Tutorial on the use of the *DEBUSSY Suite v2.0beta*

Contents

Introduction

This is a multipurpose tutorial. In the first part, the *DEBUSSY Suite v2.0beta* is used to characterize two different cases of application, which are here presented and discussed in details. The two cases refer respectively to:

1) A sample made of iron oxide nanoparticles, modelled as a population of spherical non-stoichiometric magnetite (Fe_3O_4) nanocrystals (NCs), in which magnetite partially transforms into maghemite (γ-Fe_2O_3) due to the oxidation of Fe^{2+}, the cation diffusion outwards and the formation of vacancies (*Chem. Mater.* **2013**, *25*, 4820−4827);

2) A biphasic mixture of anatase and rutile (TiO_2) nanoparticles, in which the major phase (anatase) is modelled as a bivariate population of anisotropically shaped NCs, and the minor component (rutile) is modelled as a population of spherical NCs (unpublished data, courtesy of PANanalytical B.V.). For both examples, the X-ray diffraction data have been collected in transmission mode using the Debye-Scherrer geometry and filling a glass capillary with dry powders. The data are already subtracted from glass capillary scattering contribution (and air/He scattering for synchrotron data) and corrected for absorption effects (more details are provided in the appropriate section).

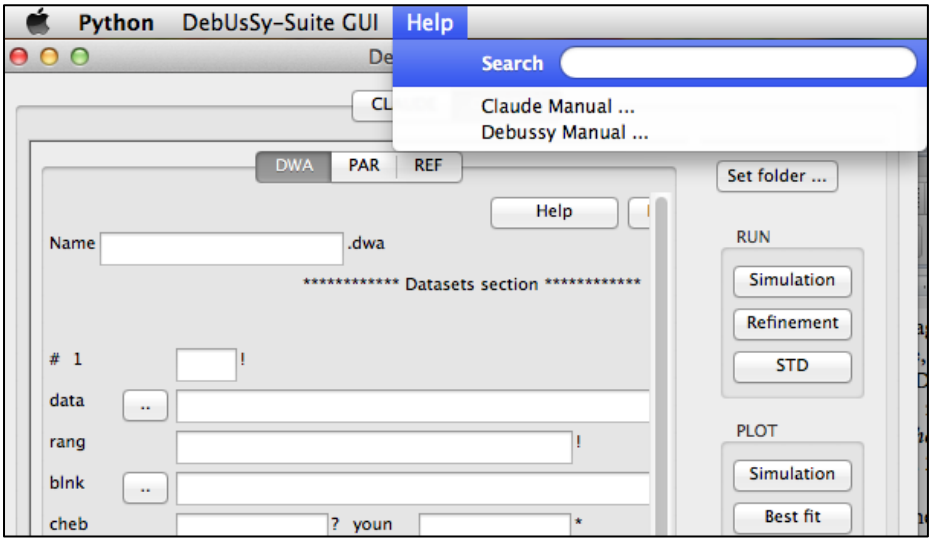
The two examples require the execution both of programs of the Claude Suite and the Debussy program.

The tutorial also provides some basic instructions for running some useful utilities of the Claude Suite:

3) Computing the DSE pattern of a single nanocrystal with selected size and shape;

4) Computing the reduced G(r) function of an experimental diffraction pattern.

Besides this tutorial, useful guides that may help in running the examples, are the *Quick Guide*, downloadable at **http://debussy.sourceforge.net/debussy/tutorial.html** and the *Claude* and *Debussy User's Manuals*, provided within the Suite package and easily accessible through the *DebUsSy Suite* GUI, by hovering over the **Help** in the upper bar of the screen:



The *TUTORIAL.tar.gz* archive, once downloaded at **http://debussy.sourceforge.net/debussy/tutorial.html** and uncompressed, includes the main folder (**TUTORIAL**) organized in three working folders (**Fe3O4/, TiO2-Panalytical/** and **CLAUDE-Utilities/**), comprehensive of all the input files needed to run the examples:

- **Fe3O4/** working folder includes two subfolders: *i*) **DB/,** in which the user will find the *magnetite.cif*

input file to be used for building the database of sampled interatomic distances of spherical magnetite NCs, following the instructions provided in this tutorial; *ii*) **DFA/,** in which the experimental data are supplied together with all the Debussy input files required to perform the optimization of the model pattern. For this example, two synchrotron X-ray diffraction patterns are provided, one for the sample (F28) and one for the amorphous component (F23).

- **TiO2-Panalytical/** working folder includes three subfolders: *i*) **DB Rut/** in which the user will find the *rutile.pha* input file to be used for building the database of sampled interatomic distances of spherical NCs for the rutile phase, following the instructions provided in this tutorial; *ii*) **DB_Anat**/ with the *anatase.pha* input needed for generating a bivariate population of rod- and plate-shaped NCs for the anatase phase, following the instructions provided in this tutorial; *iii*) **DFA/** in which the experimental data are supplied together with all the Debussy input files necessary to perform the refinement of a biphasic sample, using the databases of both structures (rutile and anatase). The X-ray diffraction pattern collected with a laboratory diffractometer is supplied for this example.
- **CLAUDE-Utilities/** working folder includes three subfolders: *i*) **MOLEC/** in which the user will find the *magnetite_r010.xyx* file to be used for building the corresponding set of sampled interatomic distances, following the instructions provided in this tutorial; *ii*) **PATTERN/** in which the user will find an example of *diffractor.inp* file along with the database required to calculate di DSE simulation of single nanocrystal*; ii*) **PDF/** in which the user will find the experimental diffraction data and an example of *dopdf.inp* file in order to calculate di reduced G(r).

EXAMPLE 1: Iron Oxide Nanoparticles

(working folder: ./**TUTORIAL/Fe3O4/**)

Overview

The aim of this example is applying the DSE analysis to a sample made of iron oxide nanoparticles, in order to extract quantitative information about the structural features (size-dependent stoichiometry and lattice expansion), the size and size distribution of the NCs.
The sample here characterized (F28) contains also an amorphous component (sub-nanometer iron oxy-hydroxides); the diffraction pattern of a similar amorphous phase was independently measured on a suitable sample (F23), added as a blank signal in the refinement process and suitably rescaled by linear least squares.
Synchrotron X-ray diffraction data of both samples (F28 and F23) were collected in transmission mode at the MS-X04SA beamline of SLS-PSI (Villigen, CH); they were properly subtracted from the scattering contributions of the glass capillary and the sample environment (air/He) (both independently measured in the same experimental conditions) and corrected for the absorption of the sample.
On the pattern modelling side, the sampled interatomic distances database is created by building a monovariate (spherical) population of NCs, starting from the structural details reported in the Crystallographic Information File (*magnetite.cif*), downloaded from the Crystallography Open Database (COD). The iron atoms in the magnetite crystal structure are treated as two distinct atomic species, accordingly to the different crystallographic sites (octahedral and tetrahedral) occupied. Such a choice allows the site occupancy factor (s.o.f.) of Fe in the octahedral site to be refined (following a size dependent law, as reported in *Chem. Mater*. **2013**, *25*, 4820−4827) while keeping fixed to 1.0 the s.o.f. of Fe in the tetrahedral site. Due to surface-induced effects, the cell parameter for this material is also refined following an inverse size dependent law.
This tutorial provides a step-by-step guide to the generation of the sampled interatomic distances database for spherical magnetite NCs (using the *CLAUDE_GUI*) and the DSE analysis of the experimental data using the previously created database (through the *DEBUSSY_GUI*).

