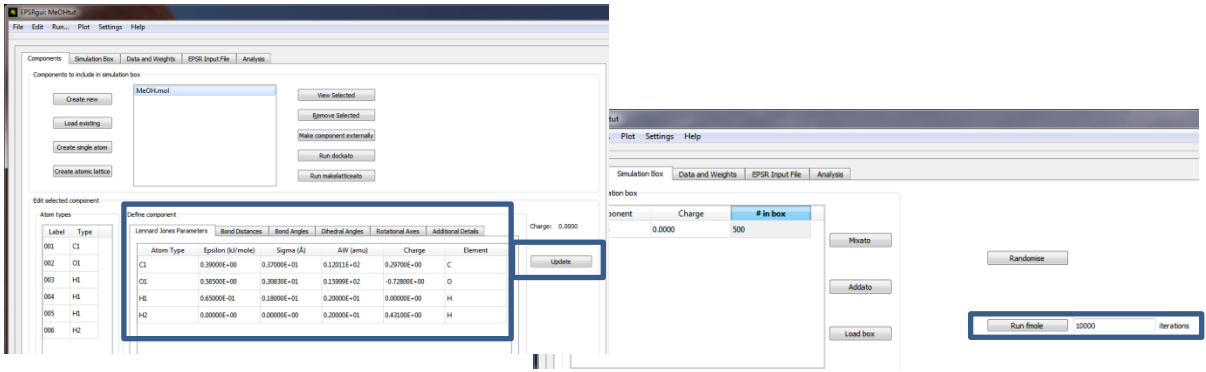


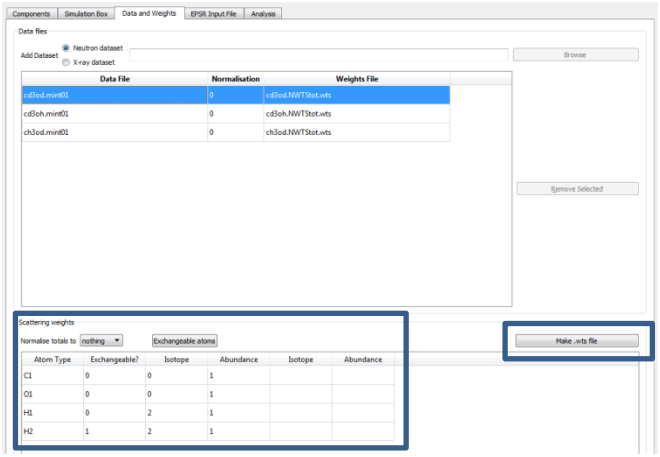


Improving the simulation – the reference potential

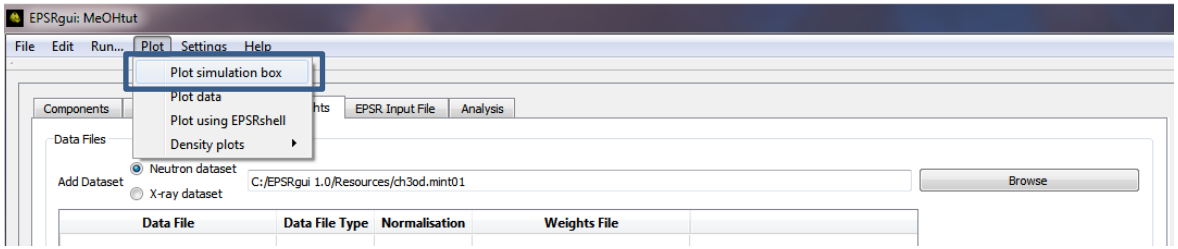
- After the box has equilibrated as far as possible without the empirical potential, stop EPSR and examine the simulation.
- In real space, are the peak positions at low r (=bond distances) correct? Are the first peak heights (=scattering weights) correct? In reciprocal space, are the peak positions approximately correct?
- If these are all approximately ok (which they should be), move on to refining the empirical potential.
- If not, edit the Lennard-Jones potentials in the Components tab, and click Update.
- Run fmole 10,000 times to apply the changes to the simulation box.
- Run EPSR again and see if this improves the fit.
- If a mistake has been made during making the weights files, correct it in the Weights files tab and click Make .wts file. In the EPSR input file tab, change ireset to 2 and then run EPSR again.



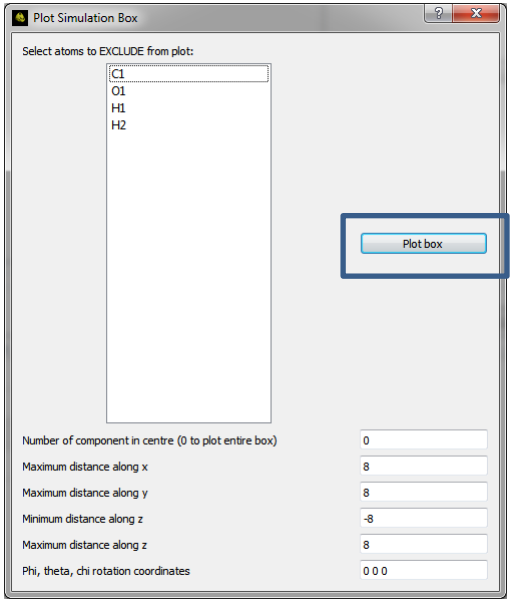


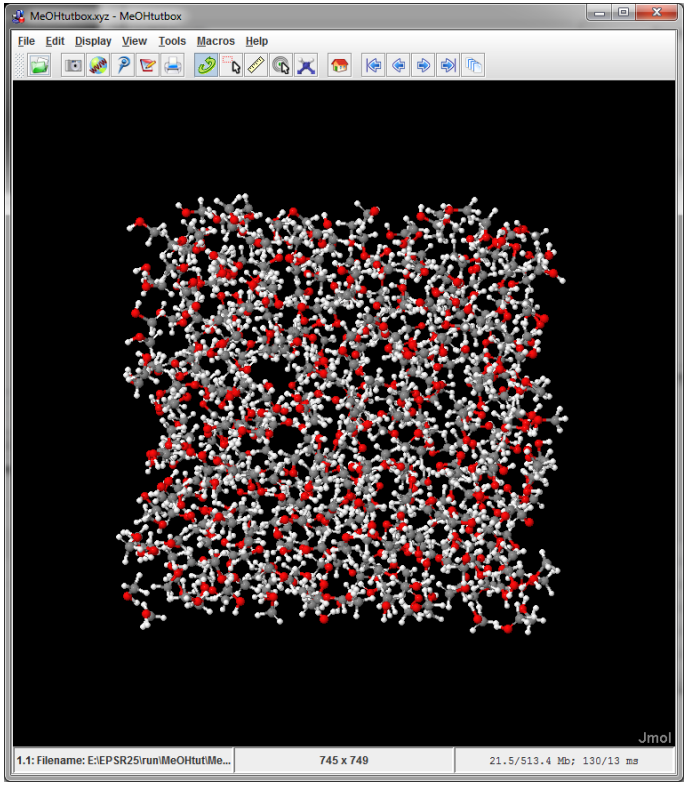


Plot simulation box



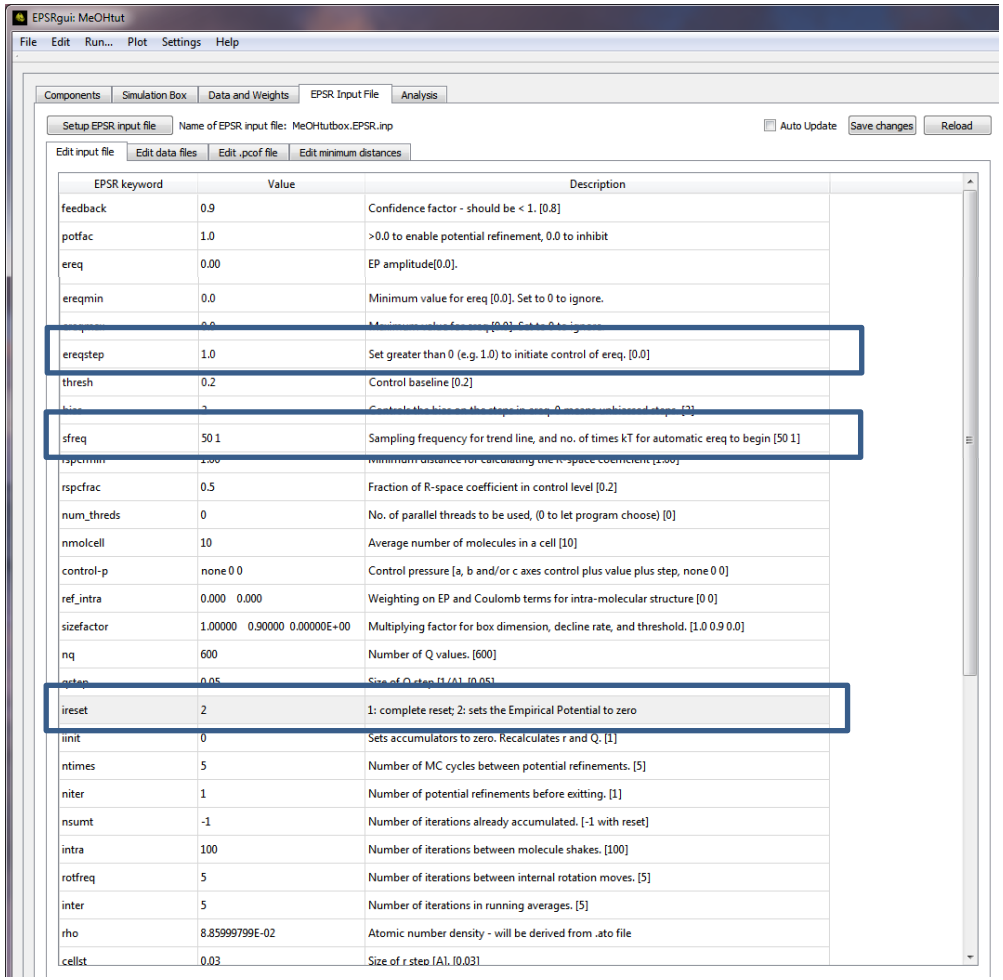
- It is a good idea to check that the molecules are behaving as would be expected in the simulation box.
- On the top menu bar click Plot-> Plot simulation box.
- In the dialog box select any atoms that you want to EXCLUDE from the plot – in this instance plot all the atoms.
- Click Plot box. The simulation box will open in a Jmol window.





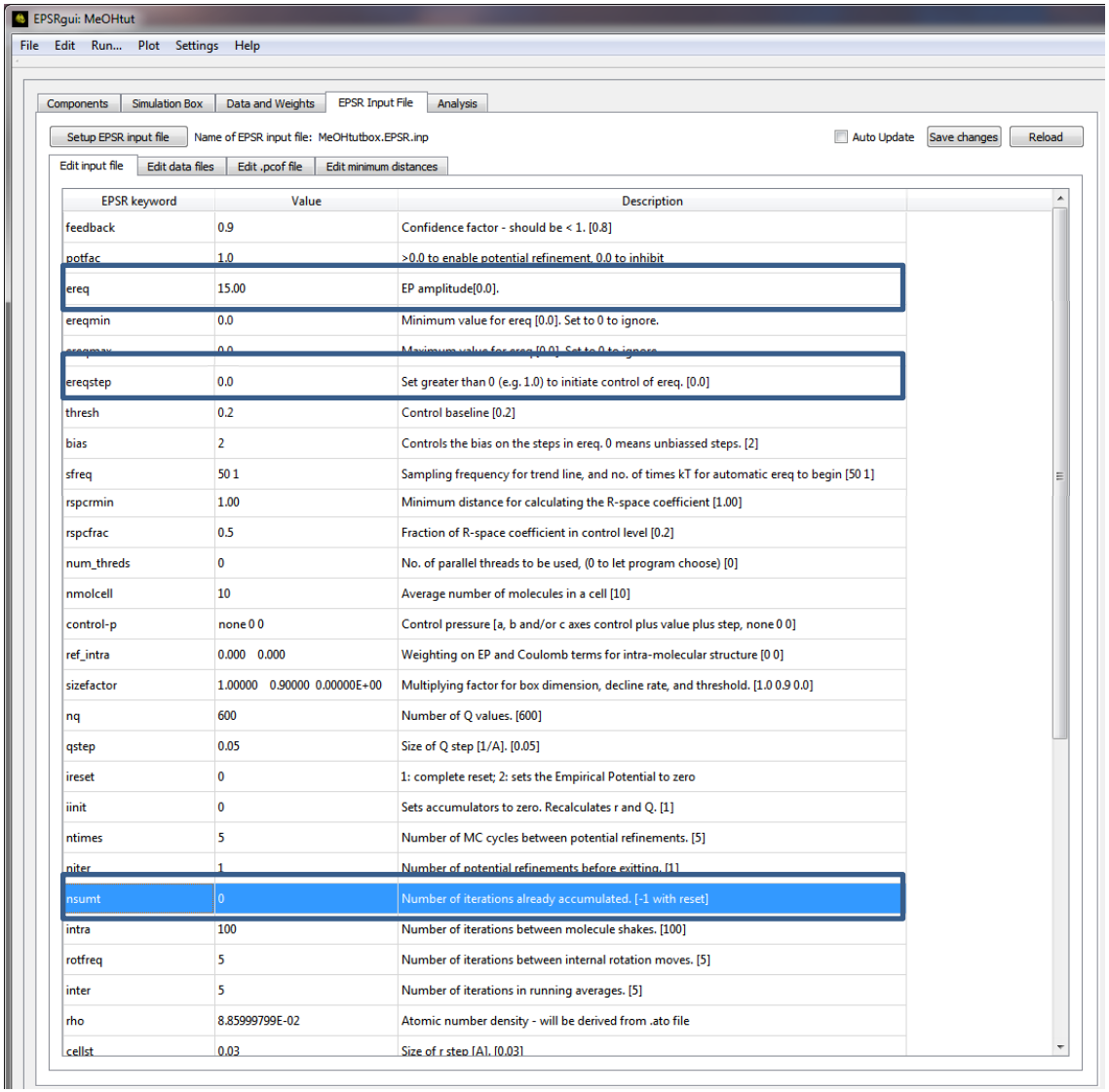
Improving the simulation – the empirical potential

- Once the fit is as good as can be obtained from the reference potential alone, it is time to start refining the empirical potential.
- If necessary, stop EPSR.
- In the EPSR input file tab, change the ereqstep value to be 1 and check sfreq is 50 1. Also, change the ireset value to be 2.
- Run EPSR again.
- EPSR will now be refining the empirical potential so as to allow the atoms to move in such a way as to get a better fit to the data. The amount of energy EPSR uses to achieve this is decided by EPSR by assessing what the recent improvement to the fit has been for a certain energy value. This can be plotted by selecting ereq from the plot drop down menu and clicking Plot.
- You may find that the empirical potential is not necessary, or that the iterative method does not find a minima. If this is the case try using a fixed value for ereq with ereqstep 0 and manually change the value of ereq – check how ereq affects the fit to the data by examining the F(Q), G(r), energy and R-factor plots.

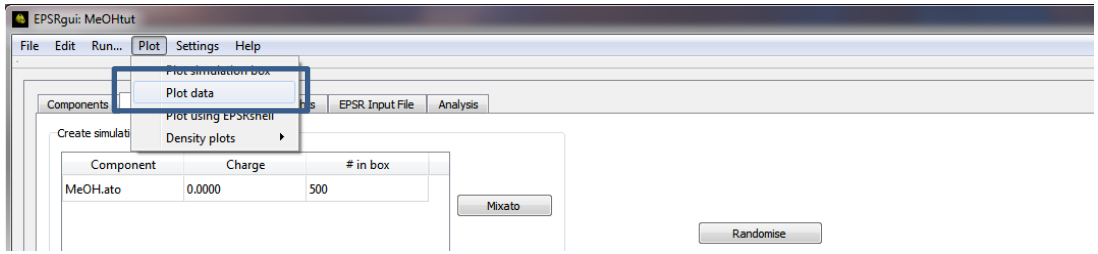


Accumulating the refined simulation box

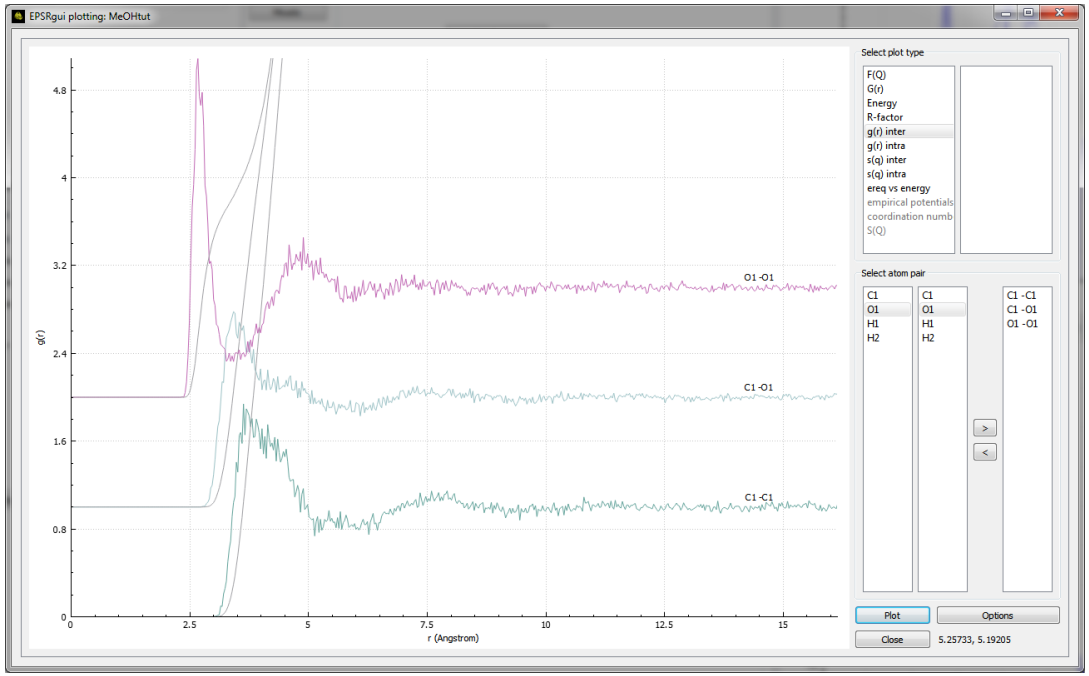
- Once the simulation has been improved as far as possible, and a good value for ereq has been identified, stop EPSR.
- In the EPSR input file tab, change ereq to be the best value identified from the ereq plot. Also change ereqstep to be 0.0.
- To start accumulating the positions of the atoms over a number of frames of the simulation (in order to improve statistics for the pair correlation functions etc), change the value of nsumt to be 0.
- We also want to set up calculations that will give insight into the structure so that they will be performed on each frame of the simulation while EPSR is running. Before we know what to setup we need to take a look at the simulation so far…



Analysing the refined simulation box – g(r)

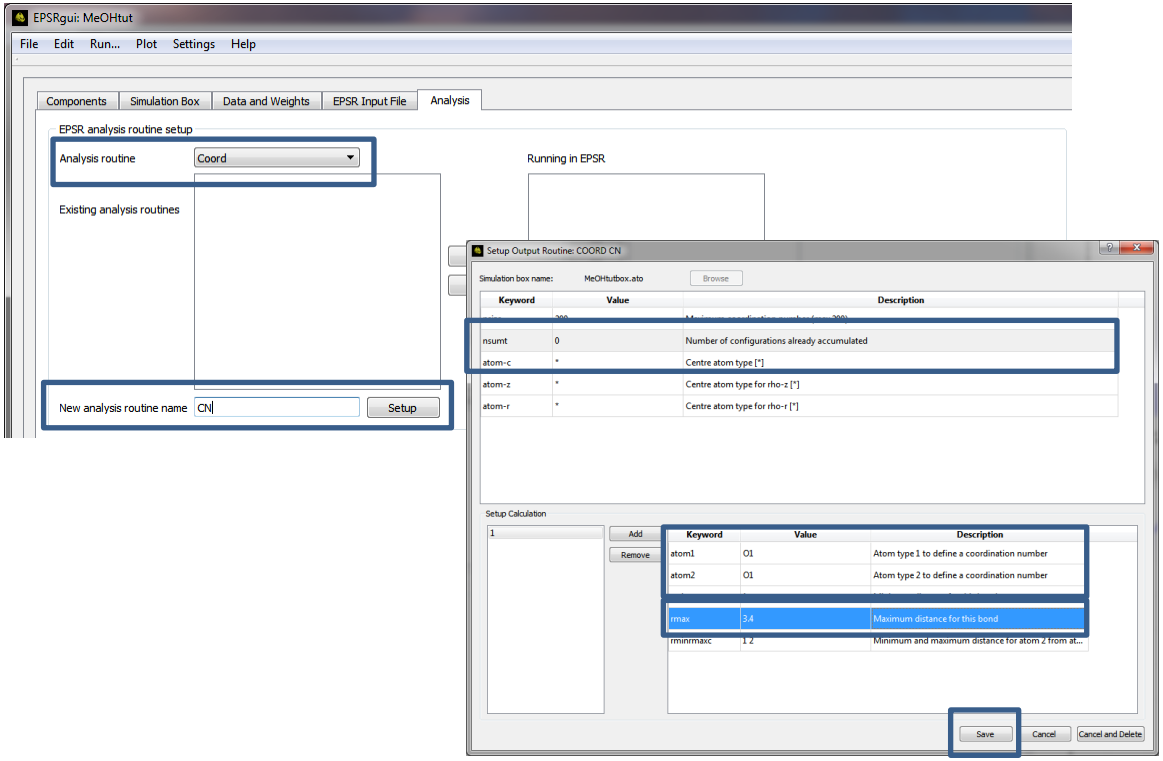


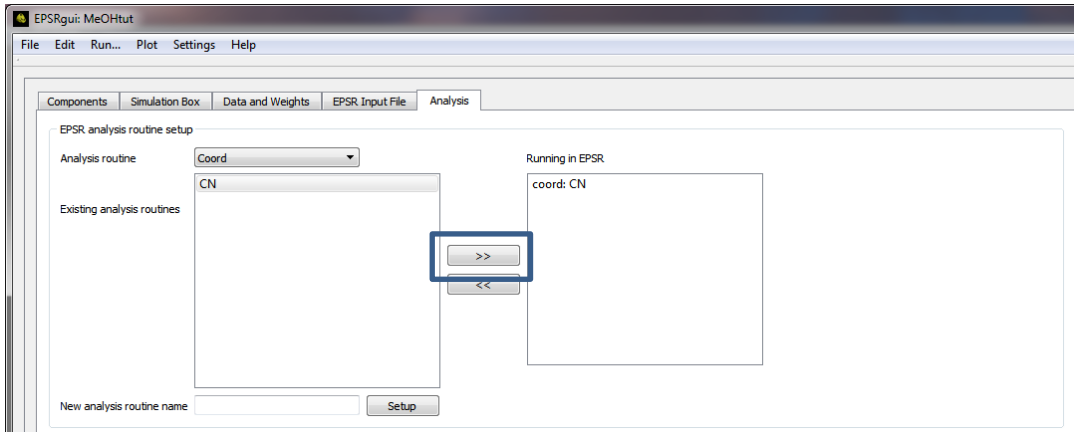
- On the top menu bar, click Plot->Plot data.
- In the plotting window that opens, click g(r) inter to plot the intermolecular pair correlation functions for selected atom pairs.
- Click on each atom in a pair and click the > button to add the pair to the list of pair correlation functions to be plotted. Repeat this for each atom pair to be plotted. To remove an atom pair, click on it and then click the < button.
- Then click Plot.
- This plots the intermolecular g(r) together with the coordination number (in grey).
- To re-position the plot, right click and drag, to zoom in and out use the mouse roller wheel. To zoom in and out along the vertical axis only, hold down Ctrl while using the mouse roller wheel. To zoom in and out along the horizontal axis only, hold down Shift while using the mouse roller wheel.
- The most commonly occurring nearest neighbour distance can be read off from the first peak maximum. Make a note of the maximum r value which could still be considered the nearest neighbour for each g(r) (usually the end of the 1st peak or the 1st minimum).