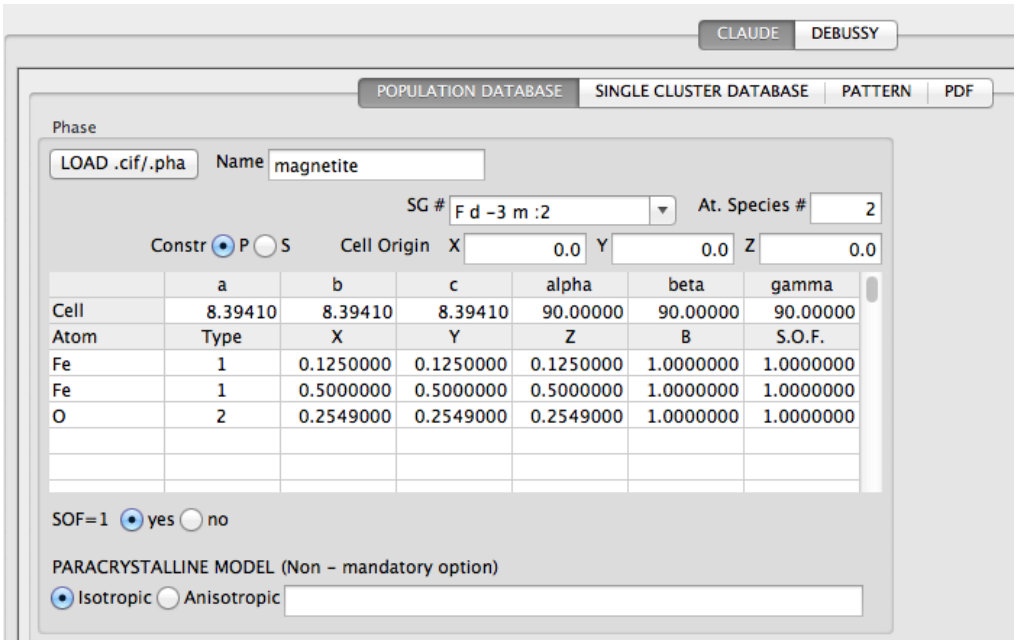
Generating a population of NCs using the *CLAUDE_GUI*

In order to start working at the database generation, the working folder (./**TUTORIAL/Fe3O4/DB/**) must be selected through the **Set Folder** button of the *CLAUDE_GUI* tab. For the *CLAUDE* step, only the *magnetite.cif* file is provided in the working folder; instructions for preparing the *magnetite.ddb* file are given below.

By loading the *magnetite.cif* file (**LOAD .cif/.pha**), the phase information contained in the cif file is written in the *magnetite.pha* file, which is then used as the input file for the NCs builder process.

With the "automatic" *.cif* to *.pha* conversion, the space group Herman-Mauguin symbol (*F d-3m*), the number of atomic species, the cell parameters and the atomic fractional coordinates of the asymmetric unit are written in the *magnetite.pha* file. All the atomic species are sorted from the highest to the lowest atomic number (Z) and all atoms with the same Z are grouped as a single atomic species. In this example, two

atomic species (Fe and O) are automatically considered. All these information are displayed in the **POPULATION DATABASE** tab, as shown below:

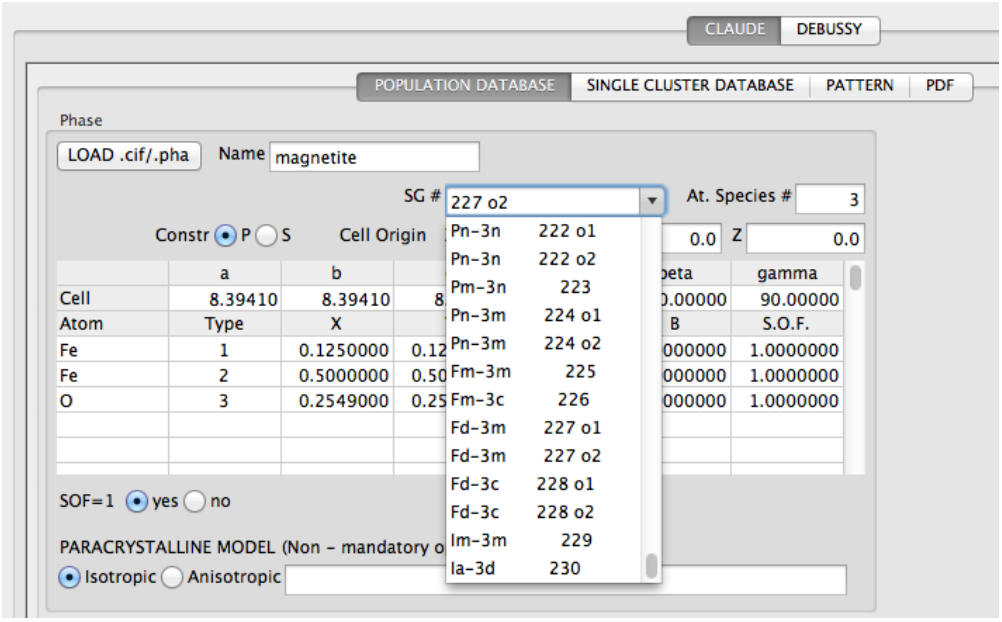


IMPORTANT: Change the content of the *magnetite.pha* file by using the **POPULATION DATABASE** tab (see figure below) by:

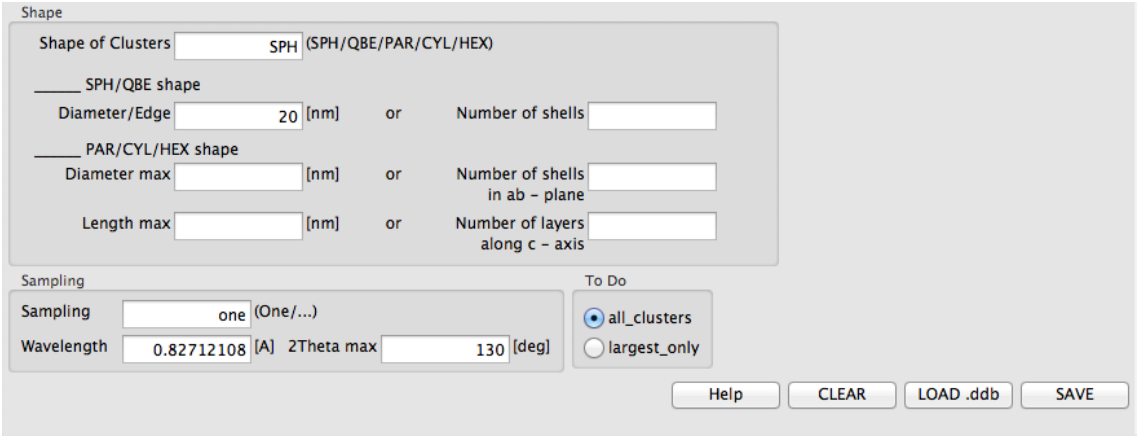
1. Selecting the Space group number (**SG #** 227) with the right origin choice (o2), through the drop-down list of the *CLAUDE_GUI.*