Calculations from the refined simulation box – coord

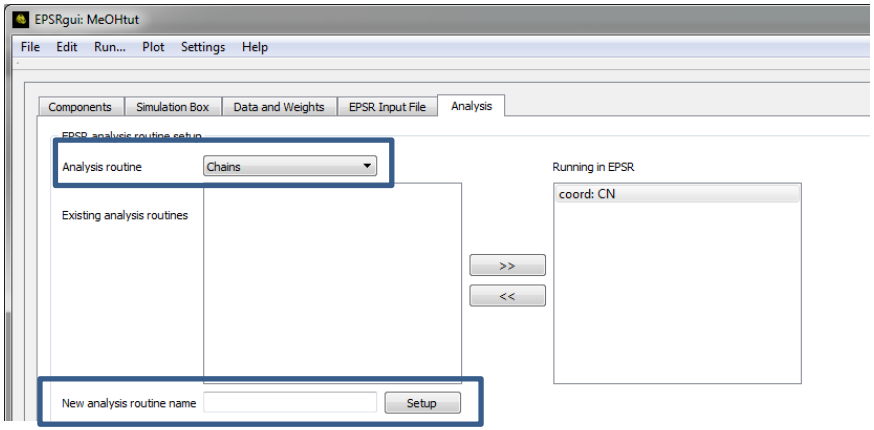
- Click on the Analysis tab.
- In the Analysis routine drop down menu, select Coord.
- In the New analysis routine name type CN and click Setup.
- In the dialog window that appears change the following values
  - nsumt: 0
  - atom1: O1
  - atom2: O1
  - rmax: <read off from g(r) plot>
- Click Add and in calculation 2 examine a different combination of atoms e.g. O1 C1 with an appropriate rmax.
- Press Save.
- The routine setup file CN will now appear in the existing outputs box. Click the >> button to add it to be run when EPSR runs.

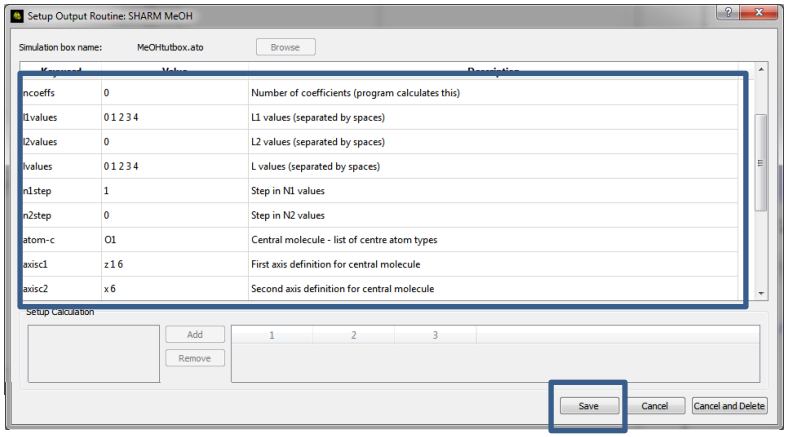


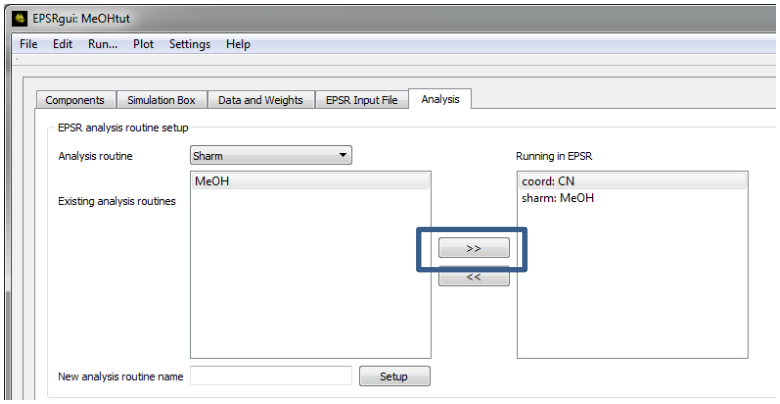


Calculations from the refined simulation box – spatial density functions

- Click on the Analysis tab.
- In the Analysis routine drop down menu, select Sharm.
- In the New analysis routine name type MeOH and click Setup.
- In the dialog window that appears change the following values
  - nsumt: 0
  - l1: 0 1 2 3 4
  - lvalues: 0 1 2 3 4
  - n1step: 1
  - atom-c: O1
  - axisc1: z 1 6
  - axisc2: x 6
  - atom-s: O1
- Press Save.
- The routine setup file MeOH will now appear in the existing outputs box. Click the >> button to add it to be run when EPSR runs.

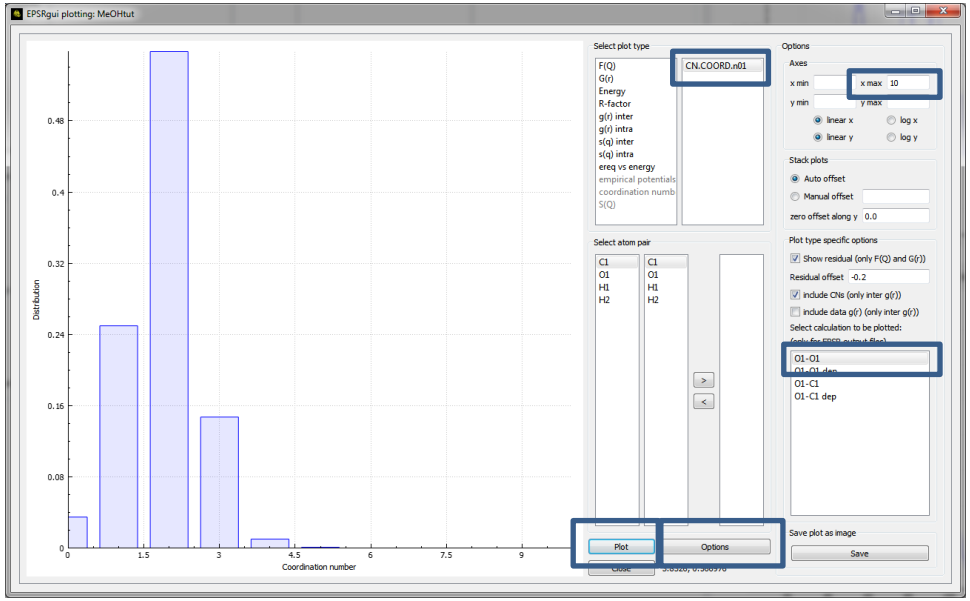


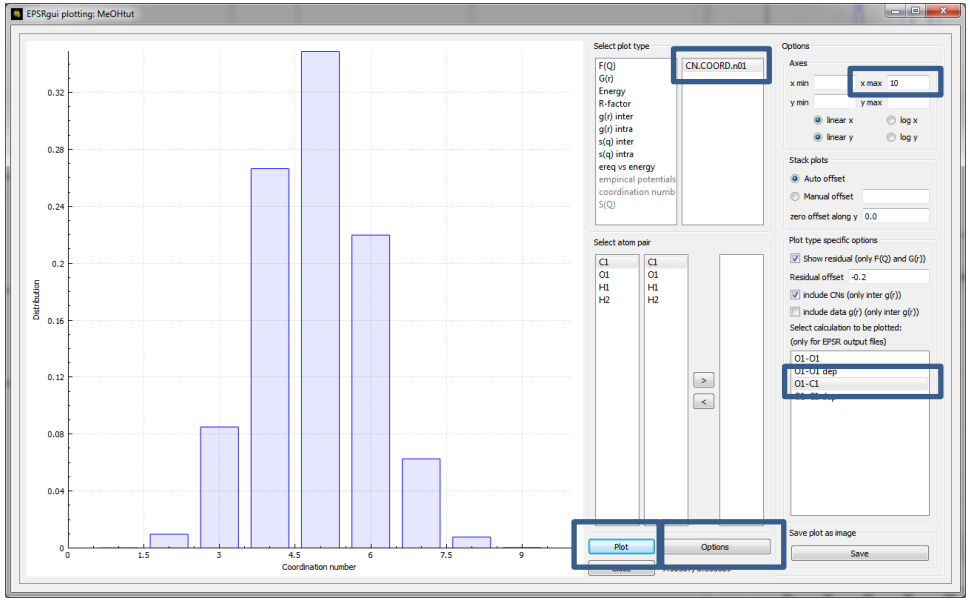




Performing calculations

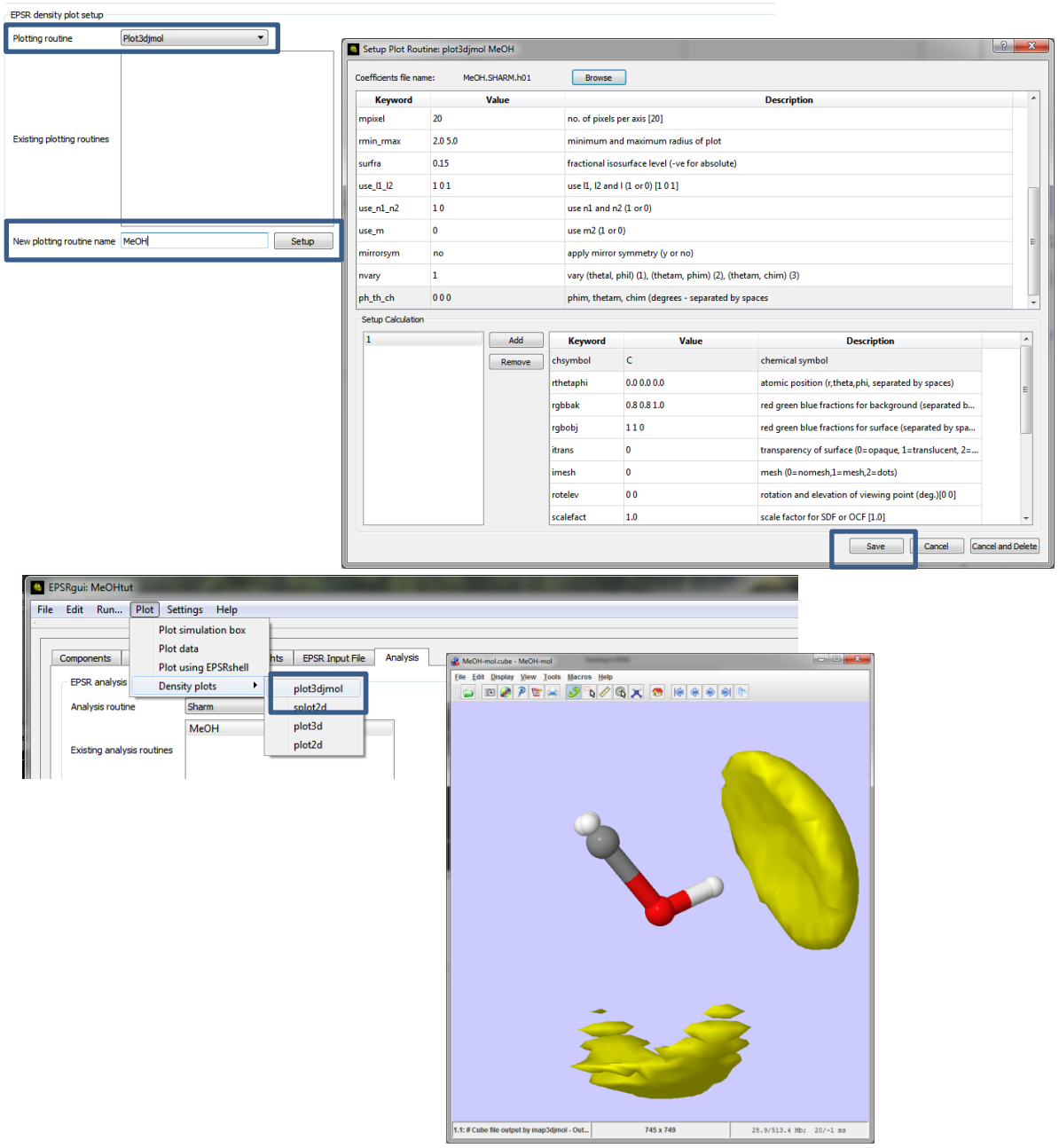
- Once all the calculations have been set up, run EPSR.
- Even while EPSR is running, the outputs from the calculations can be viewed by clicking Plot->Plot data.
- In the top right hand corner, the calculations that are running while EPSR is running are listed.
- Click on the CN.COORD calculation and click Options on the bottom right hand corner. This opens additional plotting options.
- Select the atom pair you want to see the coordination number for in the list in the Plot type specific options box and then click Plot.
- This shows a histogram of the normalised number of instances that each coordination number observed in the accumulated frames of the simulation (as defined during setting up the calculation).
- To change the maximum x value, type a value for x max and then click plot again.





Plotting spatial density functions

- Now that the sharm routine has been run, the coefficients file containing the spatial density function of O1 around O1 has been created. To view the information from this routine as a surface the plotting routine Plot3djmol needs to be setup.
- Click on the Analysis tab.
- In the Plotting routine drop down menu, select Plot3djmol.
- In the New plotting routine name type MeOH and click Setup.
- Choose the .SHARM.h01 coefficients file created by the previous analysis routine.
- In the dialog window that appears press Save.
- On the top menu bar click Plot->Plot outputs->plot3djmol.
- In the browse window that opens, select the .CUBE.txt file that has the same name as the plotting routine (MeOH) and click Open.
- The spatial density function will be plotted in Jmol as a surface around the average position of the methanol molecule. As the methyl group is rotating, it is not displayed correctly as Jmol is showing the average position of the hydrogens.



Network glass simulation – choose your own!

EPSRgui tutorial 3

Purpose of this tutorial

The goal of this tutorial is to build, refine and analyse a model of a network glass of your choice. Published data from an online repository will be used. To build this simulation, this tutorial assumes that tutorial 1 has been completed and gives pointers rather than precise instructions in how to:

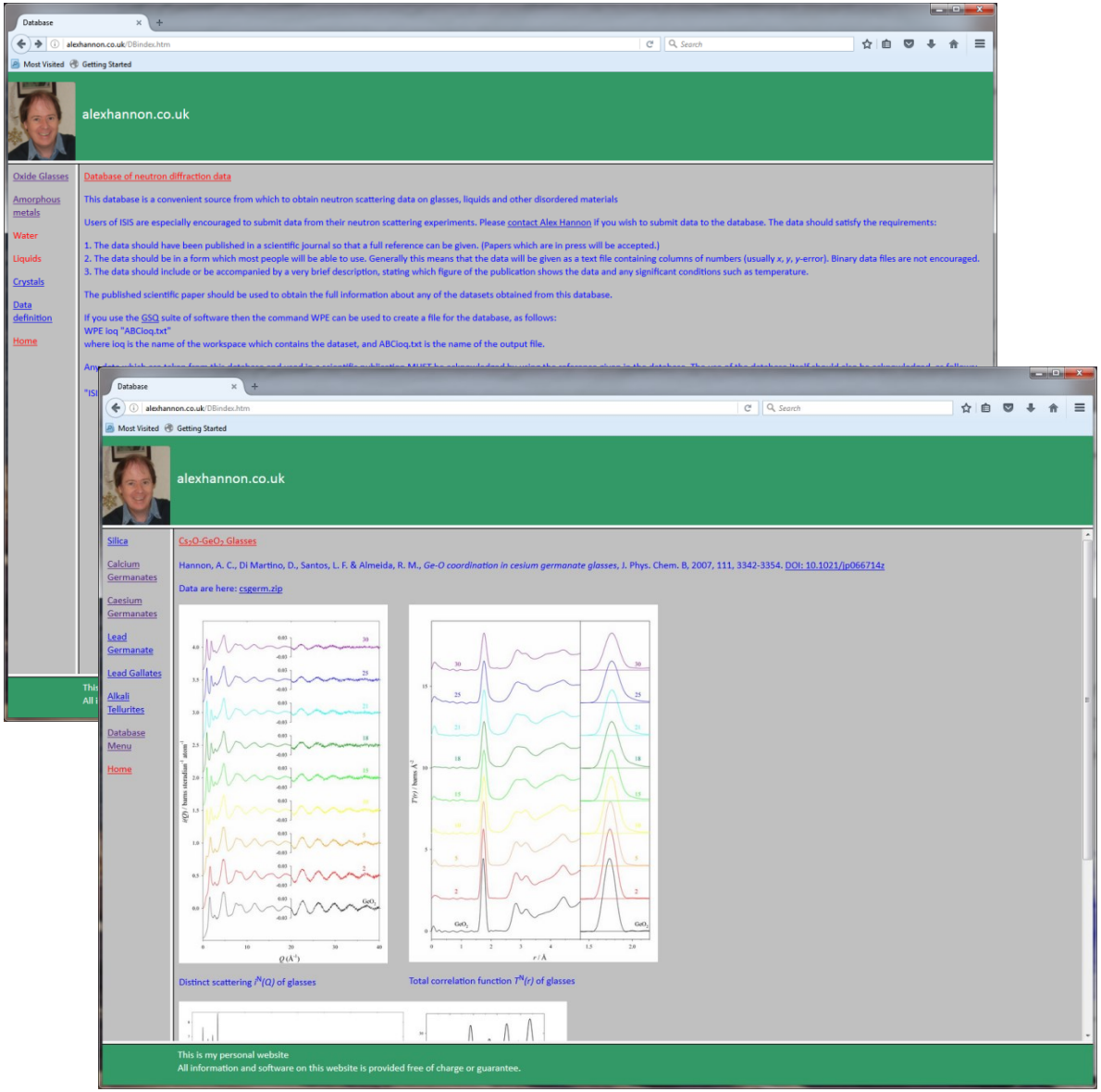
- Create the atomic components and define their Lennard-Jones potentials.
- Create a simulation box containing the components.
- Create scattering weights files for each of the experimental datasets.
- Create a simulation and run it.
- Improve the Lennard-Jones potentials as required.
- Refine the empirical potential.
- Create analysis routines to analyse the simulation
- Run analysis routines and accumulate distribution functions.
- Plot the results.

Choose a glass system

- Published experimental data for a number of glasses are listed in a database at:

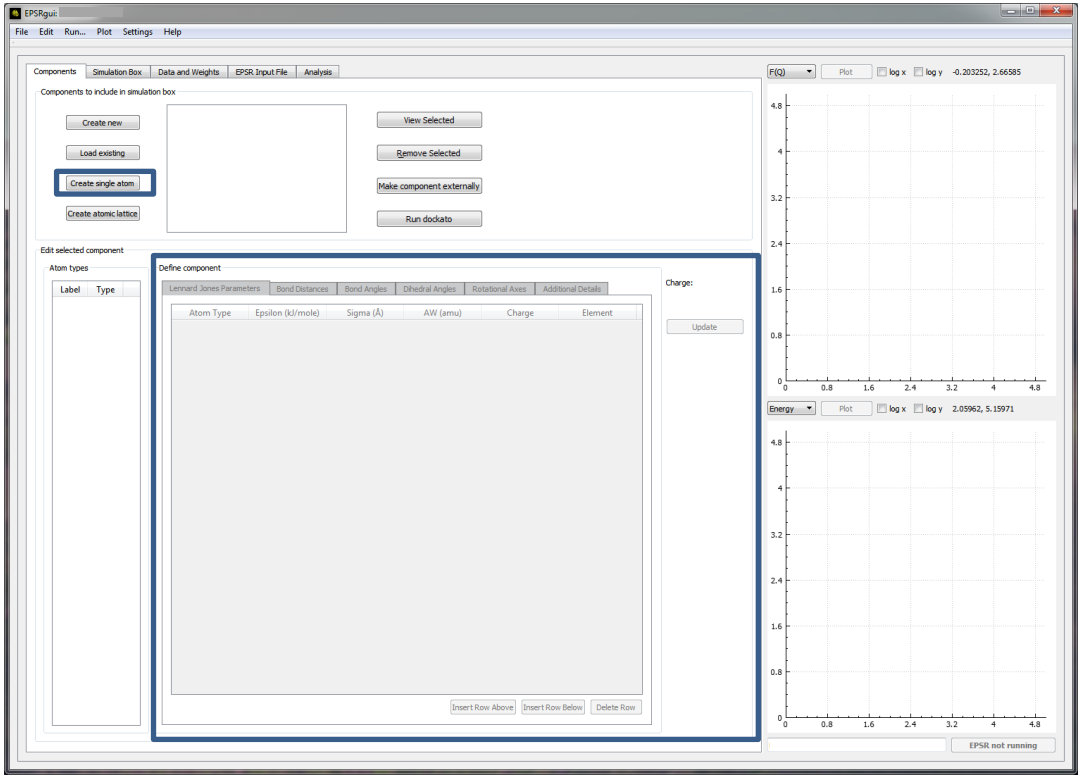
http://alexhannon.co.uk/DBindex.htm

- Click on oxide glasses and choose a system that has some experimental data. From the associated publication referenced on the webpage, note the composition of the system (including density) and how the data were normalised.



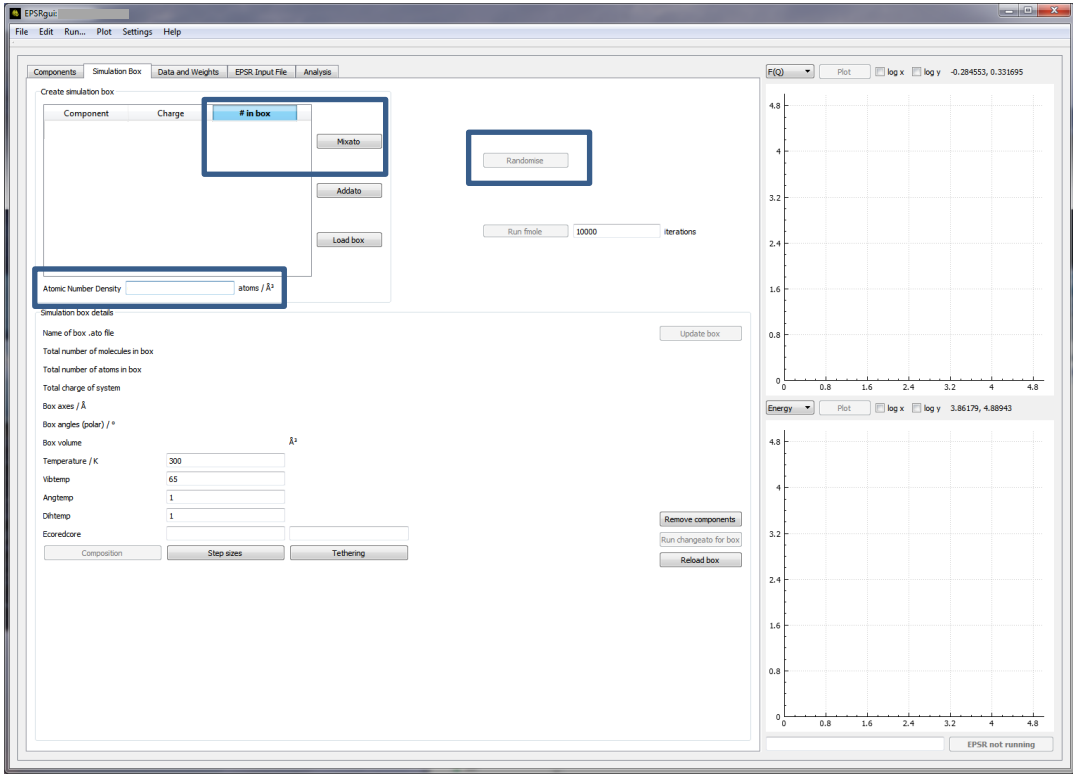
Create a new project and add components

- Create a new project via the File menu.
- In the Components tab, make the component files using Create single atom.
- If Lennard Jones parameters for the components are already in the literature, e.g. in Bowron, Procedia Materials Science 7 (2014) 38 – 52, use these as a starting point for the simulation.
- If not, use the expected bond distances to estimate appropriate sigma values for the Lennard-Jones potentials. The epsilon parameter has less effect on the simulation, so use something similar to the SiO2 simulation as a starting point.