2. Modifying the number of atomic species from 2 to 3 (**At. Species #**)

3. Marking the two Fe atoms as two different species, and the O atoms as a third one (**Type**), as shown below:



All the remaining information required for building the population of magnetite NCs are provided through the *magnetite.ddb* file. Use the **POPULATION DATABASE** tab to fill in the required information, which are specified below:



Further details about fields and numbers are provided in the following table:

`Shape Clusters:  SPH`		Shape of the NCs (SPH/QBE/HEX/CYL/PAR)
`__SPH/QBE shape`		Monovariate population of NCs: this kind of populations includes NCs of spherical (SPH) or cubic (QBE) shapes. For these shapes, the maximum size of the NCs can be provided as max diameter (SPH, max) edge (QBE) or number of shells.
`Diameter/Edge (nm) :  20`		Max limit of the cluster diameter (SPH)/ edge(QBE) in nm
`Number of shells:`		Max. number of shells
`__PAR/CYL/HEX shape`		Bivariate population of NCs: the database is built following two independent growing direction, one along *ab* plane and one along *c*
`Diameter max (nm) :`		Max. size along *ab*, in terms of the diameter of the equivalent circle of the *ab* base (in nm)
`Lenght max (nm) :`		Max. size along *c* axis (in nm)
`Number of shells in ab-plane:`		Max. number of equivalent shells in the *ab* plane
`Number of layers along c-axis:`		Max. number of unit cells along *c*
`Sampling:  one`		Sampling type
`Wavelength (Å):  0.82712108`		Wavelength (in Å)
`2-Theta Max (deg):  120.00`		*2θ* max of your experimental data
`To Do all_clusters`		Nr of clusters in the database (all_clusters/ largest_only)

Once the **POPULATION DATABASE** tab is filled, use the **SAVE** button in order to save all the information in the *magnetite.ddb* file.

Once the *magnetite.ddb* file is available, changes can be introduced by loading the existing file (by clicking on **LOAD .ddb** the information is displayed on the **POPULATION DATABASE**) and editing the appropriate field(s). After changes use the **SAVE** button to update the *magnetite.ddb* file.

The database of sampled interatomic distances for spherical NCs (up to 20 nm) is created by clicking, in the sequence specified below, on the appropriate buttons of the **MAKE** vertical menu. An X-term is automatically opened and used by the GUI for displaying messages and output information, for each action:

a) **CELL**: it generates the *magnetite.cel* file, containing all the atoms in the unit cell. The end of the run is indicated by the following message **JOB CELL DONE!** on the X-term.

b) **DATABASE:** it launches the database-builder. The program uses the unit cell content as the building block and the shape/size information supplied in the *magnetite.ddb* file. A new folder (**./DB/DISTANCES/SAMPTO180A/**) is created, storing the files containing the multiplicities of the sampled interatomic distances (*.smp*) and the associated *.smp_INFO*. Each couple of files includes

information for a single NC; the progressive number, that is the last part of the filenames, indicates the number of shells, made by lattice nodes then convoluted with the unit cell content.
Optional output files of this stage are *.xyz* and **LAT.xyz* files; each *.xyz* file contains the Cartesian coordinates of the atoms in the cluster; each **LAT.xyz* file contains the Cartesian coordinates of the lattice nodes used for building the cluster. These optional files can be generated within the *CLAUDE_GUI* by clicking on the **XYZ** button of the **MAKE** vertical menu. The **XYZ** button of the **PLOT** vertical menu launches the *Jmol* application that allows the visualization and manipulation of the *.xyz* files.
The end of the database-builder run is indicated by the message **JOB SMP-SPH DONE!** on the X-term.

Performing the DSE analysis through the *DEBUSSY_GUI*

Move from the *CLAUDE* to the *DEBUSSY* tab of the *GUI*.
For the DSE analysis of this example, all the necessary input files for the Debussy program are provided in the working folder (./**TUTORIAL/Fe3O4/DFA/**), which must be selected through the **Set Folder** button.

The following input files are supplied for this example: *magnetite.dwa*, *magnetite.par* and *magnetite.ref*.
By selecting the **DWA/PAR/REF** tabs, and by clicking on **LOAD .dwa/.par/.ref** buttons, the content of each file is displayed on the appropriate tab.

We briefly recall that:

i) *magnetite.dwa* file, contains the information on the experimental dataset, the database storing the population of NCs and the name of the files giving the model parameters (*magnetite.par*) and refinement details (*magnetite.ref*).

ii) *magnetite.par* file, includes global and atomic parameters with the lower limit for the parameter value, the actual (refined) value, the upper limit and the refinement flag (1= refine, 0 = do not refine). Global parameters are the parameters of the lognormal size distribution and the lattice expansion functions. Up to a maximum of 9 global parameters can be refined. Atomic parameters refer to the parameters used for refining atomic s.o.f.'s and Debye-Waller factors. Up to a maximum of 3+3 atomic parameters for each atom can be refined.

iii) *magnetite.ref* file contains higher level refinement flags; whereas in the *.par* file the refinement flags control each single parameter, in this file the flags can be used to control groups of parameters.

Click on the **Simulation** button in the **RUN** vertical menu in order to calculate the DSE simulation using the initial parameters reported in the *magnetite.par* file. An X-term is automatically launched and used by the program for displaying messages and information.
The end of the simulation is indicated by the **DebUsSy Simulation DONE!** message on the X-term.

The following output files are created at the end of the simulation run:

i) magnetite01_plot1D.mtx: it contains size, strain, s.o.f., Debye Waller factors of each cluster within the population. It can be visualized using the **Size/Lattice exp./S.O.F/BTH** buttons of the **PLOT** vertical menu.

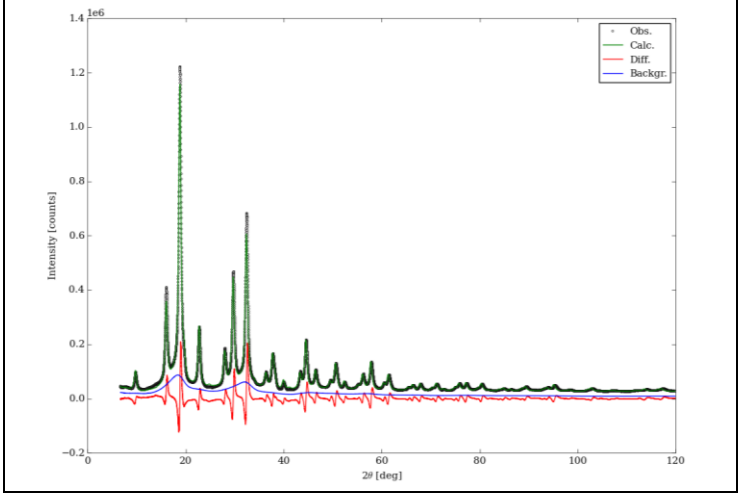
ii) *magnetite_SIM_Best.dis* reports the average diameter, mass and volume for the monovariate population

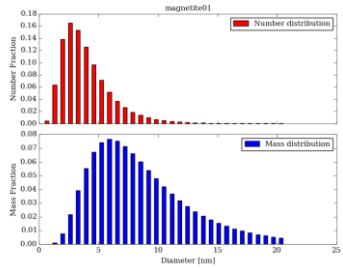
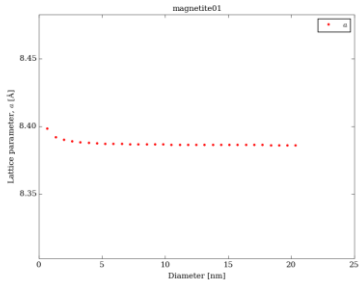
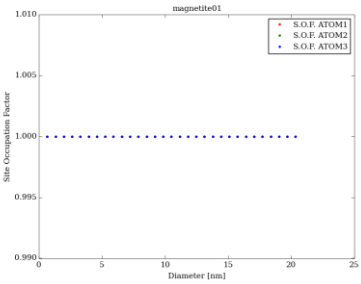
of NCs and they standard deviations. The rootname of this file (*magnetite_SIM*) is taken from the outs option in the *magnetite.dwa* file and can be changed for a new simulation run. It can be opened using a Text Editor.

iii) *magnetite_SIM_SPD#01.cal*: it contains *2θ* angle, experimental and total calculated patterns, the background curve. The rootname of this file (*magnetite_SIM*) is taken from the outs option in the *magnetite.dwa* and can be changed for a new simulation run. It can be visualized using the **Simulation** button of the **PLOT** vertical menu.

Plot of the graphical outputs of a simulation using the initial parameters reported in the *magnetite.par* file are shown below:

DSE pattern simulation



Size distributions	*Size dependent lattice parameter*	*Atomic s.o.f.*
		

In this example, some of the initial model parameters are refined against the experimental data.
The refined global parameters are: *AV1LN, SD1LN, STR_i, STR_1*.
The refined atomic parameters are the Debye-Waller factor of each atom according to a size-constant law (*BTH_I*) and the s.o.f. of Fe in octahedral site (*ATO02*) according to a size-dependent law (*OKK_I, OKK_0, OKK_L*).
A multiple refinement stages strategy, based on the COMPLEX optimization algorithm, is applied: lattice expansion parameters (*STR_i, STR_1*) are optimized in the first stage, according to an inverse-linear function (STcod=4); size distribution (*AV1LN, SD1LN*) and atomic parameters are refined in the second stage; all

parameters are simultaneously adjusted in the last and third stage.

Click on the **Refinement** button in the **RUN** vertical menu in order to start the parameters optimization run. An X-term is automatically launched and used by the program for displaying messages and information, cycle by cycle, about the refinement stages (number of parameters/data, the figure of merits, the cycles' number, etc).
The end of the refinement is indicated by the **DebUsSy Refinement DONE!** message on the X-term.

The output files created at the end of the first cycle and updated any time a new minimum of the χ^2 function is reached, are:

i) magnetite01_Best.par: it has the same format of *magnetite.par* file; here the new values of the refined parameters are automatically saved. It can be opened with the *DEBUSSY_GUI* **PAR** tab and saved as a new *.par* input file.

ii) *magnetite01_plot1D.mtx*: it contains size, strain, s.o.f., Debye Waller factors of each cluster within the population. It can be visualized using the **Size/Lattice exp./S.O.F/BTH** buttons of the **PLOT** vertical menu.

iii) *magnetite_Best.dis* reports the average diameter, mass and volume for the refined population of NCs and they standard deviations. It can be opened using a Text Editor.

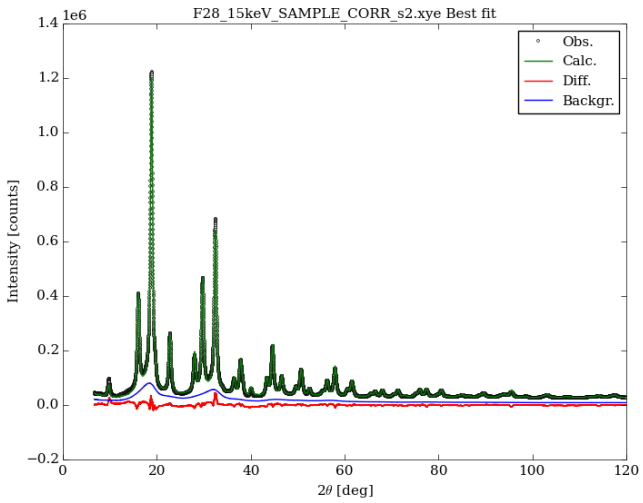
iv) F28_15keV_SAMPLE_CORR_s2_Best.cal: it is a 6 columns file with 2θ angle, experimental and total calculated patterns, the DSE simulation of the NC population, the background (polynomial) curve and the blank trace, respectively (in the example the column 5= 6, because we're are not using any polynomial coefficient to improve the background fit).
By using the **Best Fit** button in the **PLOT** vertical menu, the experimental and total calculated patterns, of the background curve and of the "Exp-Calc" difference curve are displayed.

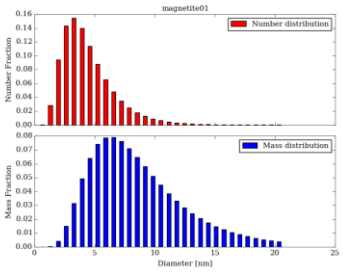
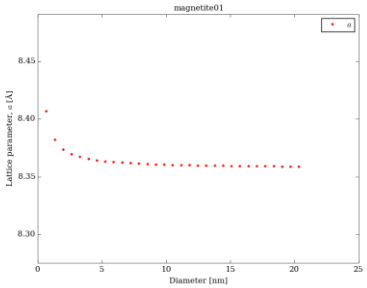
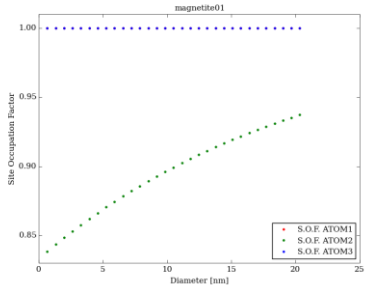
The file *magnetite_ref.sum* is created at the end of the refinement and summarizes the final results in terms of # of cycles, thresholds, CPU time (total and per cycle), final χ^2, Rwp, GoF, refined scales for the experimental pattern and its background. It can be read using a Text Editor.

At the end of each refinement stage, parallel **F_01.** files are generated for all the outputs previously described (except that for the *.mtx* file), storing the information available at the intermediate stages.

Plot of the graphical outputs at the end of the refinement are shown below:

Best Fit



Size distributions	*Size dependent lattice parameter*	*Atomic s.o.f.*
		

EXAMPLE 2: Titanium Dioxide Nanoparticles

(working folder: ./**TUTORIAL/TiO2-Panalytical/**)

Overview

The aim of this example is applying the DSE analysis to a biphasic sample of nanocrystalline titania, in order to extract quantitative information about its composition (mass fraction of anatase and rutile phases), size and size distributions of the NCs.
The experimental data here supplied were collected in transmission mode using a laboratory Panalytical Instrument (courtesy of PANalytical B.V.), subtracted from the glass capillary scattering, (measured in the same experimental conditions) and corrected for the absorption of the sample.
On the pattern modelling side, the sampled interatomic distances databases is created for a bivariate population (parallelepipeds) of NCs for anatase, while a monovariate population (spherical) is used for the rutile component.
The *DebUsSy* approach allows refining sizes and structural parameters of both phases contributing to the total scattering pattern, and their quantitative estimation.
This tutorial provides a step-by-step guide to the generation of the sampled interatomic distances databases for both structures (using the *CLAUDE_GUI*) and the DSE analysis of the experimental data (using the previously created databases) through the *DEBUSSY_GUI*.