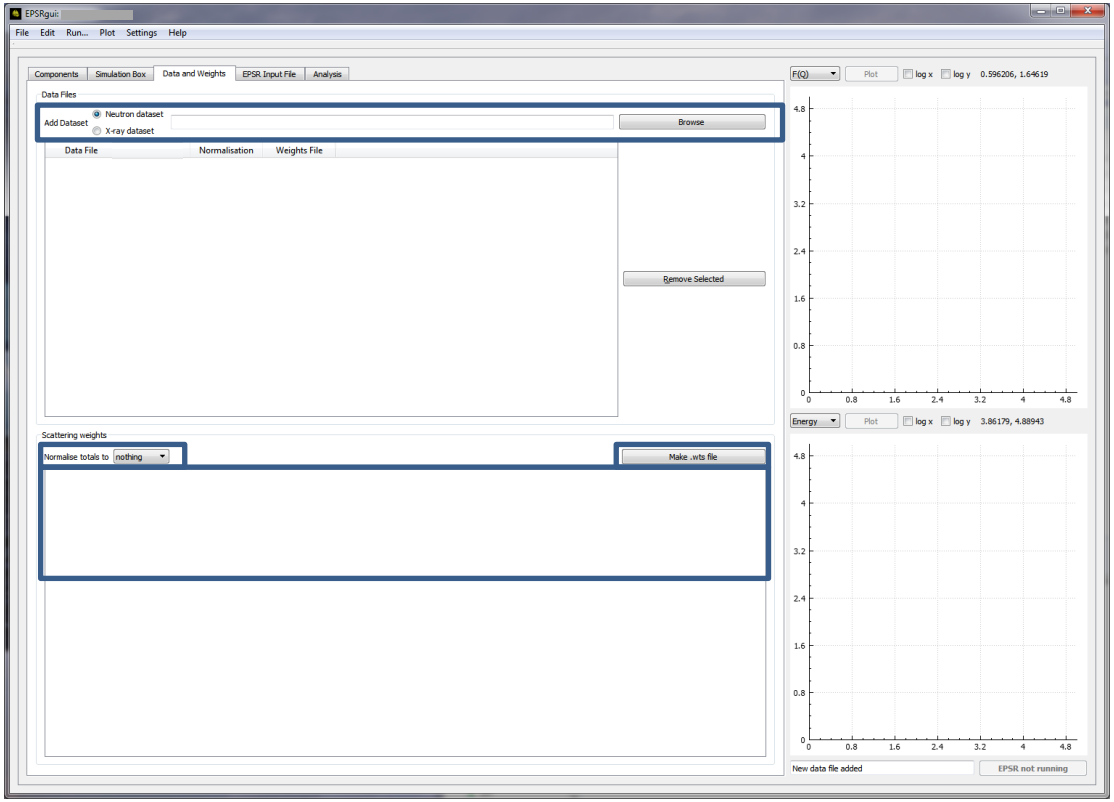
Create the simulation box

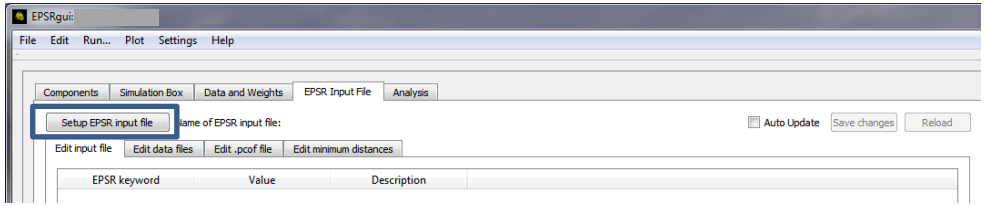
- Move on to the Simulation Box tab.
- From the atomic composition given in the associated publication, add the correct ratio of atoms to the box.
- Also from the publication, find the density of the sample and convert this to atoms/Angstrom^3.
- Ensure enough atoms are added to the box so as half the box length is larger than the longest g(r) to be assessed.
- Use Mixato to add the atoms to the box, and Randomise to distribute them randomly throughout the box.
- Check that the box is neutral in the simulation box details.



Data, scattering weights and EPSR input file

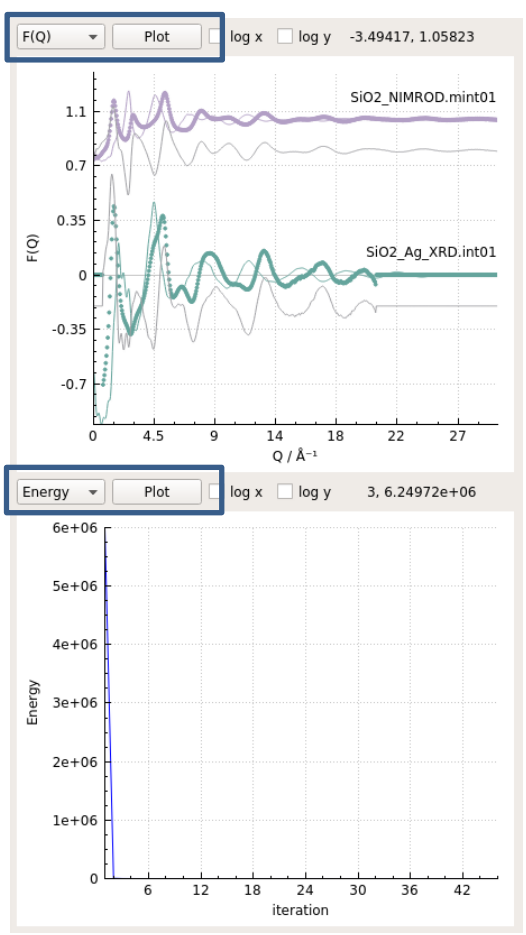
- In the Data and Weights tab, add each dataset obtained for the system, set up and then make the weights files. For this, the following information is required:
  - Are the data from X-ray or neutron scattering?
  - Which isotopes were present in the samples (for neutron data)
  - How the data were normalised
- Once complete, go to the EPSR Input File tab and setup the EPSR input file.
- Check what the format of the data file is (check the EPSR manual [Help->EPSR manual] for more information) and change the nrtype in Edit data files tab of the EPSR Input File tab accordingly.
- From the menu bar, Run EPSR.

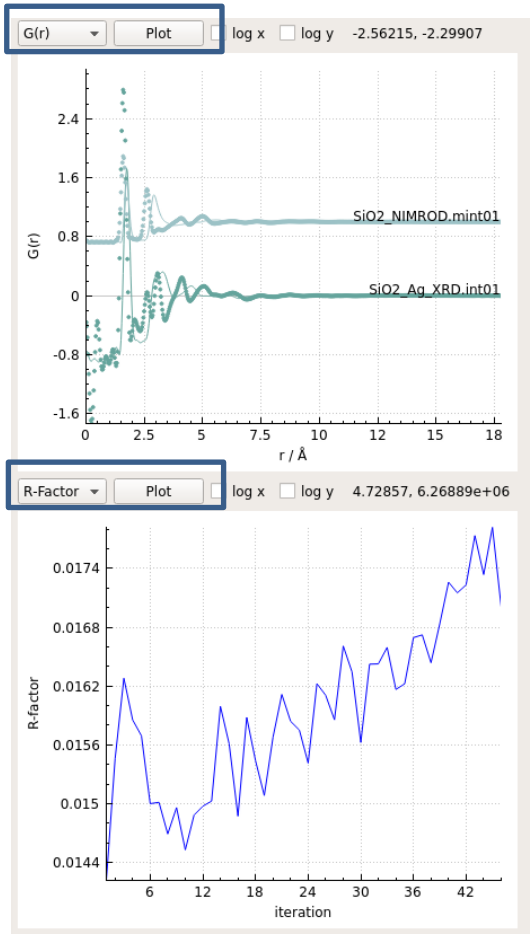




Improving the simulation

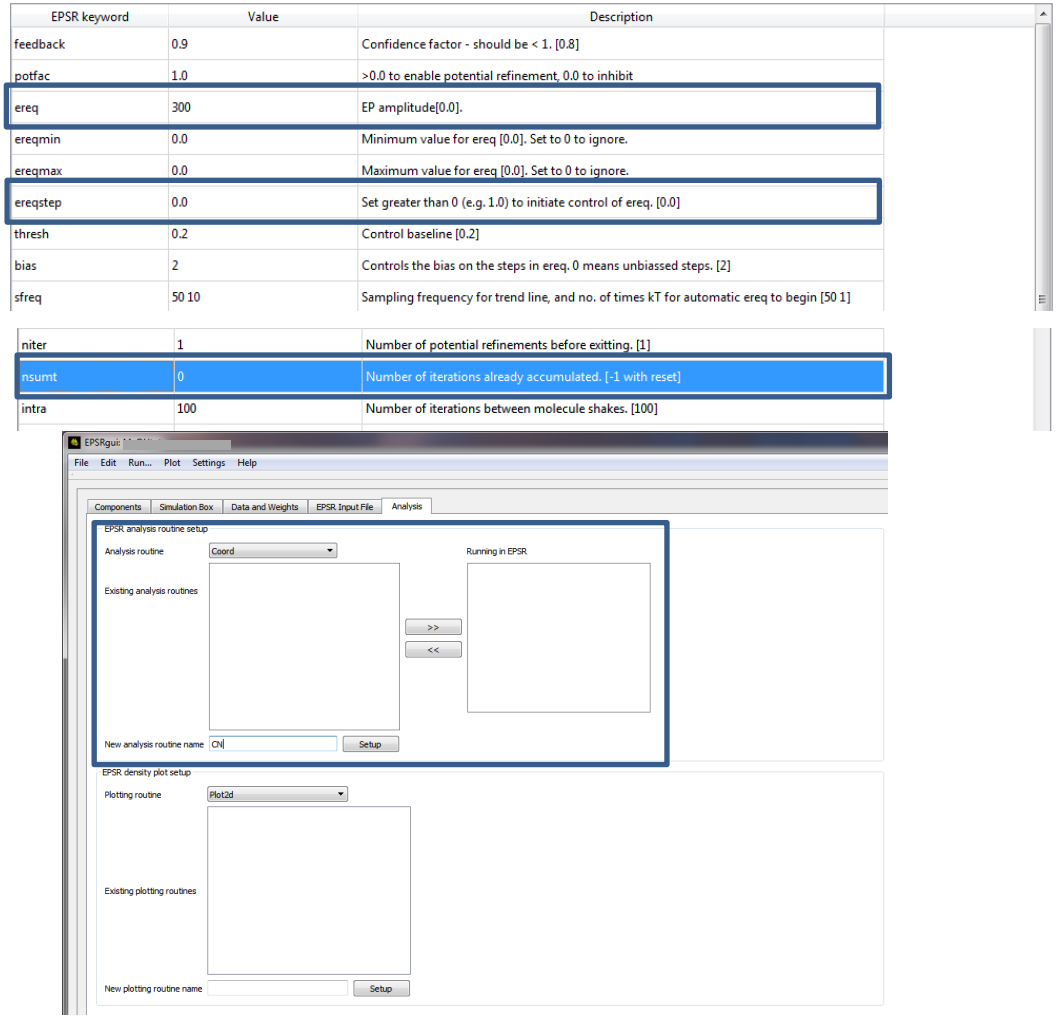
- Once the energy is negative, stop EPSR, reset the simulation (ireset 2) and start EPSR again to follow the change in energy more easily.
- Check that the model in reciprocal space (F(Q)) and real space (G(r)) bears some resemblance to the data. If it does not, check that the weights files are correct, the composition is correct, the density is correct and the values used in the component Lennard-Jones parameters are as expected (e.g. the decimal point is in the correct place).
- If all of the above are correct, use the G(r) plot to identify where the first nearest neighbours are not fitting well. Change the Lennard-Jones potentials to improve the fit.
- Once the simulation has been improved as far as possible manually, start refining ereq to make the final improvements via the empirical potential. It is important that the reference potential is improved first as the energy required to overcome a poor reference potential might otherwise be unfeasibly large.





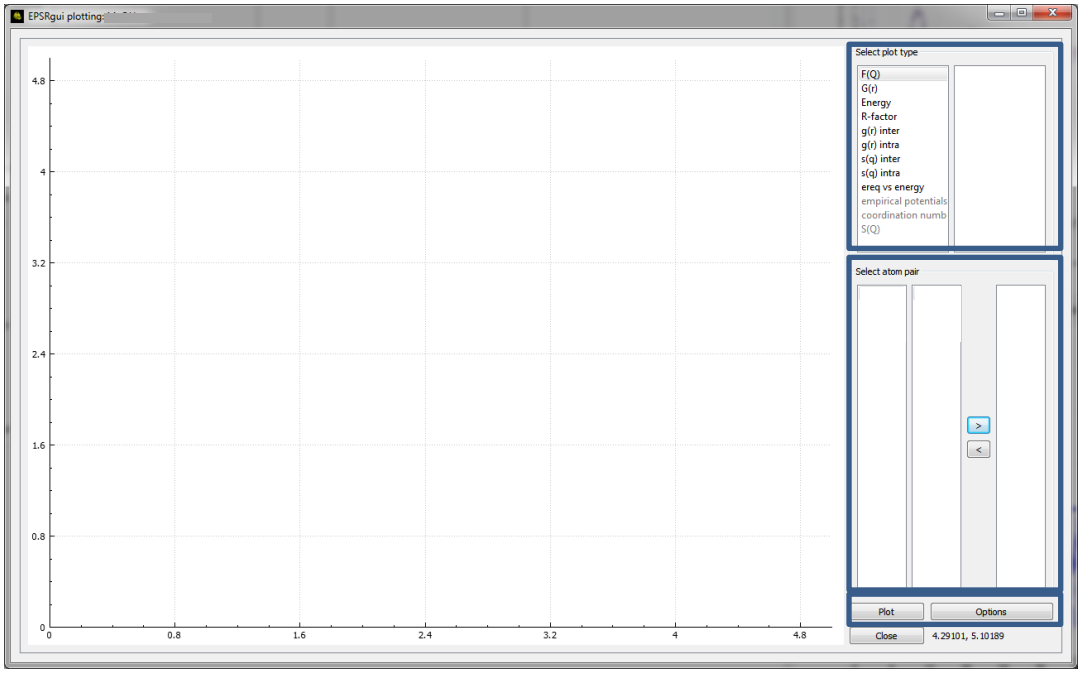
Accumulating the refined simulation box

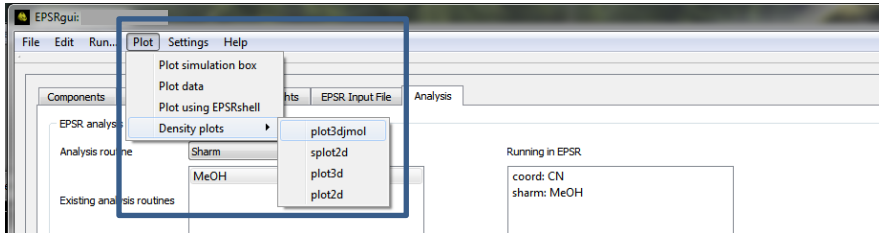
- Once the simulation has been improved as far as possible, identify a good value for ereq and stop the simulation. In the EPSR input file tab use this value of ereq as a fixed value and change the input file to start accumulating frames of the simulation.
- Identify analysis routines to be performed on the simulation while it is accumulating (use the EPSR manual for more information on each routine) and set these up in the Analysis tab before running EPSR.
- To perform additional analyses after EPSR has started, stop EPSR, setup the analysis routine and restart EPSR again. Ensure EPSR is run for sufficient iterations that the results are a good representation of the simulation.



Viewing outputs and analysis routine results

- Most outputs (e.g. pair correlation functions) and analysis routines can be plotted in the Plot data window.
- For spatial density functions (2D or 3D) a plotting routine must also be setup. Setup plotting routines in the lower section of the Analysis tab. Refer to the EPSR manual for more details on which settings to change to achieve this.

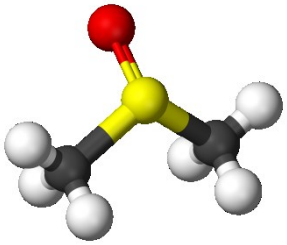




DMSO-water

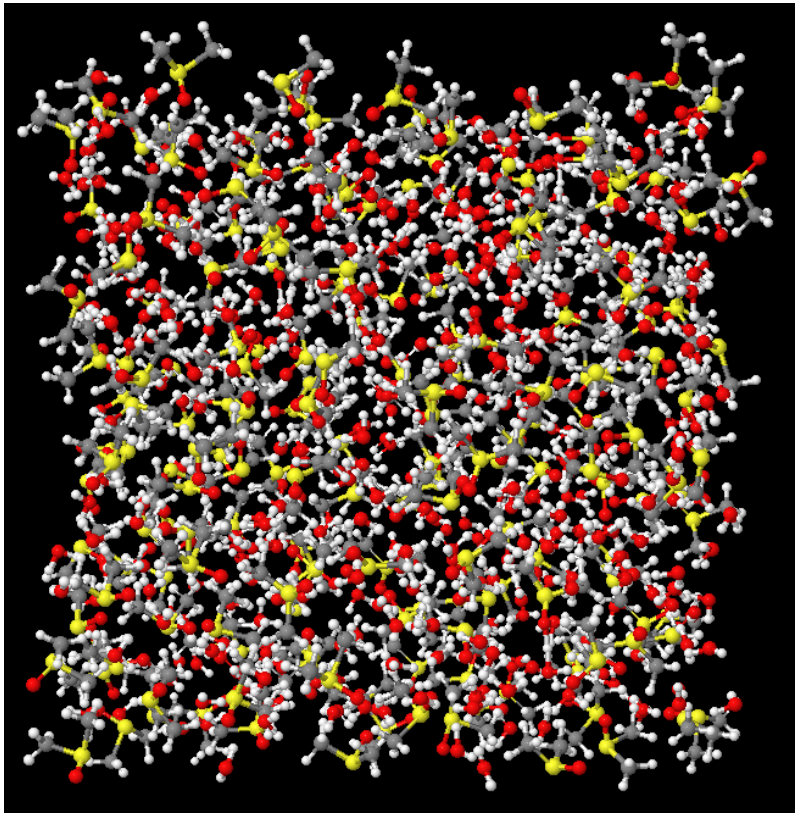
EPSRgui tutorial 4

Purpose of this tutorial



The goal of this tutorial is to build, refine and analyse a model of a the two component liquid, DMSO-water. This tutorial assumes the methanol tutorial has already been completed and gives pointers rather than precise instructions in how to:

- Create the molecular component and define the Lennard-Jones potentials or each atom type.
- Create a
- simulation box containing the component.
- Create scattering weights files for each of the experimental datasets.
- Create a simulation and run it.
- Improve the Lennard-Jones potentials as required.
- Refine the empirical potential.
- Create analysis routines to probe the simulation.
- Run analysis routines and accumulation the distribution functions.
- Plot the results.



Obtain the data and system details

- The published data are provided in the EPSRgui/Resources folder.
- Note down the composition, atomic density and data normalisation from the publication (shown on the right).
- In this instance the Lennard-Jones parameters are given in the publication, but if this was a novel system there might not be Lennard-Jones parameters so readily available. Instead these can be obtained/approximated from Jorgensen *et al.* or publications of similar systems or calculated from molecular dynamics simulations, e.g. using CHARMM.

Lennard-Jones potentials

DMSO – see Supporting Information for Jorgensen et al. in EPSRgui/Resources and pick the most appropriate potentials.