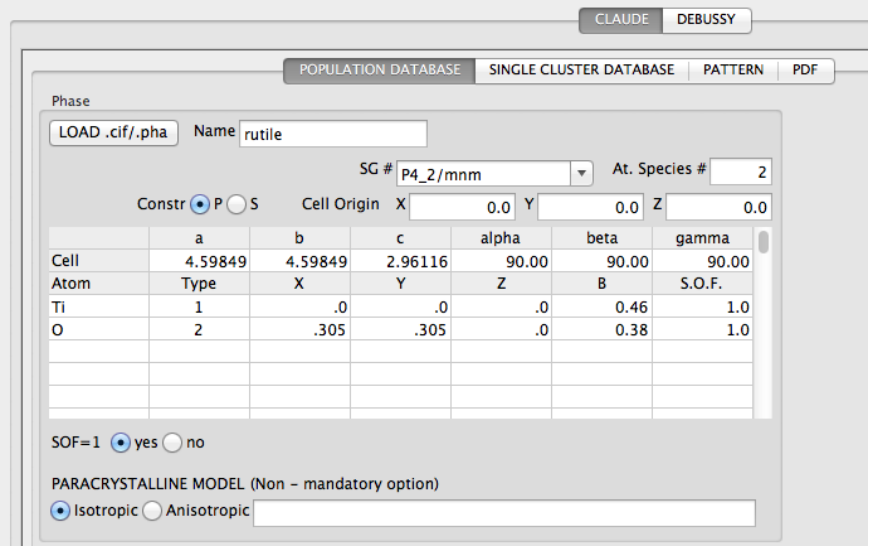
It is strongly recommended to run this tutorial after the Example 1, since the description of some basic operations/files, already reported above, are skipped here.

Generating a population of NCs using the *CLAUDE_GUI*

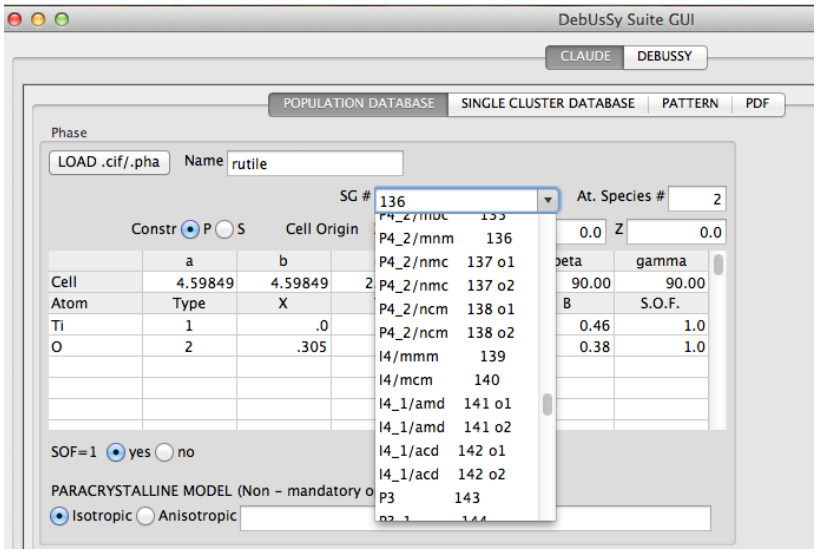
Belonging both rutile and anatase to tetratragonal crystal systems, we refined independently $a=b$ and c cell parameters with an external program. The refined cell parameters, space group symbols and the atomic coordinates for both phases are supplied in the related folders (./**TUTORIAL/TiO2-Panalytical/DB_Rut/** and ./**TUTORIAL/TiO2-Panalytical/DB_Anat/**), in the *rutile.pha* and *anatase.pha* files, respectively.

In order to start working at the two databases generation, the following operations must be performed, after selecting the *CLAUDE_GUI* tab:

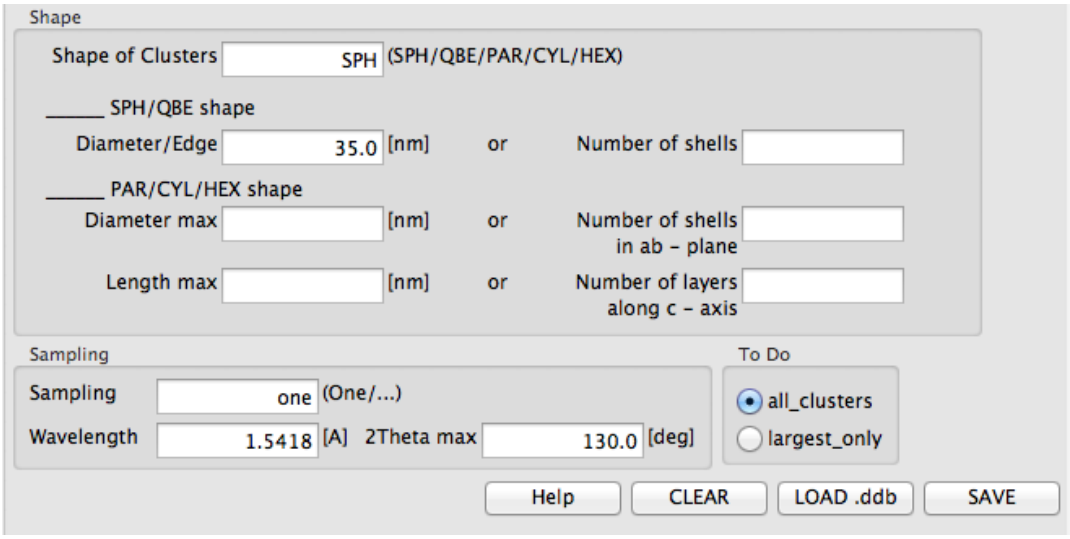
1) Building the population of spherical NCs for the rutile structure: click on **Set Folder** and select ./**DB_Rut/** working folder.
By loading the *rutile.pha* (**LOAD .cif/.pha**), the phase information contained in this file are displayed in the **POPULATION DATABASE** tab, as shown below:



Change the content of the *rutile.pha* file by using the **POPULATION DATABASE** tab (see figure below) in order to select the Space group number (**SG #** 136) instead of the Herman-Mauguin symbol, through the drop-down list of the *CLAUDE_GUI*:



All the other information required for building the spherical population of rutile NCs are provided through the *rutile.ddb* file. Use the **POPULATION DATABASE** tab to fill in the blank fields, as specified below:



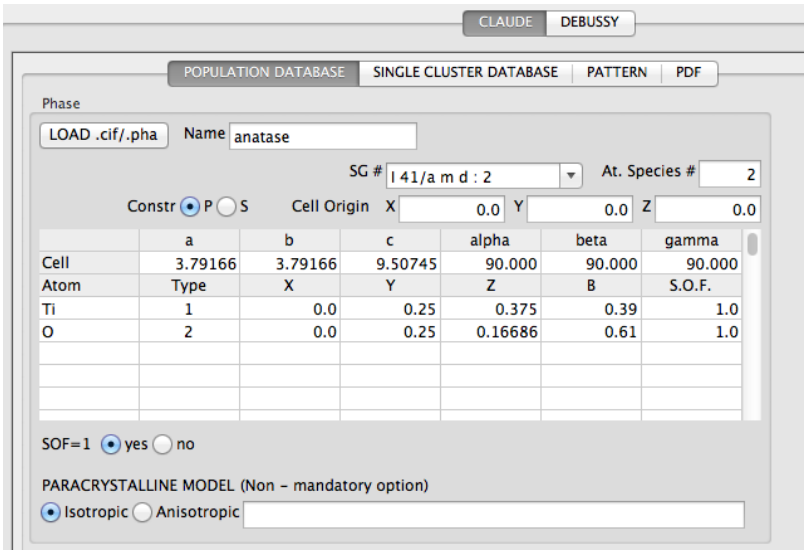
Once the **POPULATION DATABASE** tab is filled, use the **SAVE** button in order to save all the information in the *rutile.ddb* file. Once this file is created, it is possible to load it anytime (if required), by clicking on **LOAD .ddb.,** further modify and upload it through the **SAVE** button.