SPC-E water:

	Epsilon / *kJ mol^{-1}*	*Sigma / Å*	Mass / amu	*Charge / e$^-$*
Ow	0.65	3.16	16	-0.8476
Hw	0.0	0.0	2	0.4238

Ow-Hw bond distance: 0.976 Å

Hw-Ow-Hw bond angle: 104.5°

Simulation Box

Composition: 1 DMSO: 2H_2O

Atomic number density: 0.0919 atoms Å^{-3}

Data and Scattering Weights

SLS03850.mint01 – neutron, DMSO(D), H_2O

SLS03863.mint01 – neutron, DMSO(D), D_2O

SLS03871.mint01 – neutron, DMSO(D), $(H_{0.64}D_{0.36})_2O$

Data normalisation: totals not normalised

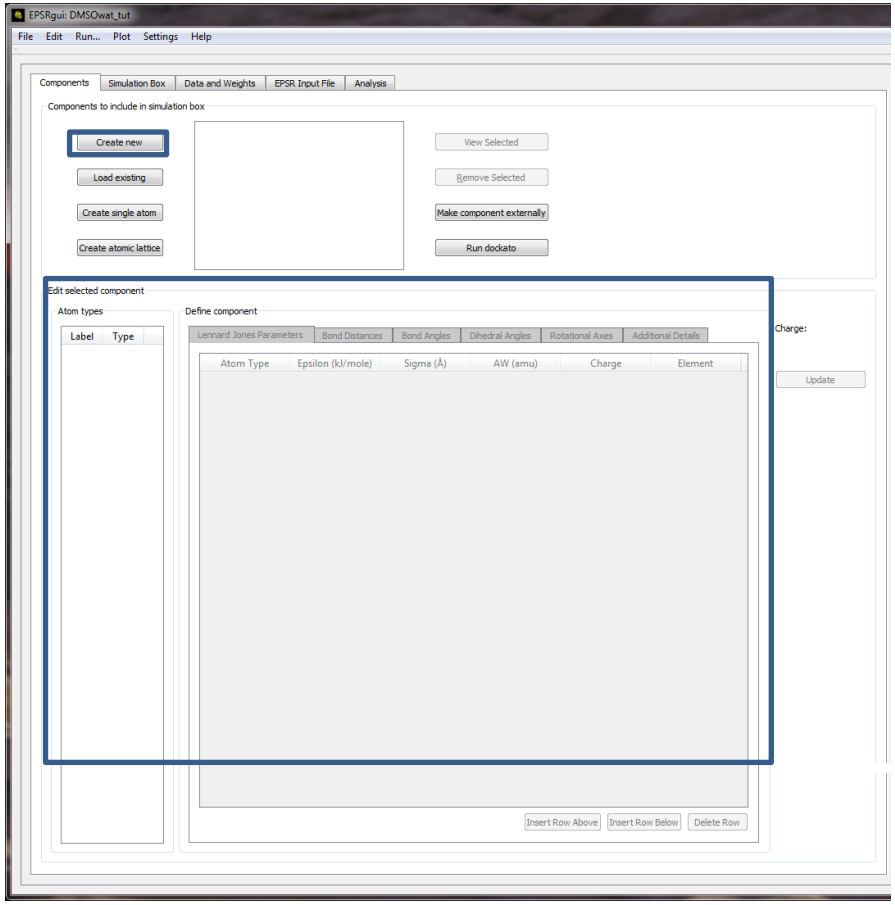
Data type: 5

References

- *A neutron diffraction study of dimethyl sulphoxide–water mixtures, A. K. Soper and A. Luzar, J. Chem. Phys. 97 (1992) 1320.*
- *Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids, Jorgensen et al., J. Am. Chem. Soc. (1996) 118, 11225-11236.*

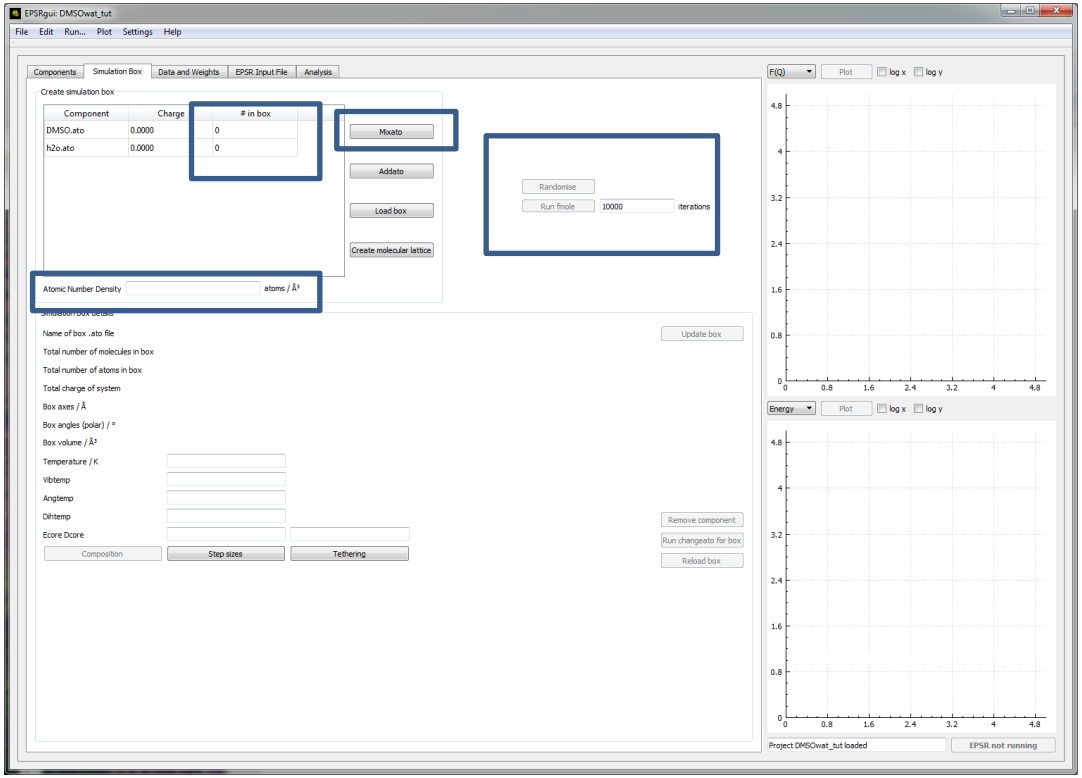
Create a new project and the components

- Create new Project.
- In the Components tab, create the molecular components. Remember to save the files as .jmol files within jmol.
- Jmol only gives a rough minimisation of the molecular structure – consider alternative sources that will provide more accurate bond distances and angles, or minimisation calculations such as MOPAC or Gaussian. To import a molecule from other software, export the molecule into a format that Jmol can read and then save the file in Jmol as a .jmol. EPSR will then convert the file to an EPSR .mol file. Remember that an EPSR .mol file does not have the same format as an MDL Molfile and cannot be used interchangeably.
- Edit the Lennard-Jones potentials for each of the atom types. Ensure that atom type names are unique to a component – the same atom type name cannot be used in more than 1 component so will often have to changed for one of the components e.g. by adding a 'w' for water atoms.
- If the molecule has rigid groups, use dihedrals to define these. If the molecule has rotatable groups, ensure there are no dihedrals restraining these, and include a rotational axis in order for fmole to rotate the group.



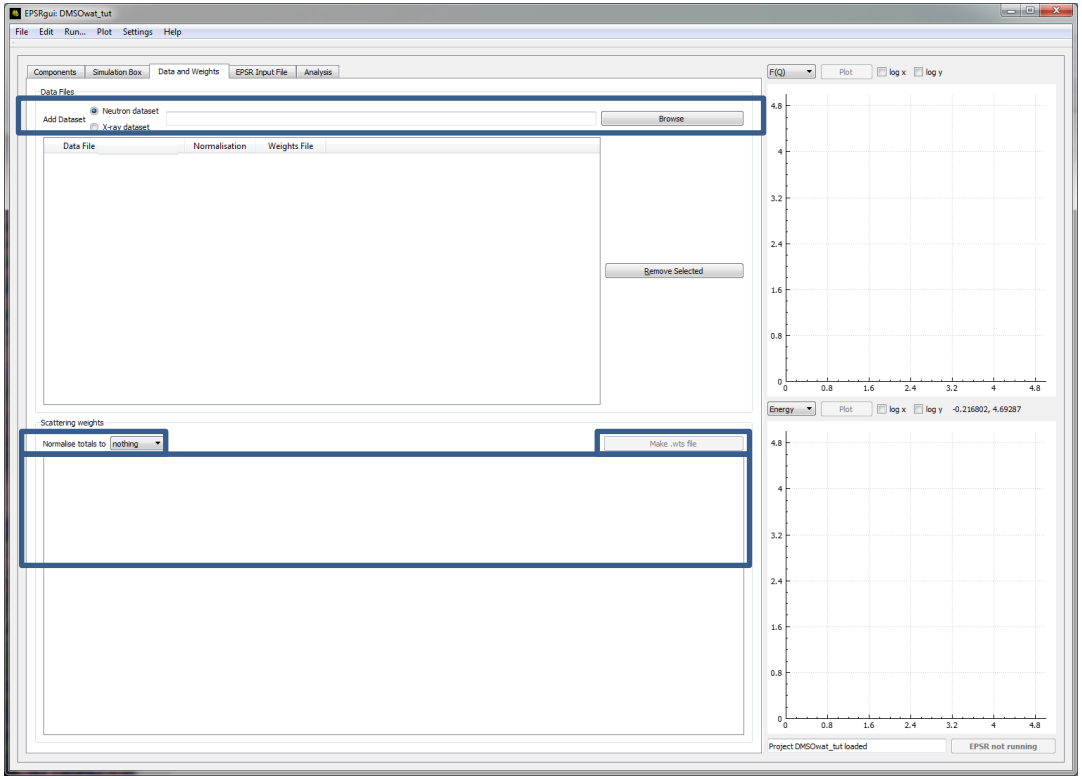
Create the simulation box

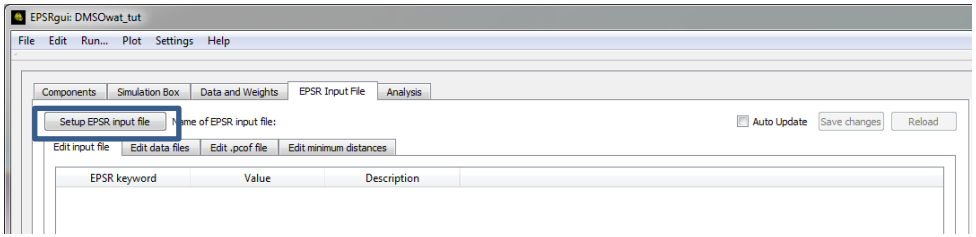
- In the Simulation Box tab, add the correct ratio of atoms to the # in box column. Ensure enough atoms are added to the box so as half the box length is larger than the longest g(r) to be assessed.
- Input the atomic number density in atoms $Å^{-3}$.
- Use Mixato to add the atoms to the box, and Randomise to distribute them randomly throughout the box.
- Check that the box is neutral in the simulation box details.
- To add some disorder to the molecule to represent the thermal motion of the atoms, click Run fmole (10,000 iterations are recommended). If necessary, change Vibtemp/Angtemp/Dihtemp (increase for more rigid restraints) and Run fmole afterwards in order for the change to be applied throughout the simulation box. If the molecule contains a flexible group, use Ecoredcore to prevent intramolecular close contacts, otherwise leave this as 0.0 0.0



Data, scattering weights and EPSR input file

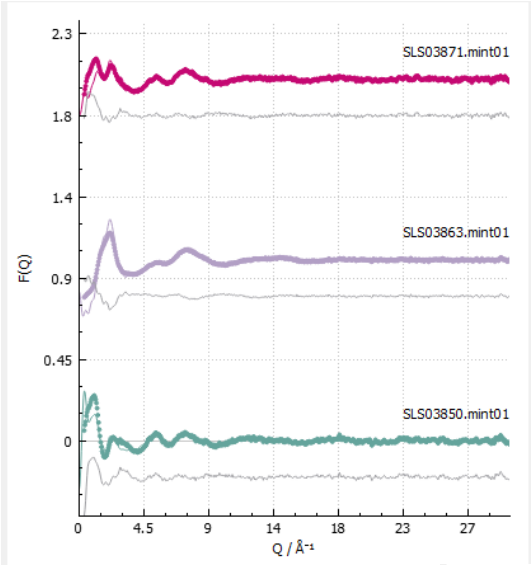
- In the Data and Weights tab, add each dataset obtained for the system, set up and then make the weights files. For this, the following information is required:
  - Are the data are from X-ray or neutron scattering
  - Which isotopes were present in the samples (for neutron data)
  - How the data were normalised
  - What the data file format is (check the EPSR manual [Help->EPSR manual] for more information).
- For exchangeable hydrogens, e.g. hydrogens bonded to O or N, use 1 in the Exchangeable column to indicate the atom will exchange and 0 if the atom will not.
- In the isotope column, use 0 for the natural isotope for a given element. For deuterium use 2 as the isotope.
- For a 50:50 H:D sample the first isotope is 0 as it is natural hydrogen and the abundance is 0.5, the second isotope is 2 as it is deuterium and the abundance is 0.5.
- In the EPSR input File tab, setup the EPSR input file and then Run EPSR.

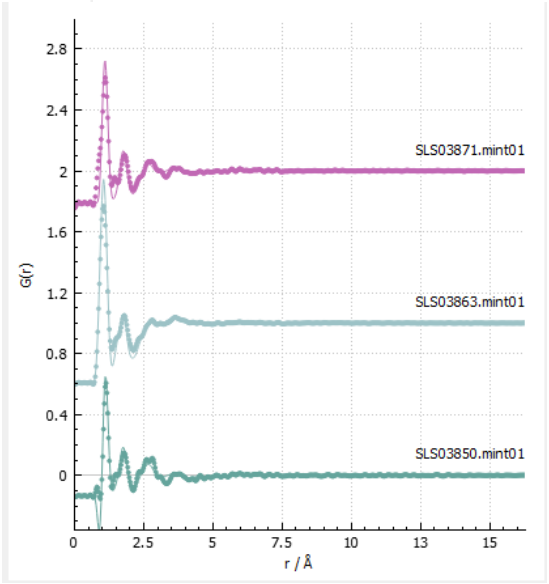




Improving the simulation

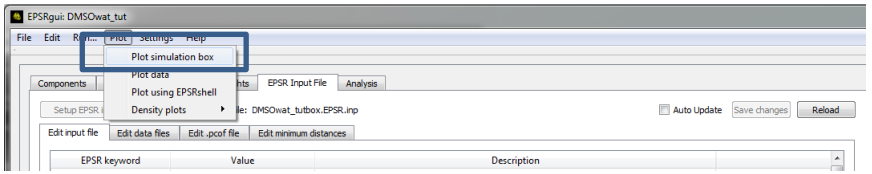
- Once the energy is negative, stop EPSR, reset the simulation (ireset 2) and start EPSR again to follow the change in energy more easily.
- Check that the model in reciprocal space (F(Q)) and real space (G(r)) bears some resemblance to the data. If it does not, check that the weights files are correct, the composition is correct, the density is correct and the values used in the component Lennard-Jones parameters are as expected (e.g. the decimal point is in the correct place).
- If all of the above are correct, use the G(r) plot to identify if the molecular structure is appropriate. If the low r peaks are shifted, try to alter the bond distances/angles for the associated atoms. Changing a single bond distance or angle can result in a distorted geometry for some molecules, e.g. ring systems. For these, try using an alternative geometry for the whole molecule.
- Remember to Run fmole 10000 times to apply the changes to the simulation box.

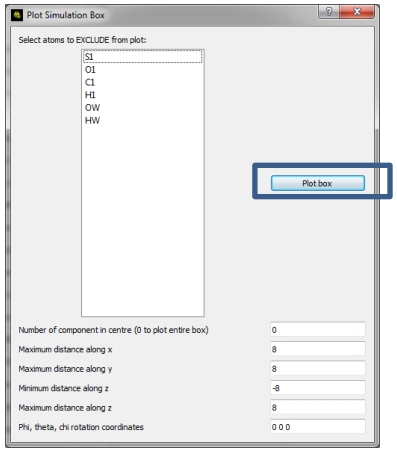




Improving the simulation

- Plot the simulation box to check that the molecules are behaving sensibly (Plot->Plot simulation box). To view just one component select the atoms of the component to be excluded from the plot and then click plot box. If a molecule has a flexible chain, check that the chain is not approaching other atoms within the same molecule too closely (i.e. short intramolecular contacts). Change Ecoredcore in the Simulation Box tab if necessary. This distance restraint is overruled by any bond and angle restraints defined for the component.
- Start refining ereq to make the final improvements via the empirical potential.



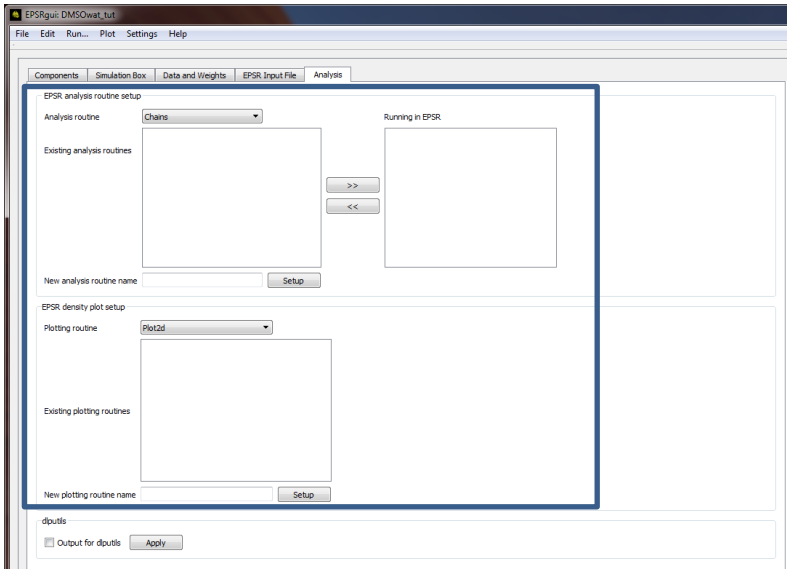


EPSR keyword	Value	Description
feedback	0.9	Confidence factor - should be < 1. [0.8]
potfac	1.0	>0.0 to enable potential refinement, 0.0 to inhibit
ereq	0.0	EP amplitude[0.0].
ereqmin	0.0	Minimum value for ereq [0.0]. Set to 0 to ignore.
ereqmax	0.0	Maximum value for ereq [0.0]. Set to 0 to ignore.
ereqstep	1.0	Set greater than 0 (e.g. 1.0) to initiate control of ereq. [0.0]
thresh	0.2	Control baseline [0.2]
bias	2	Controls the bias on the steps in ereq. 0 means unbiassed steps. [2]
sfreq	50 1	Sampling frequency for trend line, and no. of times kT for automatic ereq to begin [50 1]
rspcrmin	1.00	Minimum distance for calculating the R-space coefficient [1.00]
rspcfrac	0.5	Fraction of R-space coefficient in control level [0.2]
num_threds	0	No. of parallel threads to be used, (0 to let program choose) [0]
nmolcell	10	Average number of molecules in a cell [10]
control-p	none 0 0	Control pressure [a, b and/or c axes control plus value plus step, none 0 0]
ref_intra	0 0	Weighting on EP and Coulomb terms for intra-molecular structure [0 0]
sizefactor	1.0 0.9 0.0	Multiplying factor for box dimension, decline rate, and threshold. [1.0 0.9 0.0]
nq	600	Number of Q values. [600]
qstep	0.05	Size of Q step [1/A]. [0.05]
ireset	2	1: complete reset; 2: sets the Empirical Potential to zero
iinit	0	Sets accumulators to zero. Recalculates r and Q. [1]

Accumulating the refined simulation box

- Once the simulation has been improved as far as possible, identify a good value for ereq and stop the simulation. In the EPSR input file tab, use this value of ereq as a fixed value and change the input file to start accumulating frames of the simulation.
- With the help of the pair correlation functions (and the EPSR manual), identify analysis routines to be performed on the simulation while it is accumulating and set these up the Analysis tab before running EPSR.
- To perform additional analyses after EPSR has started, stop EPSR, setup the analysis routine and restart EPSR again. Ensure EPSR is run for sufficient iterations that the results are a good representation of the simulation.

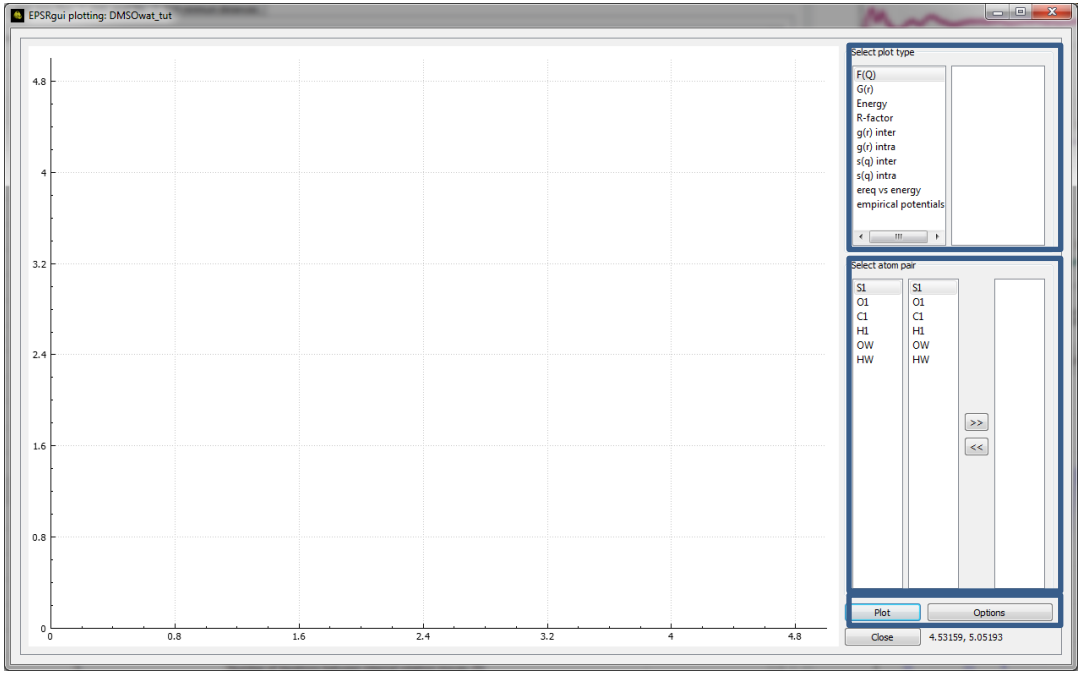
EPSR keyword	Value	Description
feedback	0.9	Confidence factor - should be < 1. [0.8]
potfac	1.0	>0.0 to enable potential refinement, 0.0 to inhibit
ereq	15.00	EP amplitude[0.0].
ereqmin	0.00	Minimum value for ereq [0.0].
ereqmax	0.00	Maximum value for ereq [0.0]. Set maximum value to 0 to ignore.
ereqstep	0.00	Set greater than 0 (e.g. 1.0) to initiate control of ereq. [0.0]
thresh	0.5	Control baseline [0.5]
niter	1	Number of potential refinements before exitting. [1]
nsumt	0	Number of iterations already accumulated. [-1 with reset]
intra	100	Number of iterations between molecule shakes. [100]

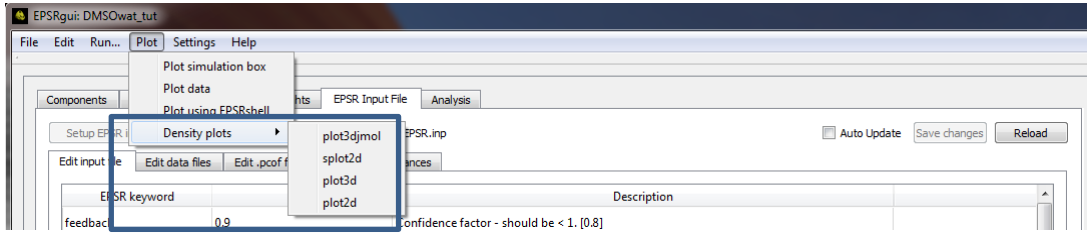


Some suggested analysis routines:
- calculate the coordination number distribution of water molecules around the O of DMSO
- calculate the coordination number distribution of water molecules around water
- Calculate the spatial density function of water around DMSO

Viewing outputs and analysis routine results

- Most outputs (e.g. pair correlation functions) and analysis routines can be plotted in the Plot data window.
- For spatial density functions (2D or 3D) a plot file must also be setup. Setup plotting routines in the lower section of the Analysis tab. Refer to the EPSR manual for more details on which settings to change to achieve this.





MCM-41

EPSRgui tutorial 5

Purpose of this tutorial

The goal of this tutorial is to build, refine and analyse a model of a porous glass, MCM-41. To achieve this, the tutorial will cover how to:

- Create the atomic components and define the Lennard-Jones potentials for each atom type.
- Create a simulation box containing the components and dummy components (Q atoms) to create pores.
- Create scattering weights files for each of the experimental datasets.
- Create a simulation that includes Bragg peak calculation and run it.
- Refine the empirical potential.
- Create analysis routines to probe the simulation – how does the structure of MCM-41 silica compare to bulk silica?
- Run analysis routines and accumulate distribution functions.
- Plot the results.