The spherical population of NCs for rutile (up to 35 nm) is created by clicking, in the sequence specified below, on the appropriate buttons of the **MAKE** vertical menu. An X-term is automatically opened and used by the GUI for displaying messages and output information, for each action:

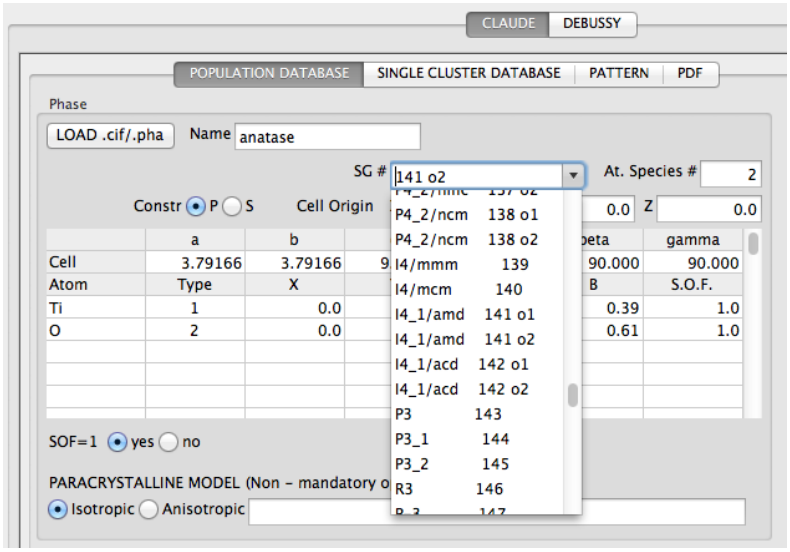
a) **CELL**: it generates the *rutile.cel* file, containing all the atoms in the unit cell. The end of this run is indicated by the following message **JOB CELL DONE!** on the X-term.

b) **DATABASE:** it launches the database-builder. The program uses the unit cell content as the building block and the shape/size information supplied in the *rutile.ddb* file. A new folder (**./DB_Rut/DISTANCES/SAMPTO330A/**) is created, storing the files containing the multiplicities of the sampled interatomic distances (*.smp*) and the associated *.smp_INFO*. Each couple of files contains information for a single NC; the progressive number, which is the last part of the filenames, indicates the number of shells, made by lattice nodes then convoluted with the unit cell content.
The end of the database-builder run is indicated by the following message **JOB SMP-SPH DONE!** on the X-term.

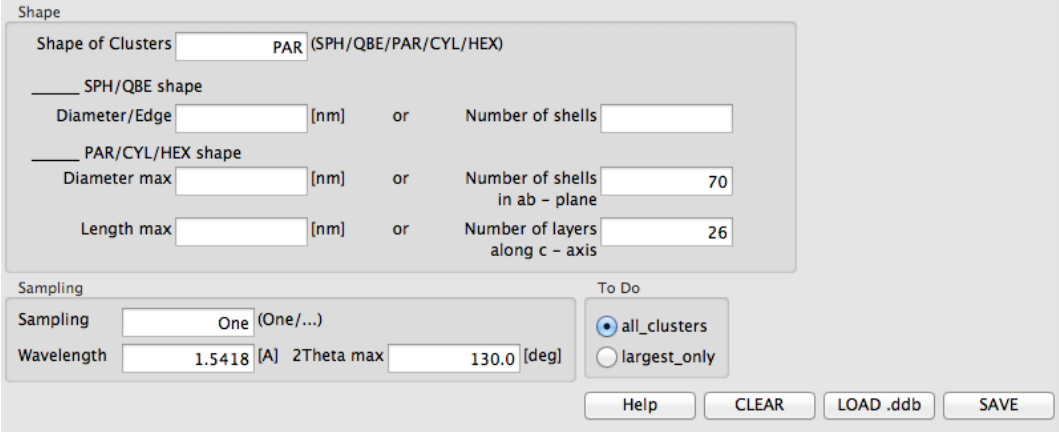
2) Building of the bivariate population of NCs for anatase structure: stay on the *CLAUDE_GUI* tab and click on **Set Folder** in order to select the ./**DB_Anat**/ working folder.
By loading the *anatase.pha* file (**LOAD .cif/.pha**), the phase information specified in this file are displayed in the **POPULATION DATABASE** tab, as shown below:



Change the content of the *anatase.pha* file, using the **POPULATION DATABASE** tab (see figure below), by selecting the Space group number (**SG #** 141) with the appropriate origin choice (o2) (through the drop-down list of the *CLAUDE_GUI)*:



All the remaining information required for building the bivariate (PAR) population of anatase NCs are provided through the *anatase.ddb* file. Use the **POPULATION DATABASE** tab to fill in the required fields, as is shown below:



Once the **POPULATION DATABASE** tab is filled, use the **SAVE** button in order to save all the information in the *anatase.ddb* file.
The bivariate population for anatase (up to 30 nm in *ab* and 25 nm along *c*) is created by clicking, in the sequence specified below, on the appropriate buttons of the **MAKE** vertical menu. An X-term is automatically opened and used by the GUI for displaying messages and output information, for each action:

a) **CELL**: it generates the *anatase.cel* file, containing all the atoms in the unit cell. The end of the run is indicated by the following message **JOB CELL DONE!** on the X-term.

b) **DATABASE:** it launches the database-builder. The program uses the unit cell content as the building block and the shape/size information supplied in the *anatase.ddb* file. A new folder (**./DB_Anat/DISTANCES/SAMPTO330A/**) is created, storing the files containing the multiplicities of the sampled interatomic distances (*.smp*) and the associated *.smp_INFO*. Each couple of files includes information for a single NC. In this PAR database, the NCs are grown following two independent directions, one along *ab* plane and the second along the *c* axis; the last part of the names of the *.smp*/*.smp_INFO* files indicates, by two progressive numbers, the clusters dimensions, being the first the number of shells (made by lattice nodes) in the *ab* plane and the second the number of unit cells along *c*. The end of the database-builder run is indicated by the following message **JOB SMP-PAR DONE!** on the X-term.

Performing the DSE analysis through the *DEBUSSY_GUI*

Move from *CLAUDE_GUI* to *DEBUSSY_GUI* tab.
For the DSE analysis of this example, all the necessary input files for the Debussy program are provided in the working folder (./**TUTORIAL/TiO2-Panalytical/DFA**/), which must be selected through the **Set Folder** button.