Lennard-Jones potentials

For Si and O use the optimised potentials used in Tutorial 1 and adapt these to make the hydroxyl group:

	Epsilon / *kJ mol^{-1}*	*Sigma / Å*	Mass / amu	*Charge / e$^-$*
Si	0.8	0.76	28	4
O	0.65	3.69	16	-2
O1	0.65	3.69	16	-2
H1	0.0	0.0	2	1

O1-H1 bond distance: 0.944 Å

Simulation Box

Composition: $SiO_{2-x}(OH)_x$ where x = 10 atom%

Atomic number density: assume SiO_2 is equivalent to bulk silica 0.066 atoms/Å^{-3} (hydrogen atoms are ignored)

Starting pore size: 40 Å diameter

Starting composition: *Si 503*
O 906
OH 200

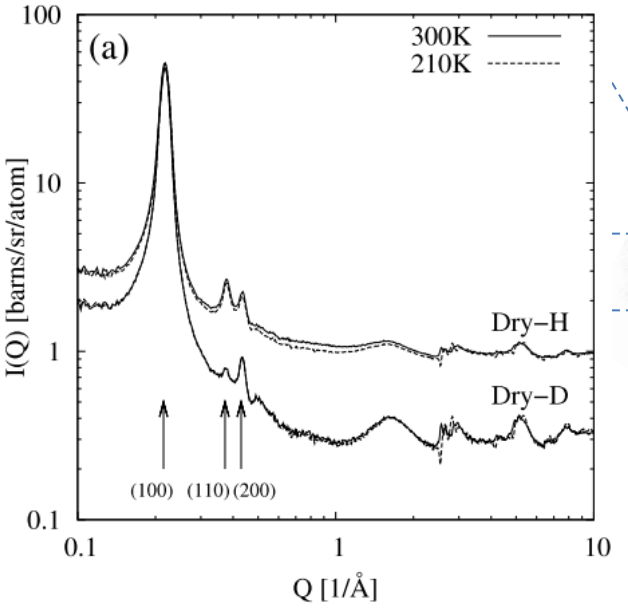
Data and Scattering Weights

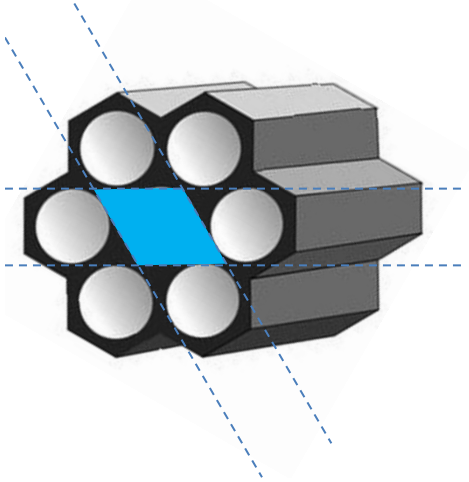
Data files – neutron, NIMROD00002401.mint01, no isotopic substitution

Data normalisation: totals not normalised

Data type: 5

MCM-41





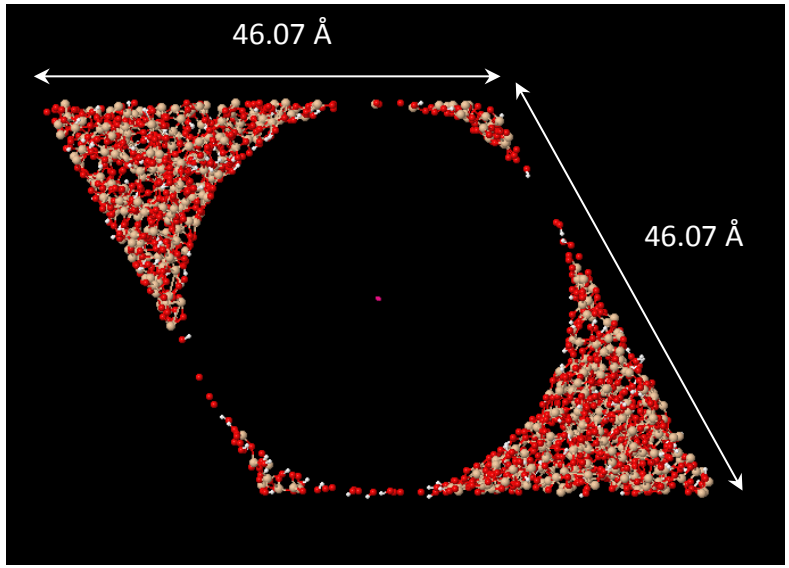
MCM-41 is an amorphous silica with cylindrical pores arranged in a hexagonal manner. As the pores are arranged in an ordered manner, this gives rise to Bragg peaks which are visible in the low Q region of data collected on NIMROD. A single hexagonal unit cell, with the pore positioned in the centre, is highlighted in blue in the adjacent image of the pore arrangement.

From the Bragg peaks, the spacing between the pores and therefore the unit cell length can be determined. As the 100 reflection is at 0.1575 $Å^{-1}$ (equivalent to a d-spacing of 39.896 Å), the spacing between the pores is therefore 46.07 Å (see Soper *J. Phys.: Condens. Matter* **24** (2012) 064107 for further details on this).

To simulate this system, we will therefore create a box where 2 sides (a and b) are 46.07 Å and there is a 120° angle between these 2 axes (γ). The third box length (c) lies along the length of the pore. We will use a relatively short (42 Å) distance for this parameter and only 1 unit cell so as to speed up the simulation for this tutorial.

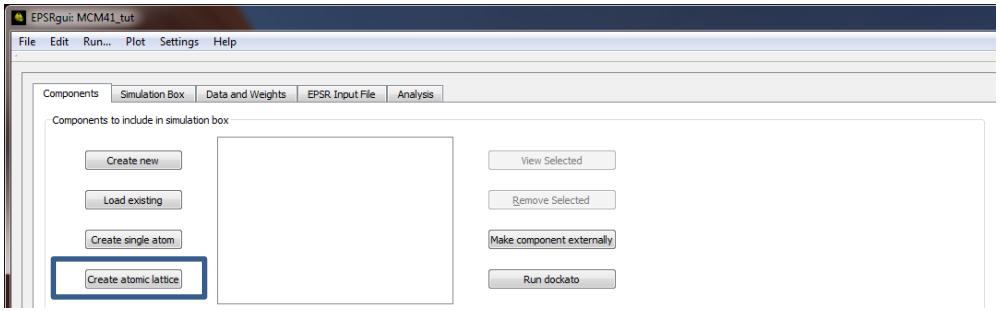
Q atoms will be used to create the pore structure. These are dummy atoms and will not contribute to the scattering in EPSR. They will be used to maintain the cylindrical structure of the pore.

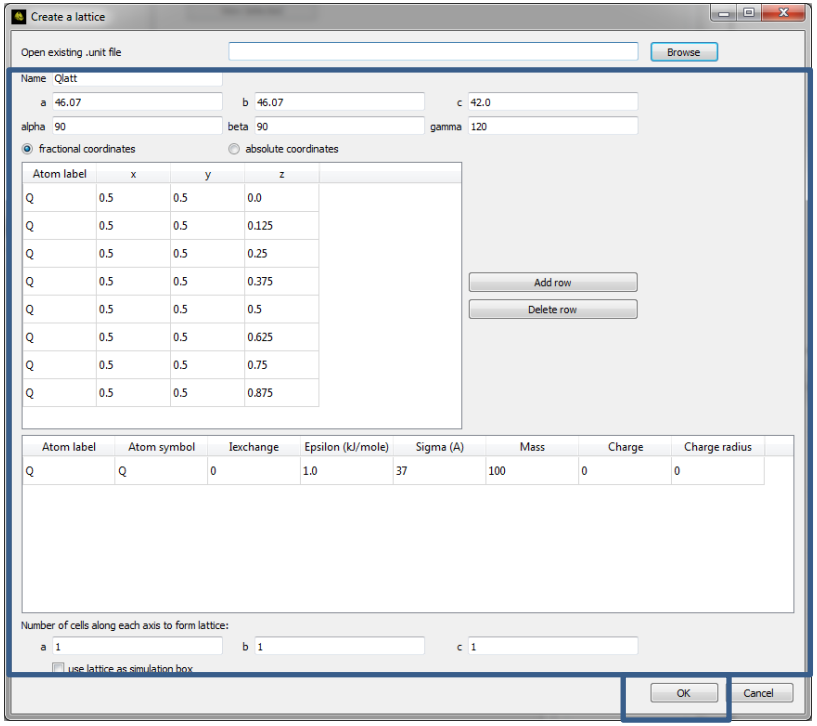
The size of the pore is not known from the initial examination of the data – only by creating a model in EPSR and comparing it to the data can the size of the pore be determined. The starting size used here is a 40 Å diameter pore. This determines the number of Si, O and OH components to add to the system in order to maintain an atomic number density of 0.066 atoms/$Å^{-3}$ (equivalent to bulk silica).



Create the components - Q atom lattice

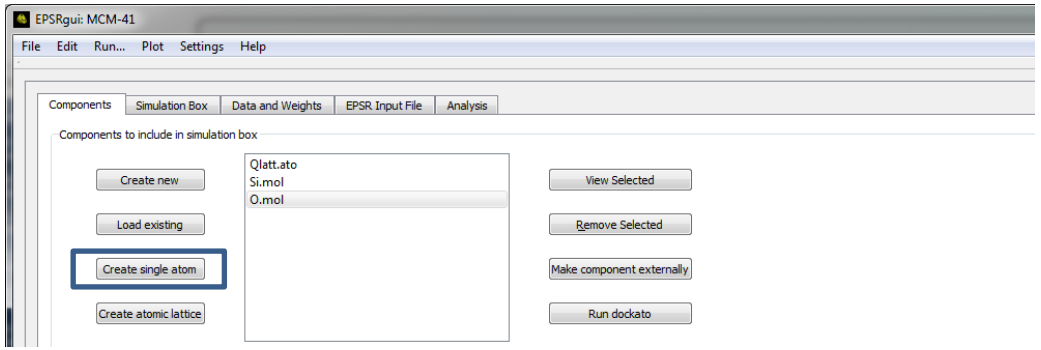
- Create new Project called MCM41_40 where the '40' represents the pore size.
- First, the lattice of Q atoms (dummy atoms) needs to be constructed.
- In the Components tab, click Create atomic lattice.
- In the Name box type Qlatt as this will be the lattice of Q atoms to create the cylindrical pores in MCM-41.
- a, b, c, alpha, beta, gamma are the lattice parameters.
- Click Add row and complete the Atom label and the atom coordinates x, y and z so as to make an effectively cylindrical pore in the centre of the cell. The spacing of the Q atoms is to make a smooth sided cylinder rather than just a few spheres next to each other.
- Fill out the Lennard Jones parameters for the Q atom. Epsilon and sigma values are used so as to create an appropriate sized pore by keeping the Si and O atoms away from the Q atoms. A larger epsilon than the pore radius is required due to the Lorentz-Berthelot mixing of the individual atom potentials.
- Use only 1 cell along each axis to form the lattice.
- Click OK.
- The lattice will appear in the Components list.

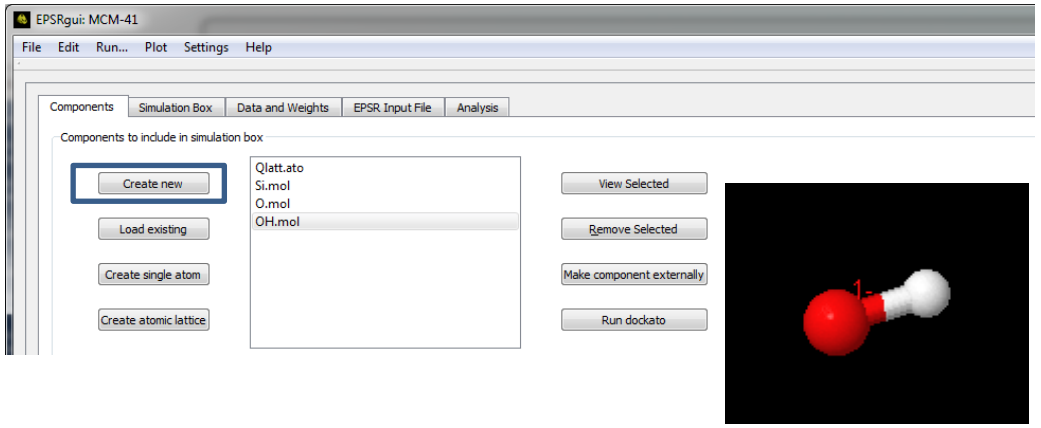




Create the components - Si, O and OH

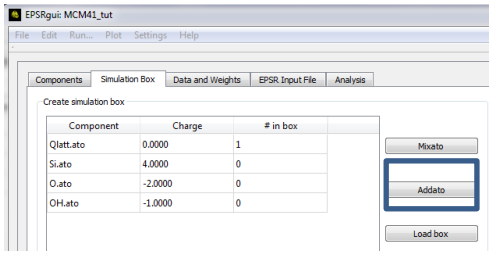
- MCM-41 is predominantly SiO2, however, studies have shown that approximately 10% of the O atoms are actually OH.
- There is evidence that these hydroxyl groups are distributed throughout the silica and are not just on the surface of the pore.
- Create the Si and O atoms using the Create single atom button. Use the potentials listed at the start of this tutorial.
- For the hydroxyl group, click Create new and make the component in Jmol. MOPAC is not necessary as the O1-H1 bond distance and Lennard-Jones parameters will be defined next anyway.
- Click on the OH component in the list and change the Lennard-Jones parameters to those listed at the start of this tutorial.
- Click Update.
- Click on the Bond distance tab and change the O1-H1 bond distance too.
- Click Update.

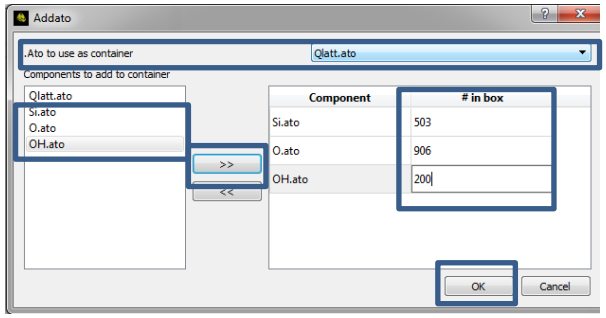


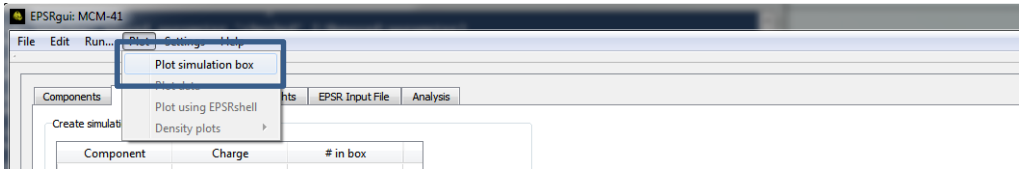


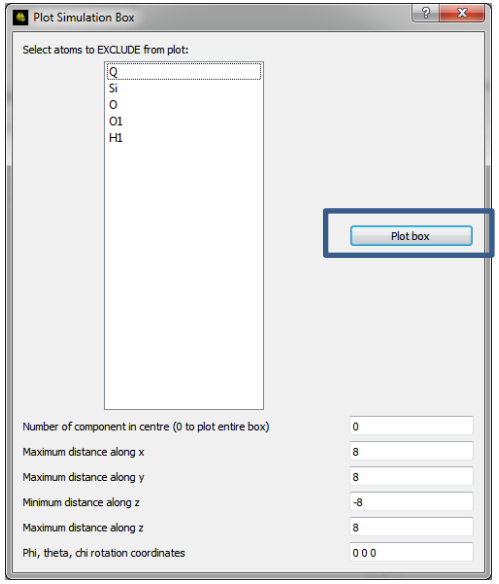
Create the simulation box

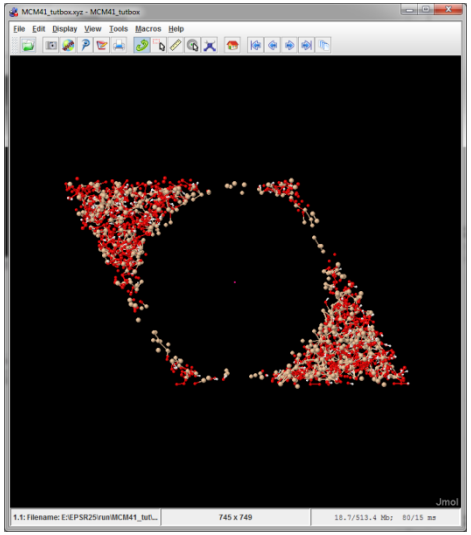
- In the Simulation box tab, click Addato.
- In the window that opens, select the Q lattice as the container.
- Then add the Si and O atoms to the table of components to be added to the container using the >> button.
- Enter the number of Si, O and OH components to be included in the box and click Ok.
- Check the box has been constructed correctly by plotting the simulation box.











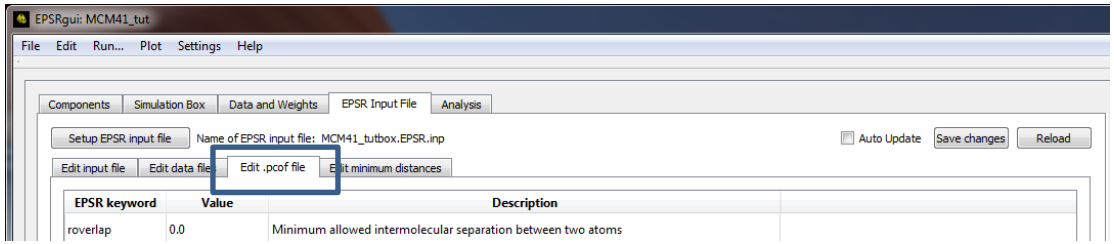
Data, scattering weights and EPSR input file

- In the Data and Weights tab add the dataset and make the weights file.
- Click on the EPSR input file tab and click Setup EPSR input file.
- In the Edit input file tab on the EPSR input file tab, change:
  - nq 2000
  - qstep 0.01
  - fwhmq 0.03
  - revlorch 1.0 0.0
  - qwidthqmax -0.003 0.6
  - hklqmin 0.01 5.5 0.0
  - qmin 0.1 0.1

- nq This is the number of Q values used in the simultaion, the default of 600 is not sufficient to cover the Q range required (0.05 to 50 $Å^{-1}$) when we use smaller binning in order to resolve the Bragg peaks. The maximum number of Q values allowed is 2000 so we will use this.
- qstep This is the size of the spacing between the simulated Q values. While 0.05 $Å^{-1}$ is appropriate for the short-range structure, it is too broad to see the peak shape of the Bragg reflections and whether they are being appropriately modelled. A value of 0.01 $Å^{-1}$ is a compromise between being able to resolve the Bragg peaks and being able to reach an appropriate Q_{max} (otherwise the data will be significantly broadened in real space).
- fwhmq This is determined by the resolution of the instrument – NIMROD has slightly lower resolution than SANDALS which is not usually noticed for liquid and glass samples without Bragg peaks, but is relevant here.
- revlorch This applies a revised Lorch function that is used to remove truncation oscillations at low Q arising from the real space data not quite reaching 1 at high r. The first value can be used to specify a constant broadening or the second value can be used to apply a Q dependent broadening.
- qwidthqmax The modulus of the first value sets the width of the calculated Bragg peaks; the shape of the peak is gaussian if qwidth is > 0 and Lorentzian if qwidth is < 0. The second value sets the maximum Q up to which the Bragg peaks will be calculated and therefore must be > 0 for any Bragg peaks to be calculated. Calculation of Bragg peaks can be very slow if there are a large number of Bragg peaks in the specified Q range, therefore only use a value up to which there are Bragg peaks.
- hklqmin The first value specifies the minimum Q for which Bragg peaks will be calculated. In this instance the Bragg peaks are present until the minimum Q value of the data (0.05 $Å^{-1}$), therefore that is used here. The second value specifies the radius in the G(r) from which the Fourier transform of the data to real space is based on the Bragg peaks. This is the point where the sharp peaks from the short range order become indistinct prior to the higher r region which will be contributed to by the long range order (Bragg peaks). The third value is the Debye-Waller factor and should be left as 0 as the thermal motion of the atoms will be included in the disorder intrinsic to the simulation.
- qmin The first value gives the smallest value of Q to be used when performing a Fourier transform. As there is Porod scattering in the data which cannot be fitted, it is sensible to use a Q value just before the start of the first Bragg peak. The second value gives the minimum Q value to be used to fit the potential and is generally the same as the first value.

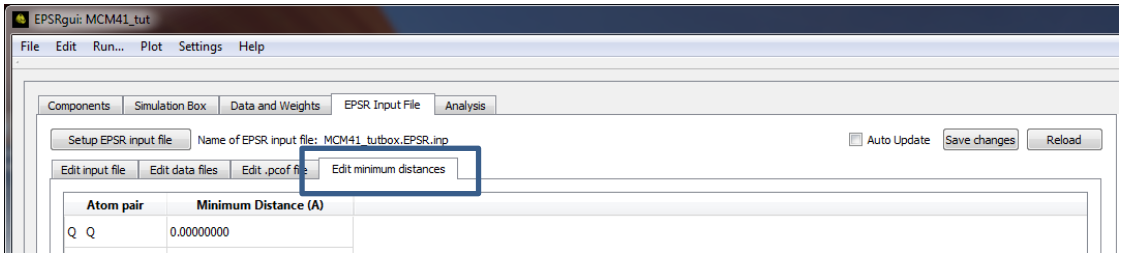
EPSR input file (continued)

- In the Edit .pcof file tab on the EPSR input file tab, change:
  - rminpt 12
  - rmaxpt 24
- As the simulation has only just been setup, ireset and iinit are 1 in order to initialise the calculation of the potential. During this initialisation values such as minimum distances are reset therefore Run EPSR once.
- Once EPSR has finished, change the minimum distances (Å) in the Edit minimum distances tab on the EPSR input file tab:
  - Q Si 19.8
  - Q O 18.0
  - Q O1 18.0
  - Q H1 17.0
- Now Run EPSR.
- Check that the energy is decreasing and that the pore remains empty of atoms.
- Once the energy is negative, Stop EPSR, change ireset to 2 and Run EPSR again.



rminpt This sets the radius at which truncation of the potential begins. It is generally half of rmaxpt.

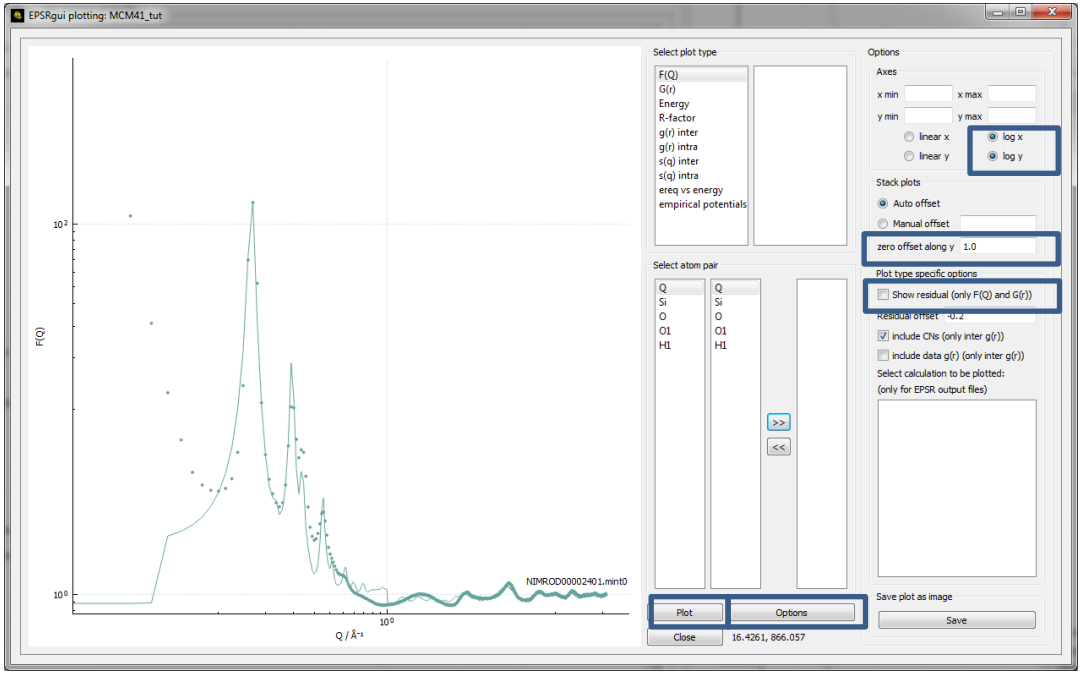
rmaxpt This sets the radius at which the potential is truncated to 0.0. It should be larger than the radius of the largest object in the box.



Consider why the minimum distances given here have been suggested.

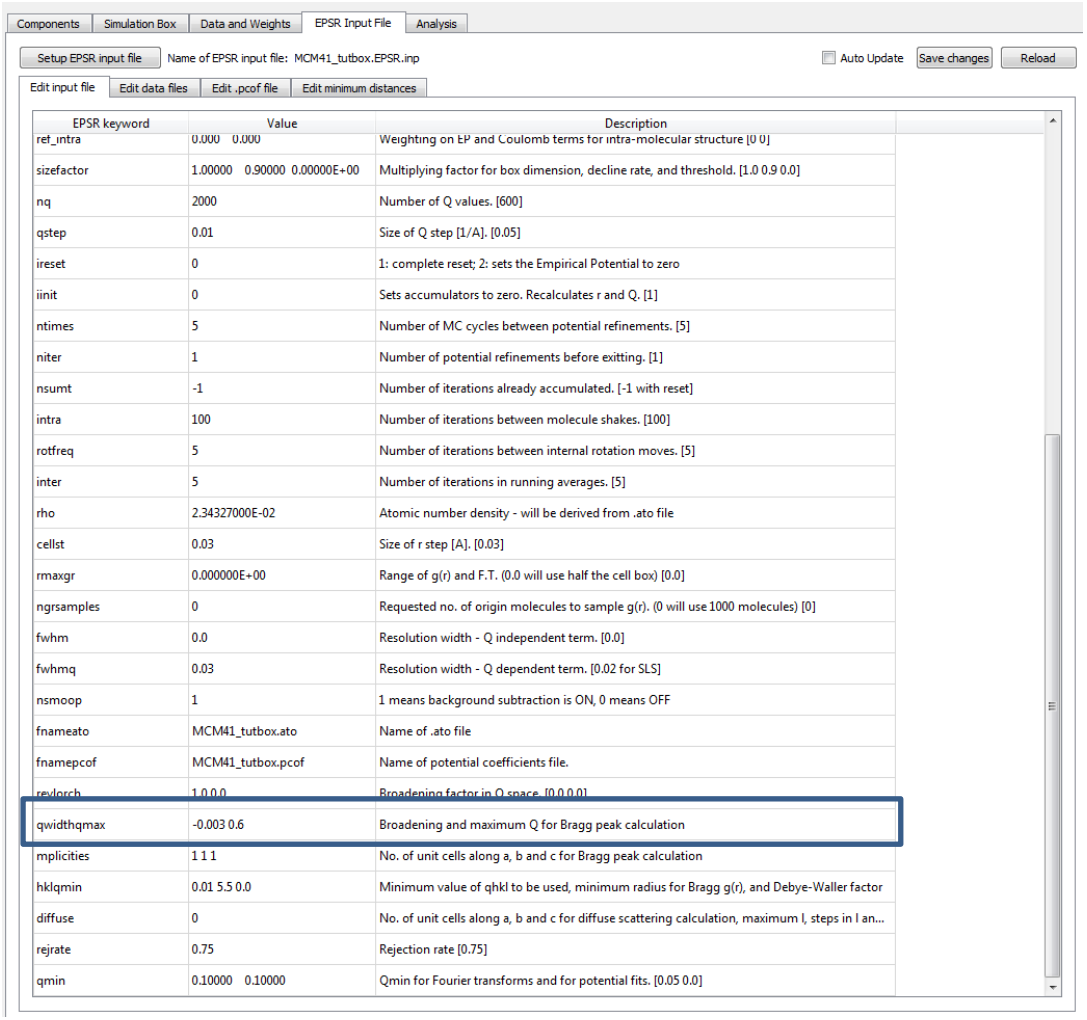
Plotting the data

- Continue running EPSR, keeping an eye on the Energy, R-factor, G(r) and F(Q) plots to check that the silica structure is forming.
- For the F(Q) plot, the large small angle scattering makes the data difficult to see on a linear scale.
- For the Quick Plots, use the log x and log y tick boxes to view F(Q) on a log scale. The data are automatically offset by 1 along y when using a log y scale.
- To view the data more clearly use the Plot->Plot data. Click on the Options button and select log x, log y and change the zero offset along y to 1.0. To remove the difference curve which can make it difficult to see the model and data at the early stages of the simulation, untick the Show residual box.
- Note that R-factor is calculated as chi-squared – the first Bragg peak has a significantly larger amplitude than the rest of the data, and, once squared, it dominates the R-factor. Therefore, while it is still of use to monitor the change in R-factor, visual inspection of the fit will be much more informative to ensure both the long range and short range aspects of the data are fitted well.



Improving the simulation – Bragg peaks

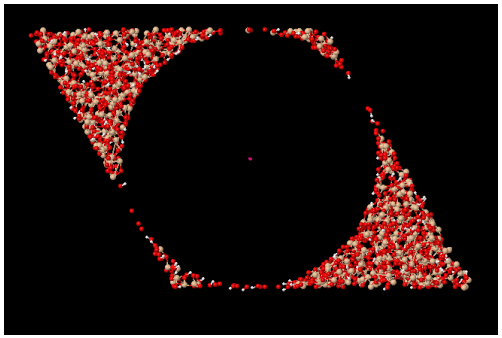
- While there may be some discrepancies in the intensities of the Bragg peaks (discussed later), the shape of the Bragg peaks can be improved first. Try changing:
  - qwidth – try using different sizes (e.g. in 0.001 steps) and also try using gaussian and lorentzian peak shapes. In order to do this, Stop EPSR, change the first value in qwidthqmax and also change ireset to 2. Allow the simulation to run for a few iterations in order for the changes to manifest completely in the Bragg peaks.
  - qmax – on inspection of the data you will notice there is a 'step' where the Bragg peak calculation stops. It is better to have this on the edge of a Bragg peak in order to minimise its effect on the data. In order to do this, Stop EPSR, change the second value in qwidthqmax to a more appropriate Q value and also change ireset to 2. Allow the simulation to run for a few iterations.

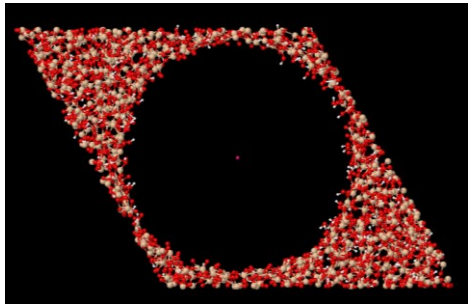


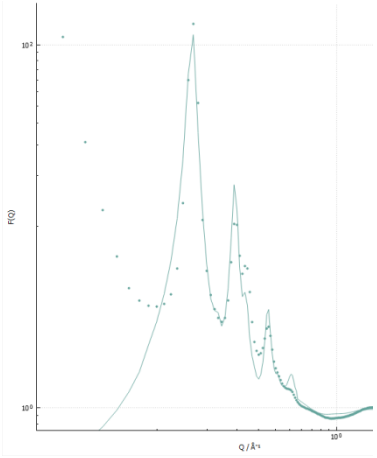
EPSR keyword	Value	Description
ref_intra	0.000 0.000	Weighting on EP and Coulomb terms for intra-molecular structure [0 0]
sizefactor	1.00000 0.90000 0.00000E+00	Multiplying factor for box dimension, decline rate, and threshold. [1.0 0.9 0.0]
nq	2000	Number of Q values. [600]
qstep	0.01	Size of Q step [1/A]. [0.05]
ireset	0	1: complete reset; 2: sets the Empirical Potential to zero
iinit	0	Sets accumulators to zero. Recalculates r and Q. [1]
ntimes	5	Number of MC cycles between potential refinements. [5]
niter	1	Number of potential refinements before exitting. [1]
nsumt	-1	Number of iterations already accumulated. [-1 with reset]
intra	100	Number of iterations between molecule shakes. [100]
rotfreq	5	Number of iterations between internal rotation moves. [5]
inter	5	Number of iterations in running averages. [5]
rho	2.34327000E-02	Atomic number density - will be derived from .ato file
cellst	0.03	Size of r step [A]. [0.03]
rmaxgr	0.000000E+00	Range of g(r) and F.T. (0.0 will use half the cell box) [0.0]
ngrsamples	0	Requested no. of origin molecules to sample g(r). (0 will use 1000 molecules) [0]
fwhm	0.0	Resolution width - Q independent term. [0.0]
fwhmq	0.03	Resolution width - Q dependent term. [0.02 for SLS]
nsmoop	1	1 means background subtraction is ON, 0 means OFF
fnameato	MCM41_tutbox.ato	Name of .ato file
fnamepcof	MCM41_tutbox.pcof	Name of potential coefficients file.
revlorch	1.0 0.0	Broadening factor in Q space. [0.0 0.0]
qwidthqmax	-0.003 0.6	Broadening and maximum Q for Bragg peak calculation
mplicities	1 1 1	No. of unit cells along a, b and c for Bragg peak calculation
hklqmin	0.01 5.5 0.0	Minimum value of qhkl to be used, minimum radius for Bragg g(r), and Debye-Waller factor
diffuse	0	No. of unit cells along a, b and c for diffuse scattering calculation, maximum l, steps in l an...
rejrate	0.75	Rejection rate [0.75]
qmin	0.10000 0.10000	Qmin for Fourier transforms and for potential fits. [0.05 0.0]

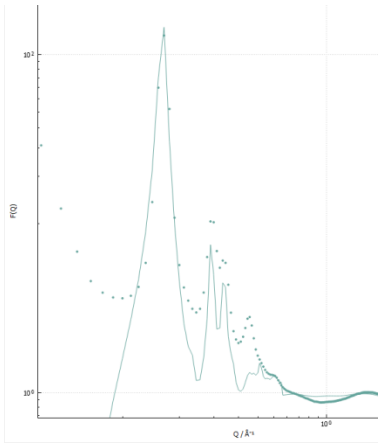
Improving the simulation – pore size

- The pore size used to start was estimated from previous studies. Although the pore size cannot be measured directly from the data, the Bragg peak intensities enable it to be determined.
- Create a new project with a 38 Å and again with a 36 Å pore diameter (make a new project for each, e.g. MCM41_38) to determine the most appropriate pore size.
- To do this, you will need to calculate the number of Si, O and OH components to include in the simulation box in order to maintain 0.066 atoms/Å^3 for the SiO2 density (ignore the H) for a given pore size.
- Use the same ratio of atoms as for the 40 Å pore but increase the total number of atoms to account for the decrease in pore size.
- Follow the steps in the previous pages but use Load existing in the Components tab to use the components you have already made.
- Change the sigma for the Q atoms to be slightly smaller so as to produce a smaller pore radius on using Addato.
- For each of the pores, after running EPSR once, change the minimum distances in the EPSR input file tab to be equivalent to the radius of the pore.
- The differences between the model and data owing to the pore size will be predominantly in the low Q region as it is the meso-scale correlation lengths that are being changed. Any discrepancies in the short range, Si-O etc, distances will be addressed later with the empirical potential.







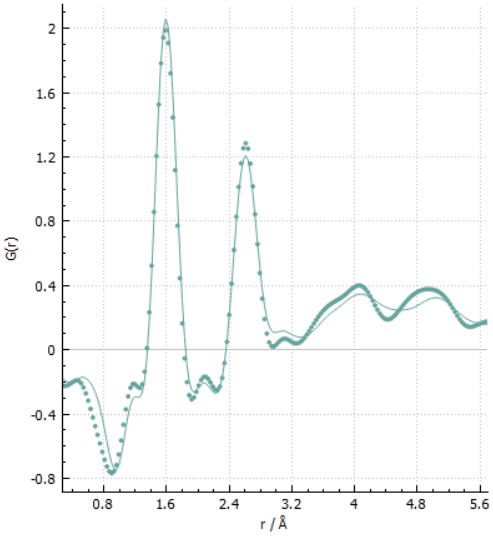


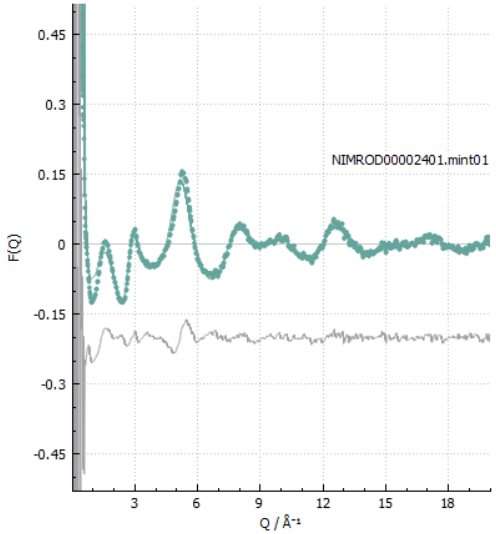
Improving the simulation – the empirical potential

- Choose the pore size with the best fit to the data to continue the tutorial with.
- If necessary, stop EPSR.
- In the EPSR input file tab, change the ereqstep value to be 1.0 and sfreq to be 50 5. Also, change the ireset value to be 2.
- Run EPSR again.
- Check how increasing ereq is affecting the structure of the silica by examining the G(r) plot. The fit to the peaks between 3 and 6 Å should be improving. Also check how EPSR is changing ereq by selecting ereq from the plot drop down menu and clicking Plot.
- You may find that the empirical potential is not necessary, or that the iterative method does not find a minima. If this is the case try using a fixed value for ereq with ereqstep 0.0 and manually change the value of ereq – check how ereq affects the fit to the data by examining the F(Q), G(r), energy and R-factor plots.
- Once the simulation has been improved as far as possible, Stop EPSR, stop refining ereq and set it to the optimum value. Start accumulating frames of the simulation (nsumt). Before starting EPSR, set up any analysis routines…

EPSR keyword	Value	Description
feedback	0.9	Confidence factor - should be < 1. [0.8]
potfac	1.0	>0.0 to enable potential refinement, 0.0 to inhibit
ereq	0.0	EP amplitude[0.0].
ereqmin	0.0	Minimum value for ereq [0.0]. Set to 0 to ignore.
ereqmax	0.0	Maximum value for ereq [0.0]. Set to 0 to ignore.
ereqstep	1.0	Set greater than 0 (e.g. 1.0) to initiate control of ereq. [0.0]
thresh	0.2	Control baseline [0.2]
biss	2	Controls the bias on the step in ereq. 0 means unbiassed steps. [2]
sfreq	50 5	Sampling frequency for trend line, and no. of times kT for automatic ereq to begin [50 1]

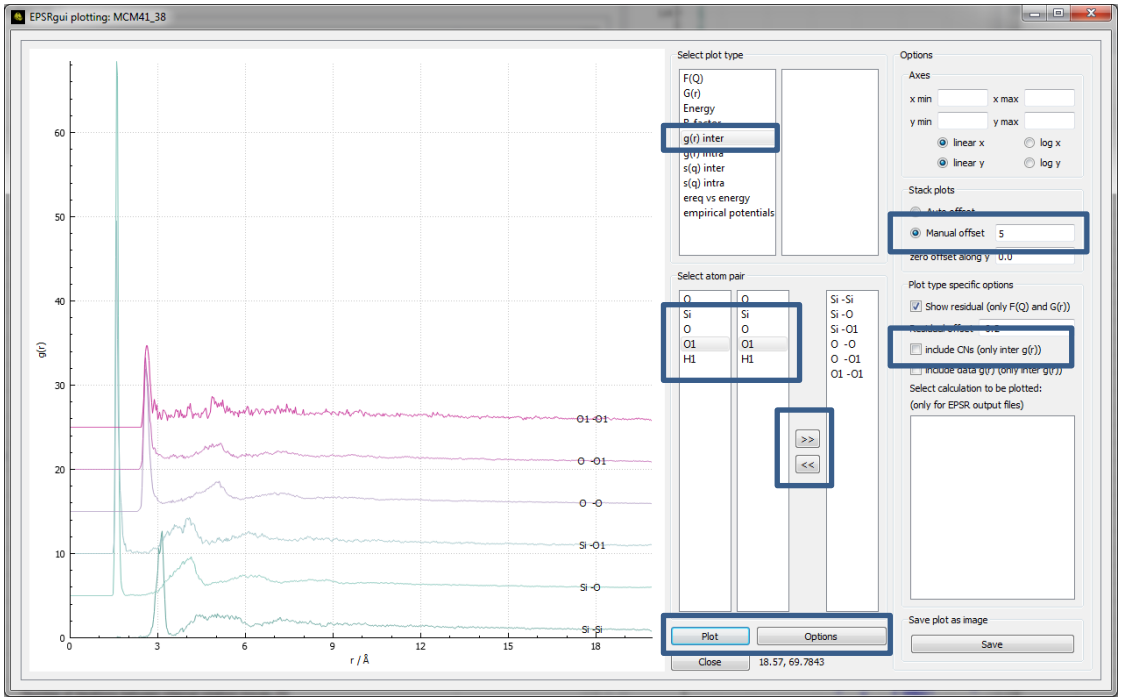
qstep	0.05	Size of Q step [1/A]. [0.05]
ireset	2	1: complete reset; 2: sets the Empirical Potential to zero
iinit	0	Sets accumulators to zero. Recalculates r and Q. [1]

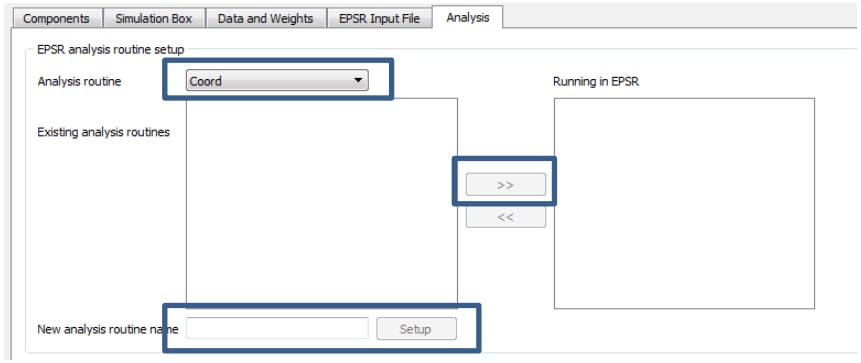




Analysing the refined simulation box

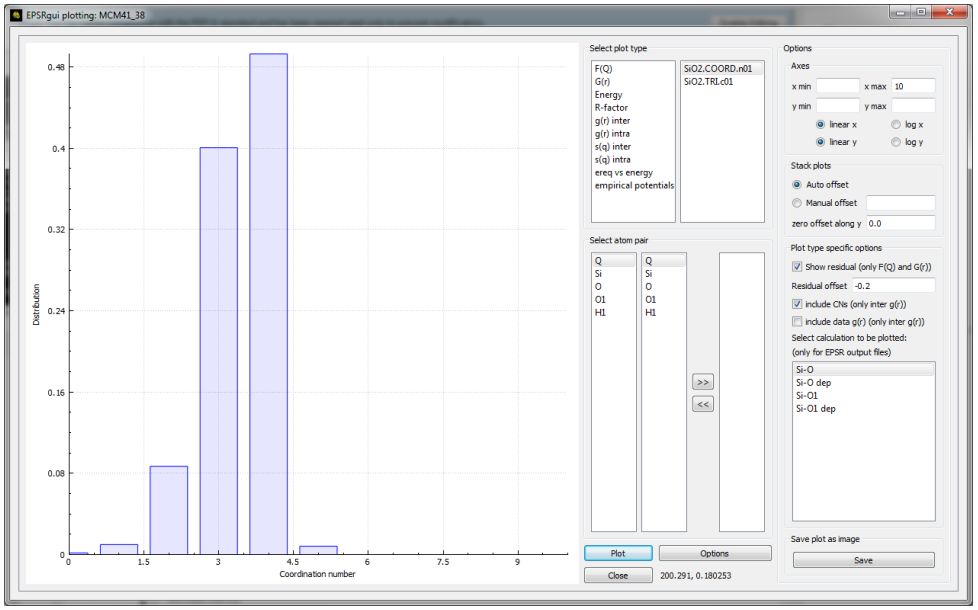
- On the top menu bar, click Plot->Plot data.
- In the plotting window that opens, click g(r) inter to plot the intermolecular pair correlation functions for selected atom pairs.
- Click on each atom in a pair and click the >> button to add the pair to the list of pair correlation functions to be plotted. Repeat this for each atom pair to be plotted. To remove an atom pair, click on it and then click the << button.
- Then click Plot.
- This plots the intermolecular g(r) together with the coordination number (in grey).
- Compare these plots with those obtained from bulk silica.
- In the Analysis tab setup analysis routines Coord and Triangles in order to compare the structure of bulk SiO2 with MCM-41.

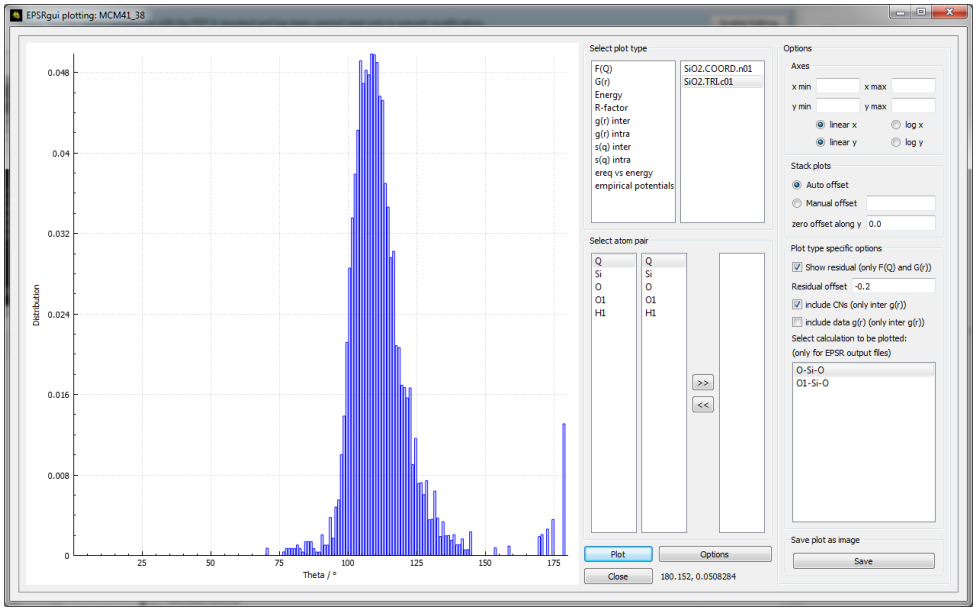




Performing calculations

- Once all the calculations have been set up, run EPSR.
- Even while EPSR is running, the outputs from the calculations can be viewed by clicking Plot->Plot data.
- In the top right hand corner, the calculations that are running while EPSR is running are listed.
- Click on the CN.COORD calculation and click Options on the bottom right hand corner. This opens additional plotting options.
- Select the atom pair you want to see the coordination number for in the list in the Plot type specific options box and then click Plot.
- Compare the results between O and O1 and with that for bulk silica. Repeat for Triangles.





Additional work

Improving the simulation – silanol group location

- While there is some evidence that the silanol groups are distributed randomly throughout the silica, there is also some evidence that they are only present on the surface of the pore.
- To examine which best fits the data, Stop EPSR.
- Make a copy of the simulation File->Save As e.g. MCM-41surf.
- Wait for the files to be copied – a message shows in the bottom right hand corner once this has been completed.
- In the menu bar, click Edit->Delete EPSR input file.
- In the Simulation Box tab, click Remove component. Select the OH.ato file and click Remove to remove the hydroxyl groups from the simulation box.
- Go to the Components tab and click Load existing to load the OH component back in to the project.
- Click on the Qlatt component, change the epsilon to be small enough to form a layer of OH around the pore and click Update.
- In the Simulation Box tab change the fmole iterations to 1 and click Run fmole. This applies the changes made in the Components tab to the simulation box.