The following input files are supplied for this example: *TiO2.dwa*, *rutile.par* and *anatase.par*, *TiO2.ref*.
By selecting the **DWA/PAR/REF** tabs, and by clicking on **LOAD .dwa/.par/.ref** buttons, the content of each file is displayed on the appropriate tab.

We briefly recall that:

i) *TiO2.dwa* file contains the information on the experimental dataset, the databases storing the population of NCs and the name of the files giving the model parameters (*rutile.par* and *anatase.par*) and the refinement details (*TiO2.ref*). In this example two phases are refined (each phase has its own parameter file), labelled by the symbol % in this file and mandatorily specified following the order of the database code (first monovariate, *db03* code, then bivariate, *db04* code, populations). See the *Debussy User's Manual* for further details.

ii) *rutile.par* and *anatase.par* files, are the parameters files for each phase. These files have the same structure already described in the Example 1, containing the (9) global and (6) atomic parameters for Ti and O: for each of them the lower limit for the parameter value, the actual (refined) value, the upper limit and the refinement flag (1= refine, 0 = do not refine) are reported.

iii) *TiO2.ref* file contains higher level refinement flags to control groups of parameters; the refinement flags for each phase are separated by the symbol %, indicating the phase number, in the same order as reported in the *TiO2.dwa* file.

Click on the **Simulation** button in the **RUN** vertical menu in order to calculate the DSE simulation using the initial parameters specified in the *rutile.par* and the *anatase.par* files. An X-term is automatically launched and used by the program for displaying messages and information.
The end of the simulation is indicated by the **DebUsSy Simulation DONE!** message on the X-term.

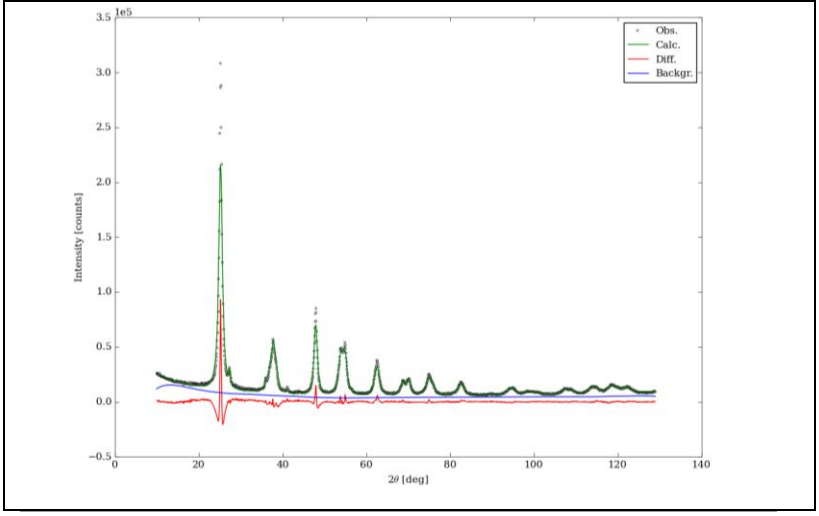
The following outputs are created at the end of the simulation run:

i) rutile01_plot1D.mtx and *anatase02_plot2D.mtx*: they report size, strain, s.o.f., Debye Waller factors of each cluster within the mono- (rutile) and bivariate (anatase) populations. They can be visualized using the **Size/Lattice exp./S.O.F/BTH** buttons in the **PLOT** vertical menu.

ii) *TiO2_SIM_Best.dis* indicates the size and size distributions information for each phase (reported following the same order of the *TiO2.dwa* file) and their global mass fractions.
For rutile, it reports the average diameter, mass and volume for the monovariate population of NCs and they standard deviations.
For anatase, the average diameter, mass and volume, together with the size and size distribution functions projected along the two normal growing directions (*ab* plane and *c* axis) their covariance matrix and correlation angle are indicated.
The rootname of this file (*TiO2_SIM*) is taken from the outs option in the *TiO2.dwa* file and can be changed for a new simulation run. This file can be opened using a Text Editor.

iii) *TiO2_SIM_XPD#01.cal*: it contains 2θ angle, experimental and total calculated patterns and the background curve (12 Chebyshev coefficients are used in this example, as specified in the *TiO2.dwa* file).
The rootname of this file (*TiO2_SIM*) is taken from the outs option in the *TiO2.dwa* file and can be changed for a new simulation run.
This file can be visualized using the **Simulation** button in the **PLOT** vertical menu; it is shown below:

DSE pattern simulation



In this example, some of the initial model parameters are refined against the experimental data.
Being the rutile structure (phase % 1) the minority phase found in a very small amount within the titania sample, we provide its *rutile.par* file with all the global parameters (*AV1LN*, *SD1LN*) already refined: the refinement of these parameters can be considered an advanced option for this tutorial, and can be reached (optionally) using a multistage refinement. The Debye-Waller factors of Ti and O are however refined, following a size-constant law (*BTH_I*).
The refined global parameters for the anatase (phase % 2) are: *AV1LN, SD1LN, AV2LN, SD2LN, PHILN.* The refined atomic parameters are the Debye-Waller factors of each atom (Ti and O) according to a size-constant law (*BTH_I*).

In the strategy that we propose here, the refinement can be carried on by a unique stage (as reported in *TiO2.ref* file), using the COMPLEX optimization algorithm: only the Debye-Waller factors of both atoms (Ti and O) are refined for rutile structure (%1), while size distributions and atomic parameters are refined for the anatase (%2).

Click on the **Refinement** button in the **RUN** vertical menu in order to start the parameters optimization run. An X-term is automatically launched and used by the program for displaying messages and information, cycle by cycle, about the refinement stages (number of parameters/data, the figure of merits, the cycles' number, etc.).
The end of the refinement is indicated by the **DebUsSy Refinement DONE!** message on the X-term.

The output files created at the end of the first cycle and updated any time a new minimum of the χ^2 function is reached are:

i) rutile01_Best.par and *anatase02_Best.par*: here the new values of the refined parameters are automatically saved. They can be opened with the *DEBUSSY_GUI* **PAR** tab and saved as new *.par* input files.

ii) *rutile01_plot1D.mtx* and *anatase02 plot2D.mtx* : they contain size, strain, s.o.f., Debye Waller factors of each cluster within the mono- (rutile) and bivariate (anatase) populations. They can be visualized using the **Size/Lattice exp./S.O.F/BTH** buttons in the **PLOT** vertical menu.
The **Size** button allows the visualization of the monovariate number- and mass- based size distributions for rutile. A 2D map is plotted for the bivariate size distribution of the anatase (as shown in the pictures below): the horizontal axis reports the diameter (D_{ab}) of the circle of area equivalent to the base of the

prism (in the crystallographic *ab*-plane), and the vertical axis the length (L_c) of the prism (along the crystallographic *c*-axis); the color-code indicates the number/mass fractions of the *i-th* cluster of the database.
Looking at these maps, we can state that the morphology of these NCs can be approximated by platelets, that the size dispersion is higher in the *ab*-plane and the correlation between the two growing directions is not negligible (the correlation angle approaches the 45° degrees).