Additional work
Improving the simulation – silanol group location

- When Addato adds components to a container, it uses the epsilon and sigma values of any tethered components to work out where to put the additional components.
- Therefore, in the Simulation Box tab, click on the Tethering button and change each of the atoms listed to T with a tether atom '0' (zero). Click Update box.
- Click Addato and select MCM-41surfbox.ato as the container from the dropdown list and select OH.ato as the component. Add the number of OH to include and click Ok.
- In the composition box that appears, check that the correct number of OH components have been added to the box. If some are missing this is because there was not enough space for them in the box given the sigma values of OH and the tethered components.
- Now untether the Si and O atoms by changing the tethered column to F and clicking Update box.
- As the scattering weights files already contain the O1 and H1, they are fine to continue using.
- In the EPSR input file tab, click Setup EPSR input file. Change the input and .pcof file parameters for the Bragg peak calculation and Run EPSR once. Change the minimum distances and Run EPSR again.
- Examine which has the best fit to the data – the simulation box with the silanols distributed randomly, or the simulation box with the silanols at the surface of the pore.

MCM-41 loaded with N_2

EPSRgui tutorial 6

Purpose of this tutorial

The goal of this tutorial is to refine a model of a vapour deposited in MCM-41. This tutorial assumes tutorial 5 (MCM-41) has already been completed and uses the refined model of the MCM-41 system as the starting point for this tutorial. This tutorial will cover how to:

- Remove Q atoms.
- Add components to a pre-existing simulation box.
- Create scattering weights files for each of the experimental datasets.
- Create a simulation and run it.
- Refine the empirical potential.
- Create analysis routines to probe the simulation.
- Run analysis routines and accumulate distribution functions.
- Plot the results.

Lennard-Jones potentials

	Epsilon / *kJ mol^{-1}*	*Sigma / Å*	Mass / amu	*Charge / e$^-$*
N1	0.31013	3.31	14	0

N1-N1 bond distance: 1.11 Å

Simulation Box

Composition: $SiO_{1.9}(OH)_{0.1}$. $0.31N_2$

Data and Scattering Weights

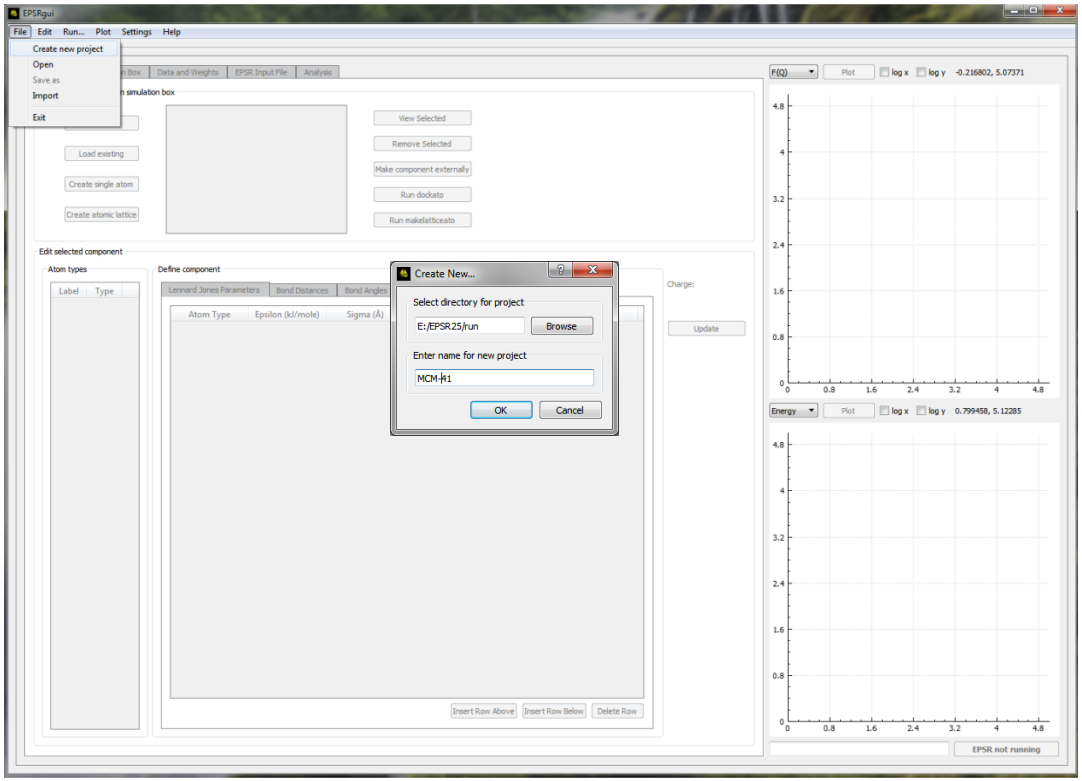
Data files – neutron, NIMROD00002404.mint01 , no isotopic substitution

Data normalisation: totals not normalised

Data type: 5

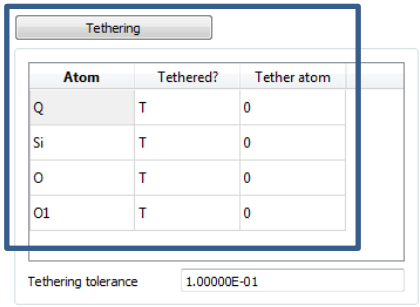
Save an existing project with a new name

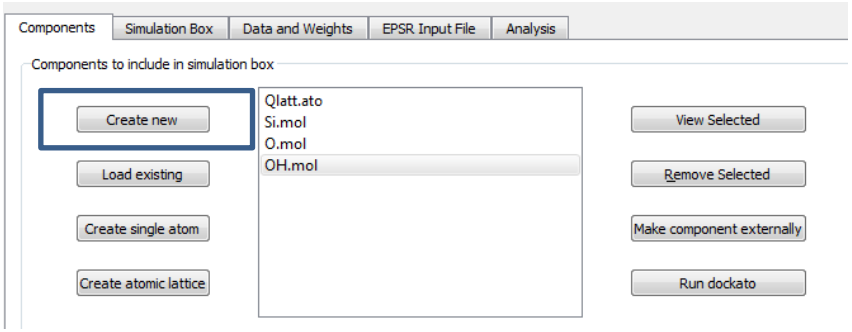
- First, open the existing project: on the top menu bar, click File -> Open…
- Open the project from Tutorial 5 that had the best fit to the data.
- On the top menu bar, click File -> Save As…
- Type the name for the new project, e.g. MCM41_N2 and click OK.
- The EPSR input file for the bare MCM-41 will not be applicable to the loaded MCM-41, therefore click Edit->Delete EPSR input file.
- In the Data and Weights tab, Remove the data file as new data and weights files are required.

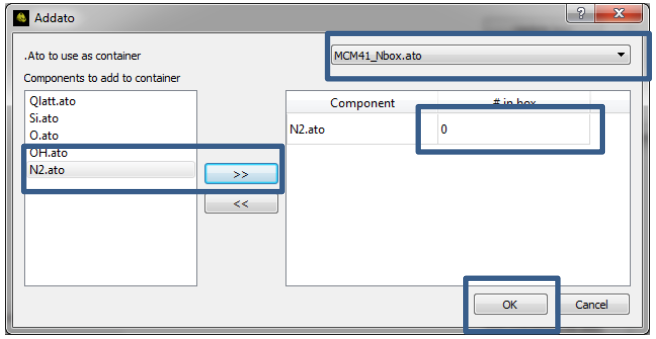


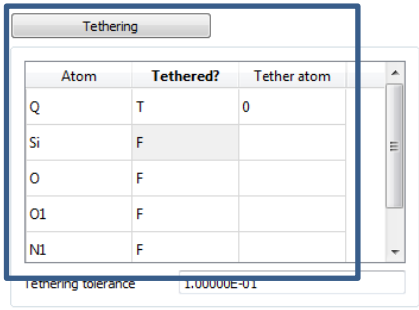
Preparing the simulation

- In the Simulation box tab, tether (T) each of the components using 0 as the tether atom.
- In the Components tab, click Create new and create N_2 in Jmol.
- Once created, edit the Lennard-Jones parameters and the bond distance to be those stated at the start of this tutorial and click Update.
- Edit the sigma and epsilon values of the Q atoms in Qlatt to 0.0 and 0.0 so as there is space for the N_2 molecules in the pore
- In the Simulation box tab, Run fmole once to apply the new sigma and epsilon values to the box.
- Calculate the number of nitrogen molecules added to the pore given the molar ratio at the start of this tutorial and the number of Si atoms used to create the box in the last tutorial.
- Click Addato and choose the simulation box as the container and add the appropriate number of nitrogen molecules and click Ok.
- Check the simulation box looks Ok.
- Untether Si, O and OH by typing 'f' in the Tethered? column and deleting the entry in the tether atom column. Click Update box.



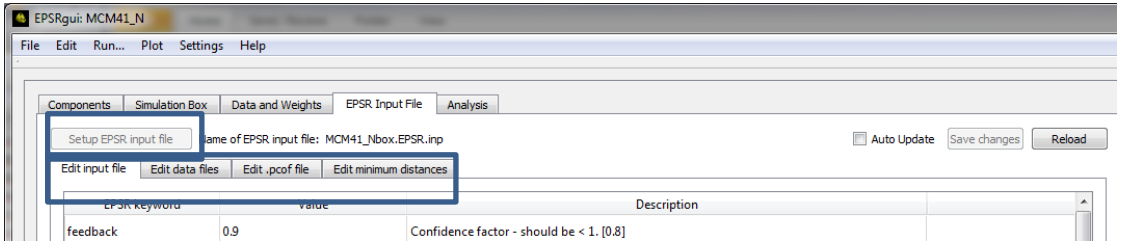


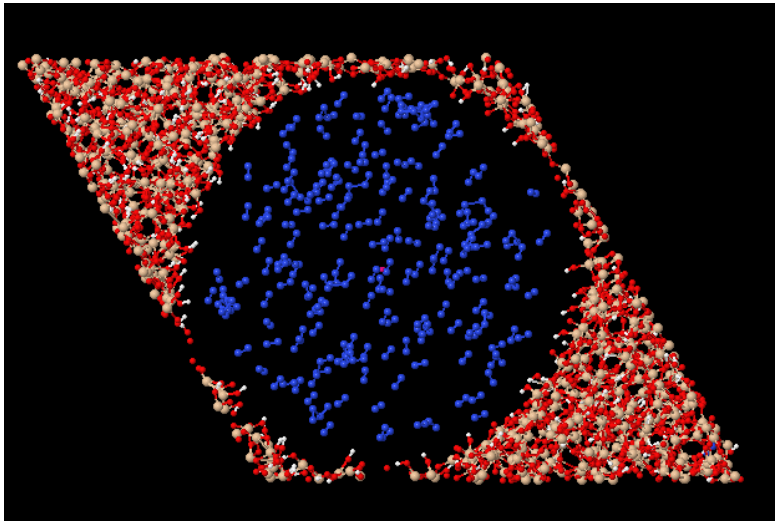




Data, scattering weights and EPSR input file

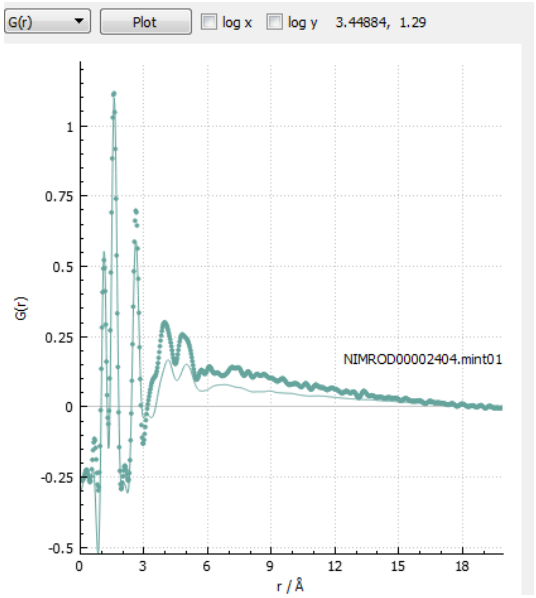
- In the Data and Weights tab add the dataset and make the weights file.
- Click on the EPSR input file tab and click Setup EPSR input file.
- Change the parameters in the Edit input file tab and Edit .pcof file tab to be consistent with those used to generate the best fit in the in the empty MCM-41 tutorial.
- Run EPSR once.
- Once EPSR has finished, change the minimum distances (Å) in the Edit minimum distances tab on the EPSR input file tab:
  - Q Si 19.8
  - Q O 18.0
  - Q O1 18.0
  - Q H1 17.0
- Now Run EPSR.
- Check that the energy is decreasing and that the pore only contains nitrogen molecules.
- Once the energy is negative, Stop EPSR, change ireset to 2 and Run EPSR again.

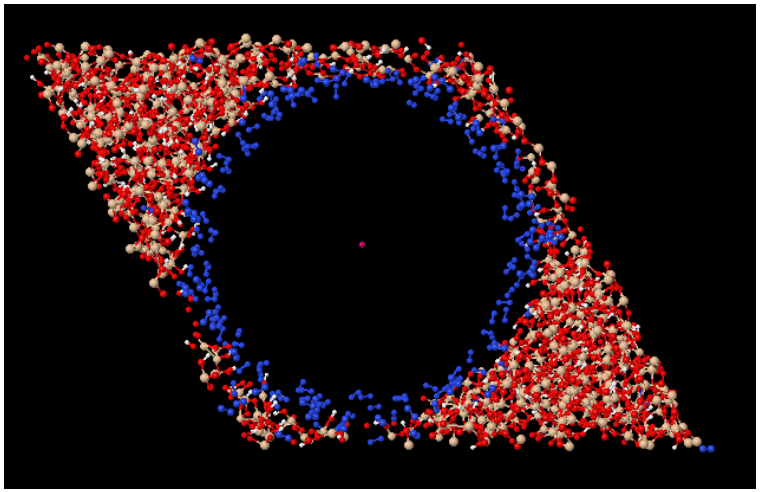




Improving the simulation

- Inspect the data in real space. There is a large mismatch between the model and the experimental data in the mid r region.
- As the nitrogen molecules have been added to the whole pore but are likely on the surface, use a minimum distance to move the nitrogen molecules away from the centre of the pore.
- Try different values to see which provides the best fit.
- Examine the data in reciprocal space – adjust the Bragg peak calculation parameters to account for the change in Bragg peaks.
- Once optimised and the box has equilibrated increase the value of ereq (iteratively or manually) using the previous value of ereq for bare MCM-41 as a guide.





Accumulating and analysing the refined simulation box

- Once the simulation has been improved as far as possible, consider which analysis routines could be used to examine the simulation box.
- Set these up and also start accumulating the simulation.
- Plot the results.

Ice

EPSRgui tutorial 7

Purpose of this tutorial

The goal of this tutorial is to build, refine and analyse a model of a disordered solid, ice at 220K. To achieve this, the tutorial will provide suggestions on how to:

- Create the atomic components and define the Lennard-Jones potentials for each atom type.
- Create a simulation box containing the components already on their lattice positions.
- Create scattering weights files for each of the experimental datasets.
- Create a simulation that includes Bragg peak calculation and run it.
- Improve the simulation and refine the empirical potential.
- Create analysis routines to probe the simulation – how does the structure of ice compare to that of water (e.g. from the DMSO-water tutorial or pure water from the literature.)
- Run analysis routines and accumulate distribution functions.
- Plot the results.

Lennard-Jones potentials

SPC-E water:

	Epsilon / $kJ\ mol^{-1}$	*Sigma / Å*	Mass / amu	*Charge / e⁻*
O1	0.65	3.16	16	-0.8476
H1	0.0	0.0	2	0.4238

O1-H1 bond distance: 0.976 Å

H1-O1-H1 bond angle: 104.5°

Simulation Box

Composition: H_2O

Atomic number density: determined by crystal structure

Data and Scattering Weights

Data files – neutron, SLS03449.mint01, natural hydrogen

neutron, SLS03460.mint01, null water

neutron, SLS03468.mint01, fully deuterated

Data normalisation: totals not normalised

Data type: 5

Neutron scattering lengths

https://ncnr.nist.gov/resources/n-lengths/

Neutron scattering lengths and cross sections							
Isotope	conc	Coh b	Inc b	Coh xs	Inc xs	Scatt xs	Abs xs
H	---	-3.7390	---	1.7568	80.26	82.02	0.3326
1H	99.985	-3.7406	25.274	1.7583	80.27	82.03	0.3326
2H	0.015	6.671	4.04	5.592	2.05	7.64	0.000519
3H	(12.32 a)	4.792	-1.04	2.89	0.14	3.03	0

Ice at 220K

The data for this tutorial are from:

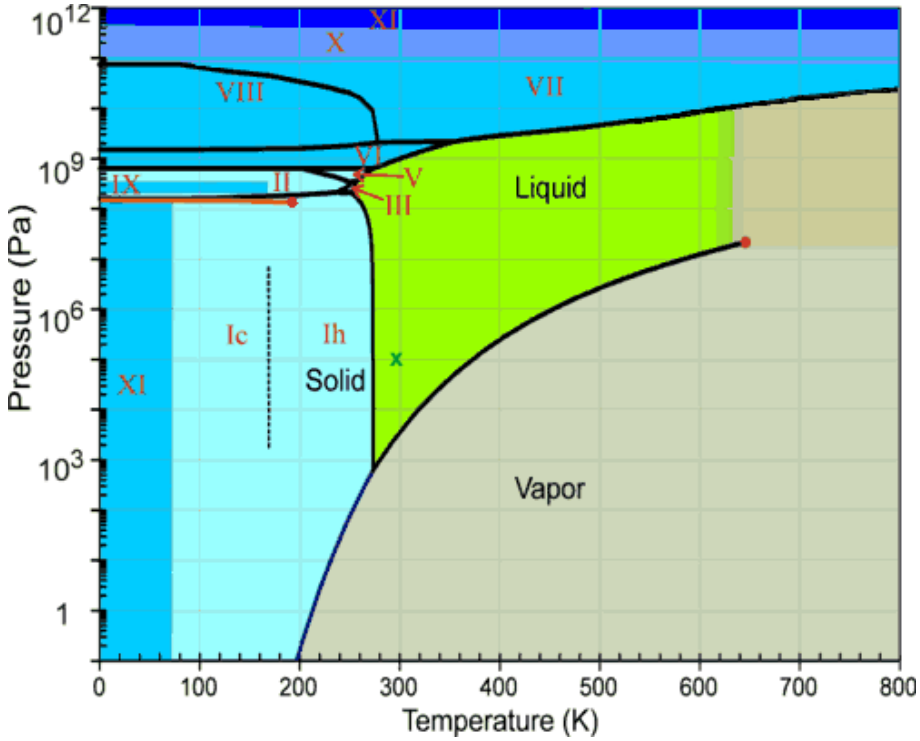
Proceedings of the International School of Physics “Enrico Fermi”. Course 187 “Water: Fundamentals as the Basis for Understanding the Environment and Promoting Technology”, edited by P. G. Debenedetti, M. A. Ricci and F. Bruni (IOS, Amsterdam; SIF, Bologna) 2015

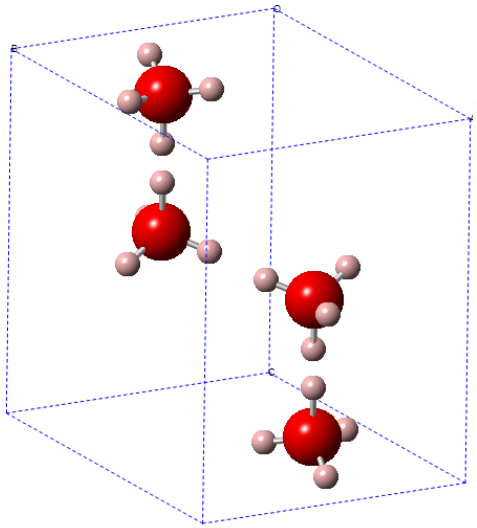
DOI 10.3254/9781-61499-507-4-151

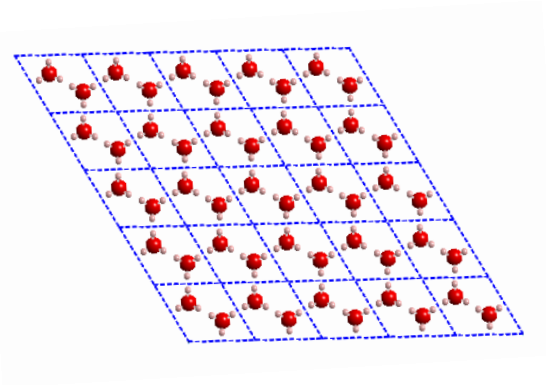
Ice has a complex phase diagram with various hydrogen bonded arrangements of the water molecules as well as proton ordered and proton disordered forms of each arrangement (except for one of the phases… http://ergodic.ugr.es/termo/lecciones/water1.html).

These data were obtained by crash cooling liquid water to 220K, resulting in a disordered form of ice 1h. Data were collected five times for each sample – the sample was heated to 298K in between each data collection before being crash cooled again. This was to remove any effects of preferred orientation of the ice crystals from the data.

Ice 1h is a proton disordered form and therefore has four half occupancy hydrogen atoms per water molecule. The structure of ice 1h can be obtained from the ICSD (*icsd.cds.rsc.org/)* or the CCDC (*https://www.ccdc.cam.ac.uk/)* in the form of a cif file (crystallographic information file). The cif file contains the atom positions for the asymmetric unit which are then multiplied by the symmetry operators to produce the unit cell. The unit cell is repeated by translation to produce the crystal lattice.

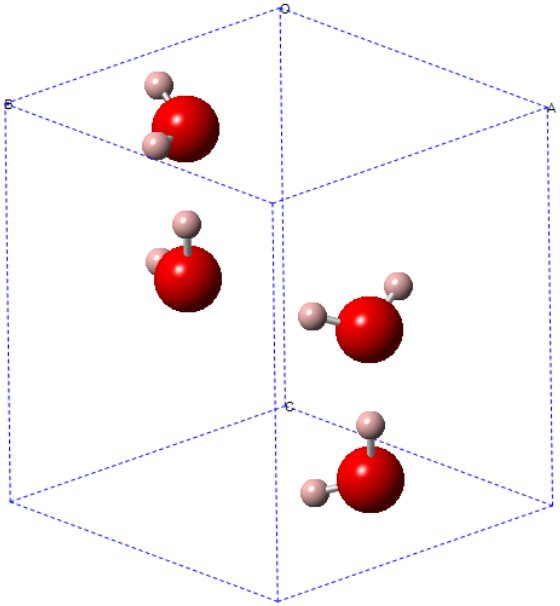


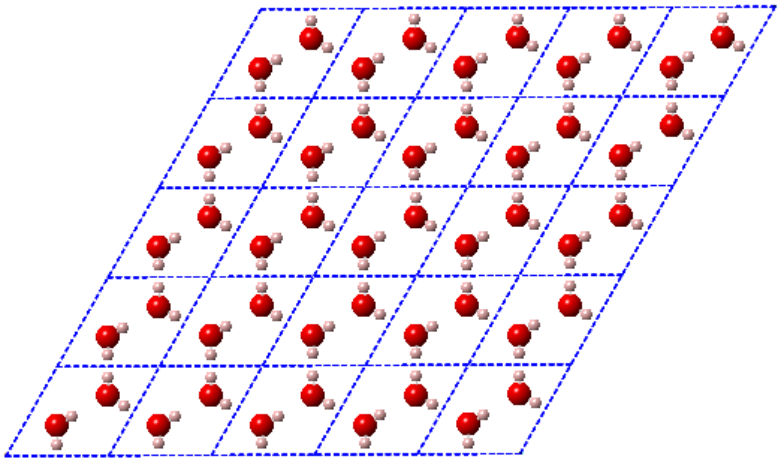




Preparing the components

- To use the cif file, first the structure must be converted into the space group P1 which does not contain any symmetry. This can be done by multiplying out the atom positions with the symmetry elements, or, in software such as CrystalMaker, using 'Transform cell' to convert to P1. This has already been done in the file ice_1h_P1.cif
- EPSR does not account for half occupancy hydrogen atoms, therefore to use the cif file as a starting point, the additional hydrogen atoms must be removed. This can be done manually, or by deleting them via software such as CrystalMaker. This has already been done in the file ice_1h_P1.cif
- What might be problematic when deleting the hydrogen atoms?
- In order to use the unit cell in EPSR, it must be in the format of an EPSR .ato file. Therefore Aten has been used to convert the unit cell to a .ato file. For this, the unit cell in P1 with no half occupancy atoms, and the Lennard Jones potentials for each of the atoms are required. After creating the .ato file, open it with a text editor and scroll to the bottom of the file. Where it says moltypeXX, delete the moltypeXX and replace it with water. This is the name of the component that will be used in EPSR. The resulting file is in the Resources folder.





Optional

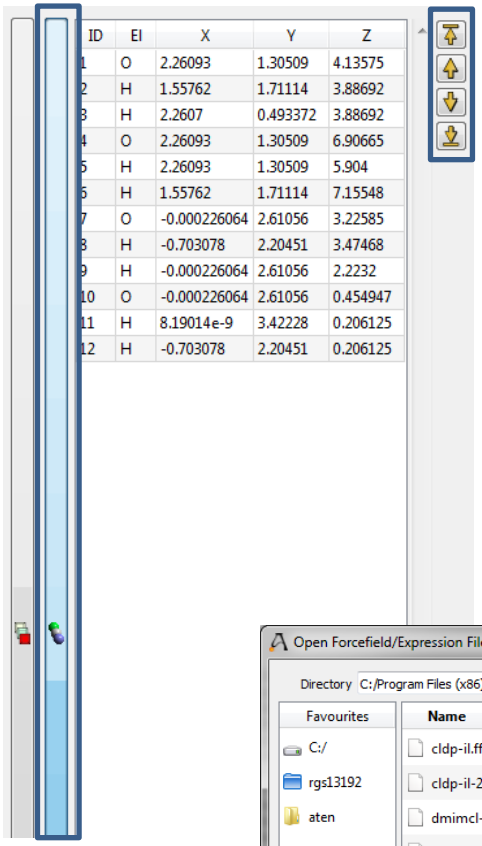
Preparing the components
- using Aten to create a .ato file

- Open Aten and open the file ice_1h_P1.cif.
- On the left hand side of the screen click the vertical bar that has 3 atoms in it. This shows the atoms present in the structure. Reorder the atoms (by clicking on an atom in the list and using the arrow buttons) so that the atoms for each molecule are consecutive and the oxygen atom is first.
- Click on the Forcefields tab and click Open. Click on the aten folder in the Favourites list and go to the ff folder, select the spce.ff file and click Open. The forcefield SPC-E water will now be shown in the list. To the right of this list, click Assign.
- Click on the Home tab and Save the structure as a .ato file, e.g. ice_1h_P1.ato, in the project folder.
- Check that the following message in red does not appear:

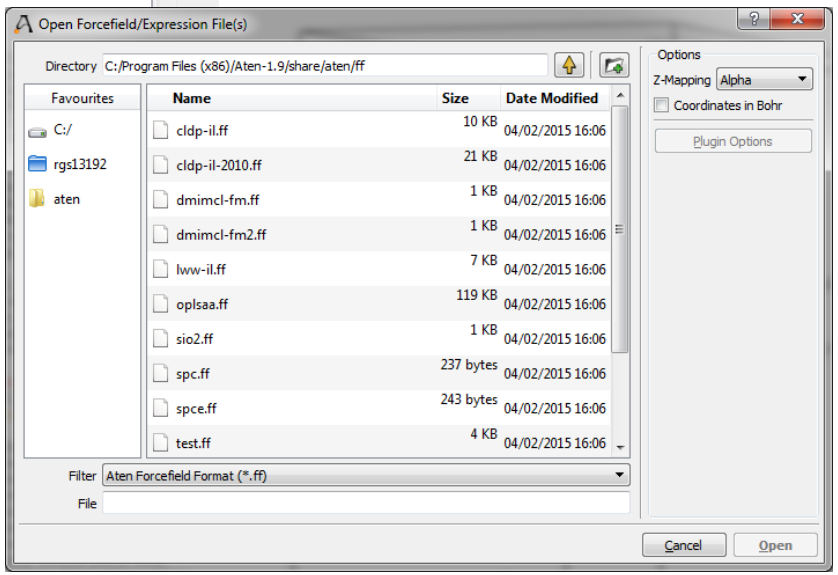
Pattern creation failed because of bad atom ordering of the presence of additional bonds.

Problem occurred in pattern 1 whilst selecting from atom X.

- If it does, amend the atom ordering and try saving the file again.
- Otherwise, open the file in a text editor. At the bottom of the file there will be a line that says moltypeXX or OH2. Change this word to be the name of the component.
- Check that the atom types used in the .ato file are the same as the labels used in the component (change the component if necessary).
- The .ato file is now ready for loading into EPSRgui using Load box.

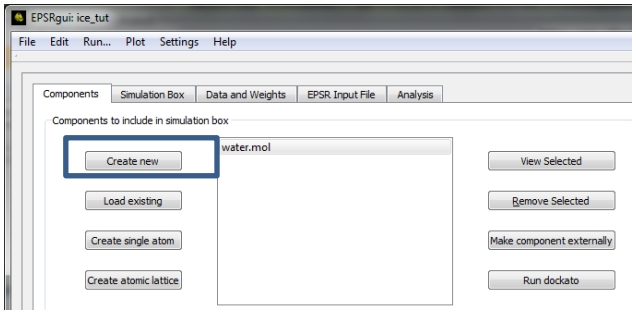


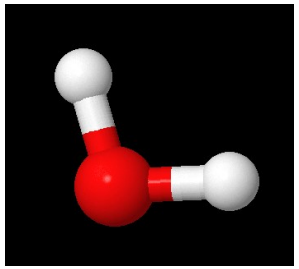
ID	El	X	Y	Z
1	O	2.26093	1.30509	4.13575
2	H	1.55762	1.71114	3.88692
3	H	2.2607	0.493372	3.88692
4	O	2.26093	1.30509	6.90665
5	H	2.26093	1.30509	5.904
6	H	1.55762	1.71114	7.15548
7	O	-0.000226064	2.61056	3.22585
8	H	-0.703078	2.20451	3.47468
9	H	-0.000226064	2.61056	2.2232
10	O	-0.000226064	2.61056	0.454947
11	H	8.19014e-9	3.42228	0.206125
12	H	-0.703078	2.20451	0.206125

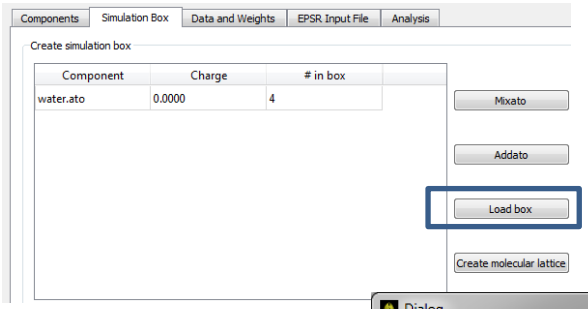


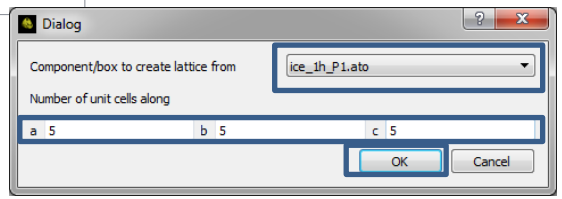
Create the components and simulation box

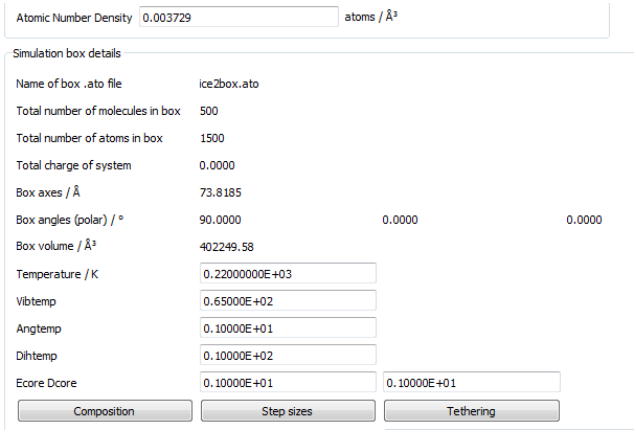
- Create new project called ice_tut.
- Click Create new and make a water molecule named water.jmol.
- Change the Lennard Jones potentials, charge, bond distance and bond angle to be appropriate to SPC-E water (given at the start of this tutorial). Change the atom types to be the same as are listed in ice_1h_P1.ato (i.e. OW and HW). Click Update.
- In the Simulation Box tab click Load box. Click Ok to the message box that 'moltypeXX' has been changed to the name of the component. Open the ice_1h_P1.ato file.
- In the Simulation box details the unit cell parameters will be shown. The structure can be checked further by plotting the simulation box.
- To create a large box out of this small unit cell, click Create molecular lattice. Select ice_1h_P1.ato from the dropdown list and expand the unit cell 5 times in each direction.
- The simulation box is now called ice2box and the details are shown in the Simulation Box tab.







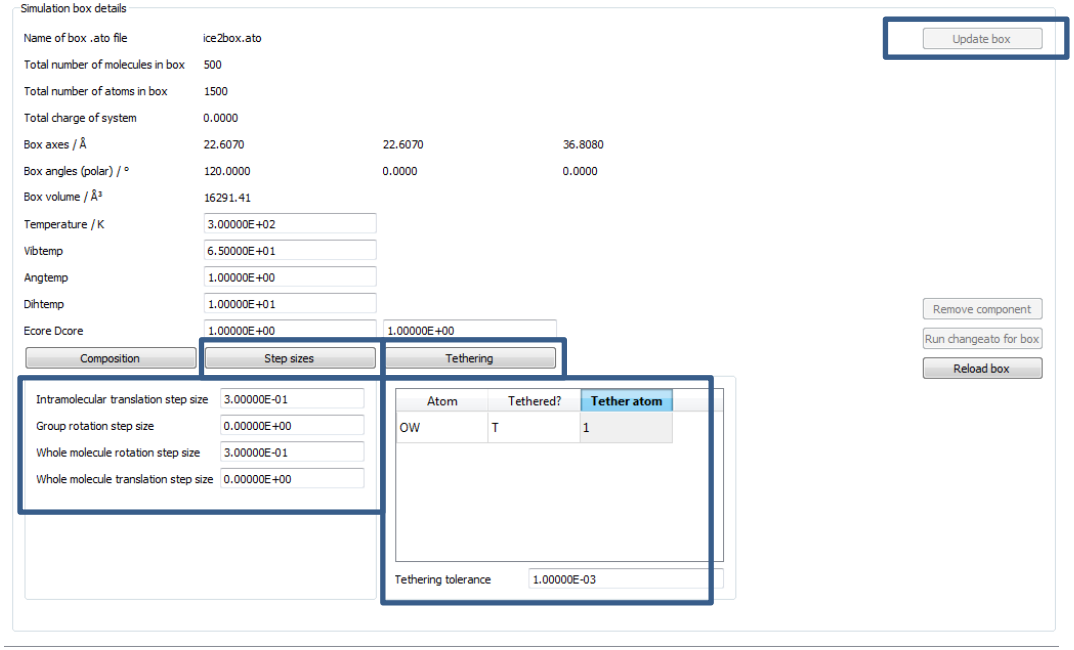


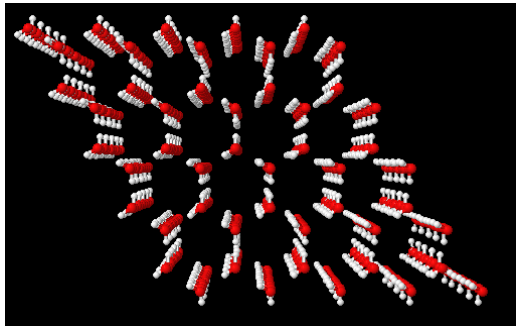


Create the simulation box (continued)

- Click Tethering and tether the water molecules via the oxygen atoms. Use a 'T' in the Tethered? column and type the atom label for the oxygen atom, '1', (as the lattice of oxygen atoms is not disordered) in the Tether atom column. Change the Tethering tolerance to 0.1.
- Click Step sizes and change:
  - Intramolecular translation ss: 0.3
  - Group rotation ss: 0.0
  - Whole molecule rotation ss: 0.3
  - Whole molecule translation ss: 0.0

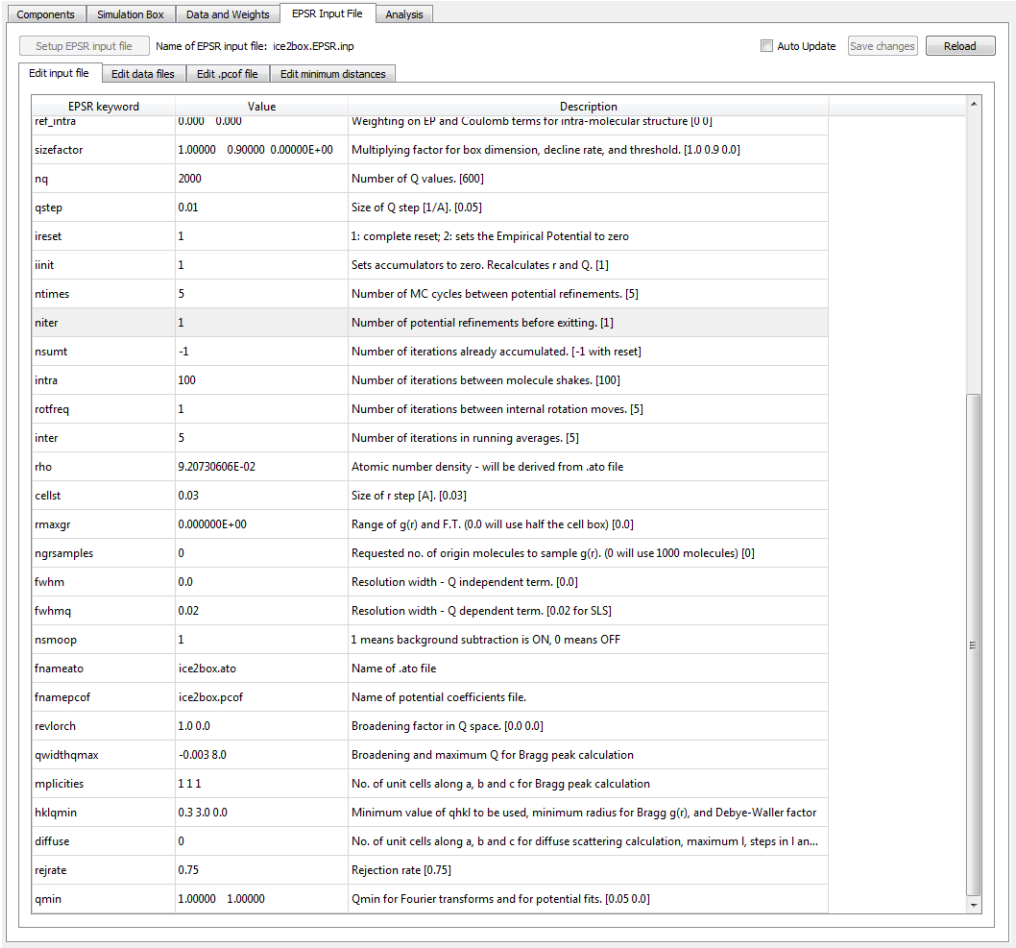
  This changes the size of each step EPSR will move the molecules – the smaller moves will prevent the structure from becoming too disordered too quickly, and the 0.0 step sizes will prevent these moves from occurring.
- Click Update box.
- To make sure the water molecules have the correct Lennard-Jones parameters and bond distance and angles, Run fmole 10000 times.
- Check the simulation box looks Ok.





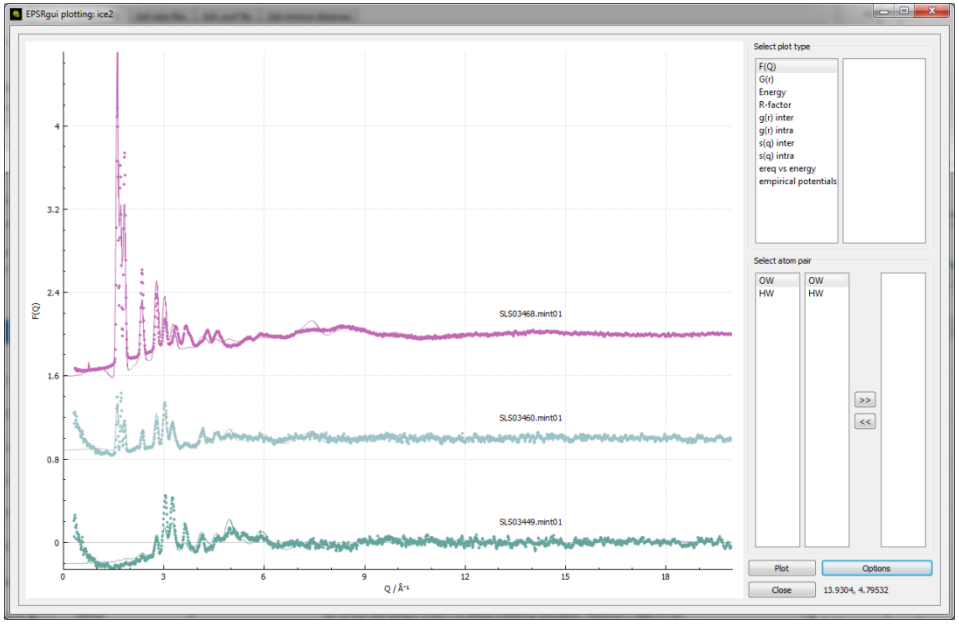
Data, scattering weights and EPSR input file

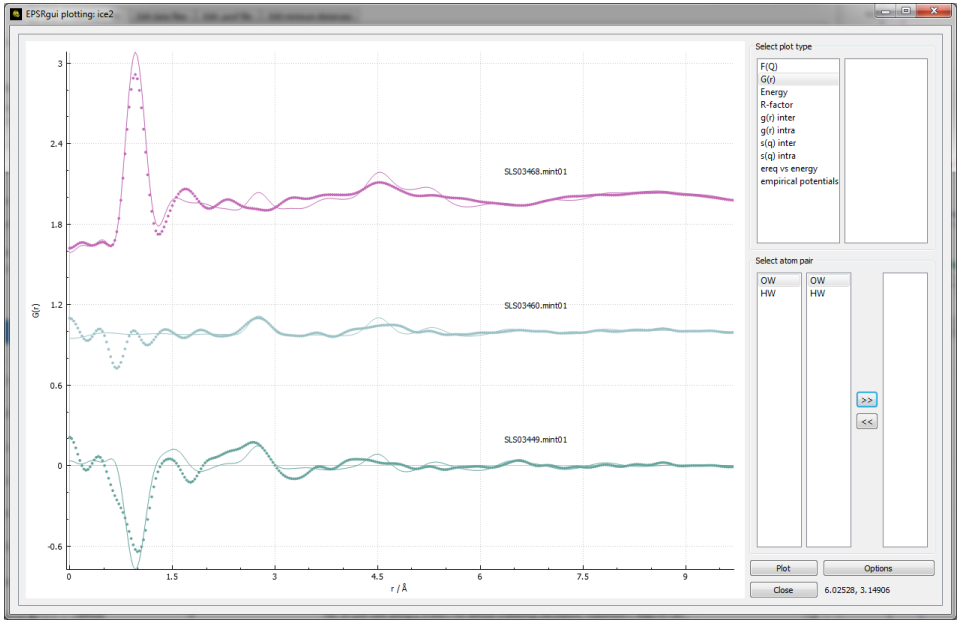
- In the Data and Weights tab add the dataset, fil out the exchangeable and isotopically substituted atoms and make the weights file.
- Click on the EPSR input file tab and click Setup EPSR input file.
- In the Edit input file tab on the EPSR input file tab, change:
  - nq 2000
  - qstep 0.01
  - rotfreq 1 (this is the number of iterations between rotation moves; as rotation is what the water molecules need to do to fit the data, it is useful to perform rotations every iteration)
  - qwidthqmax -0.003 8.0
  - hklqmin 0.3 3.0 0.0
  - qmin 1.0 1.0
- Now Run EPSR.



Improving the simulation

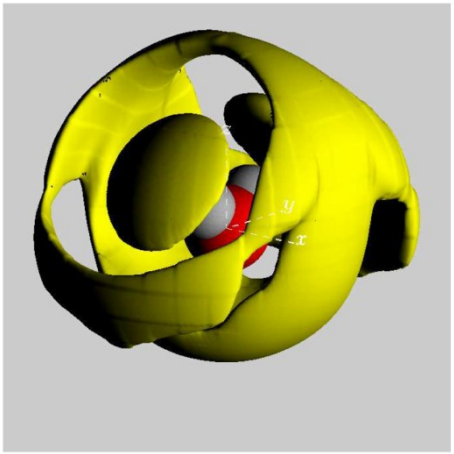
- Check the fit to the data in reciprocal and real space and how the energy and R-factor are changing. Periodically check how the simulation box is changing.
- Areas to consider for improvement:
  - How crystalline is the O atom lattice? Try changing the Tethering tolerance and see how this affects the model.
  - Are the Bragg peak calculation parameters appropriate? Try changing qwidthqmax, hklqmin and mplicities. mplicities can be used to split the simulation box into smaller unit cells for the Bragg peak calculation. For instance, 2 2 2 would mean that a unit cell of ½ a, ½b and ½c would be used for the Bragg peak calculation. Reducing the cell size reduces the number of Bragg peaks calculated, but also loses information about the diffuse scattering.

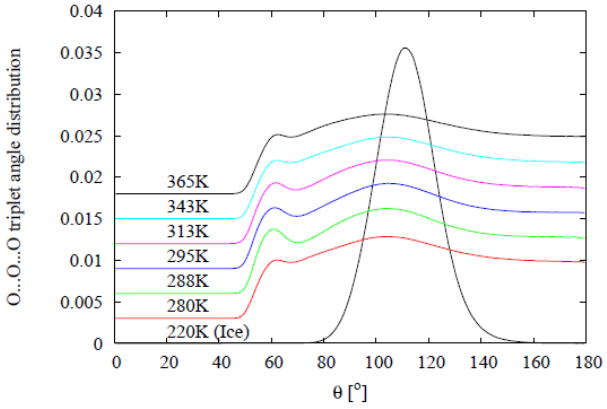


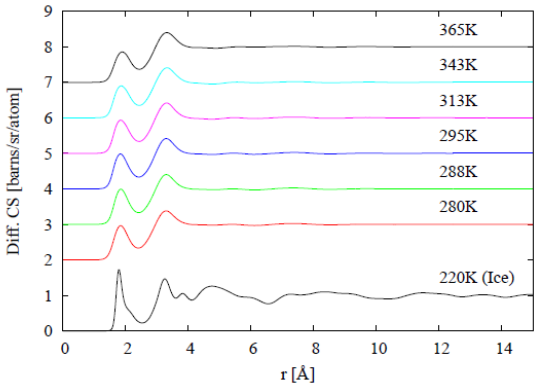


Analysing the refined simulation box

- Using the EPSR manual, consider which analysis routines will probe the ice structure and set these up to run while EPSR is accumulating.
- Compare the radial distribution functions with literature data.
- Plot the results.







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