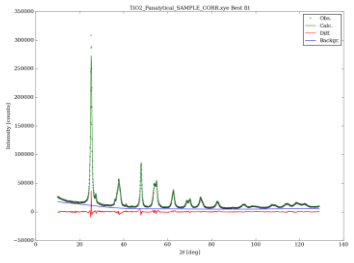
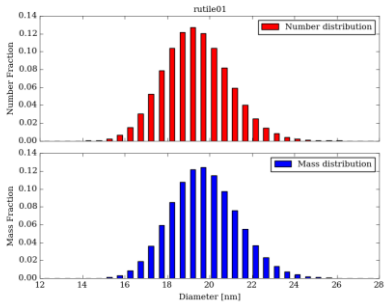
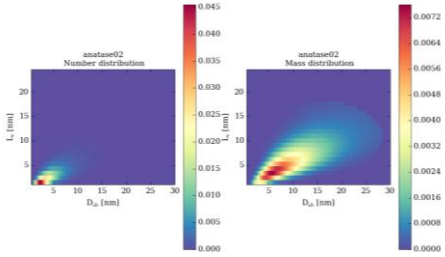
iii) *TiO2_Best.dis* reports the size and size distribution information for each phase (specified following the same order of the *TiO2.dwa* file) and their global mass fractions. It can be opened using a Text Editor. For structure % 1 (rutile) the average number- and mass- based sizes and sizes distributions are supplied. For anatase (structure % 2) together with the average sizes, also the number- and mass- based mean sizes and size distributions along the two growth directions are given. The considerations about the anatase NCs morphology and their different distribution along the two growing directions, made by looking at the 2D maps above, can be confirmed reading this file.
At the end of the *TiO2.dis* file, the global mass fractions of the two phases are supplied, giving 3.9% for rutile and 96.1% for anatase.

iv) *TiO2_Panalytical_SAMPLE_CORR_Best.cal:* it is a 7 columns file with 2θ angle, experimental and calculated total DSE patterns, the single DSE simulation of each phase (rutile and anatase), the background (polynomial) curve and the blank trace (being 0.0 in this example, because no blank curve is used), respectively

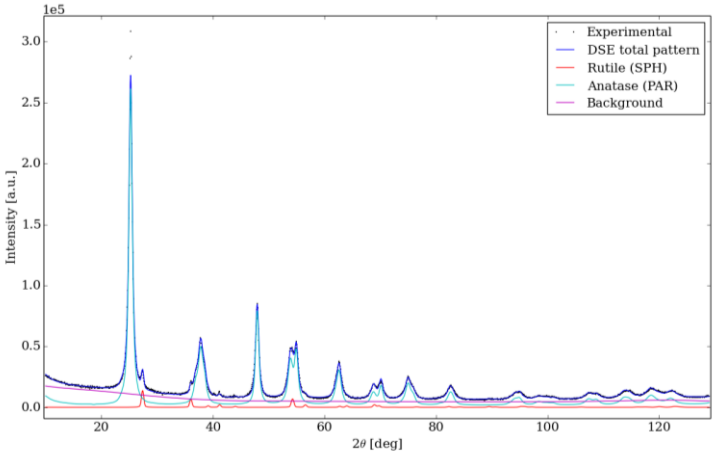
The file *TiO2_ref.sum* is created at the end of the refinement and summarizes the final results in terms of # of cycles, thresholds, CPU times (total and per cycle), final χ^2, Rwp, GoF, refined scales for the experimental pattern and its background. It can be read using a Text Editor.

At the end of this unique refinement stage, parallel **F_01.** files are generated for all the outputs previously described (except that for the .mtx file).

Plot of the graphical outputs at the end of the refinement are shown below:

Best Fit	*SPH size distributions for rutile*	*PAR size distributions for anatase*
		

By using the **CUSTOM** plot button in the **PLOT** vertical menu, the visualization of each component of the *TiO2_Panalytical_SAMPLE_CORR_Best.cal* file is allowed (see the **HELP** button in the **CUSTOM** window for details):


1e5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Intensity [a.u.]
20
40
60
80
100
120
2θ [deg]
Experimental
DSE total pattern
Rutile (SPH)
Anatase (PAR)
Background

EXAMPLE 3: DSE pattern simulation of a Single Cluster

(working folder: ./**TUTORIAL/CLAUDE-Utilities/PATTERN**)

Overview

The aim of this example is calculating the DSE pattern simulation for a single cluster of selected size and shape, rather than a population of nanocrystals of diverse size and shape. This option can be used both for ordered nanocrystals (as the examples provided in this tutorial) and disorder/amorphous clusters, since it requires the list of Cartesian coordinates of the particle, collected in a single *.xyz* file.
Here the *.xyz* files for two nanocrystalline samples (spherical magnetite and parallelepiped anatase) are supplied:

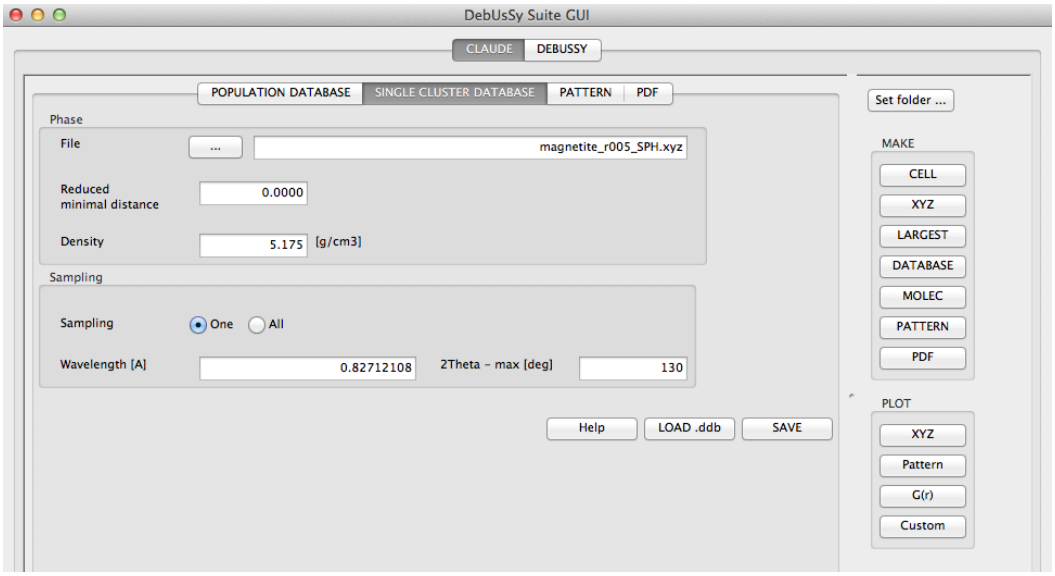
i) *Magnetite NCs*: SPH clusters of two different sizes (*magnetite_r005_SPH.xyz* and *magnetite_r010_SPH.xyz*, 3.3 and 6.6 nm, respectively), in order to highlight the size-induced effects on the DSE pattern of isotropically shaped clusters.

ii) *Anatase NCs*: PAR (anisotropic) clusters with comparable volume and different shape. *anatase_a005_c014_PAR.xyz* exhibits a rod-like shape, *anatase_a011_c003_PAR.xyz* a platelet-like shape. The two nanocrystals are here used to show shape-induced effects on the DSE patterns.

Starting from these input files provided in the working folder, the sampled interatomic distances will be computed through the *CLAUDE_GUI* and following the instructions provided in the tutorial; the input file (*diffractor.inp*) for calculating the corresponding DSE simulation is also available in the same folder.

DSE simulation of a single magnetite cluster

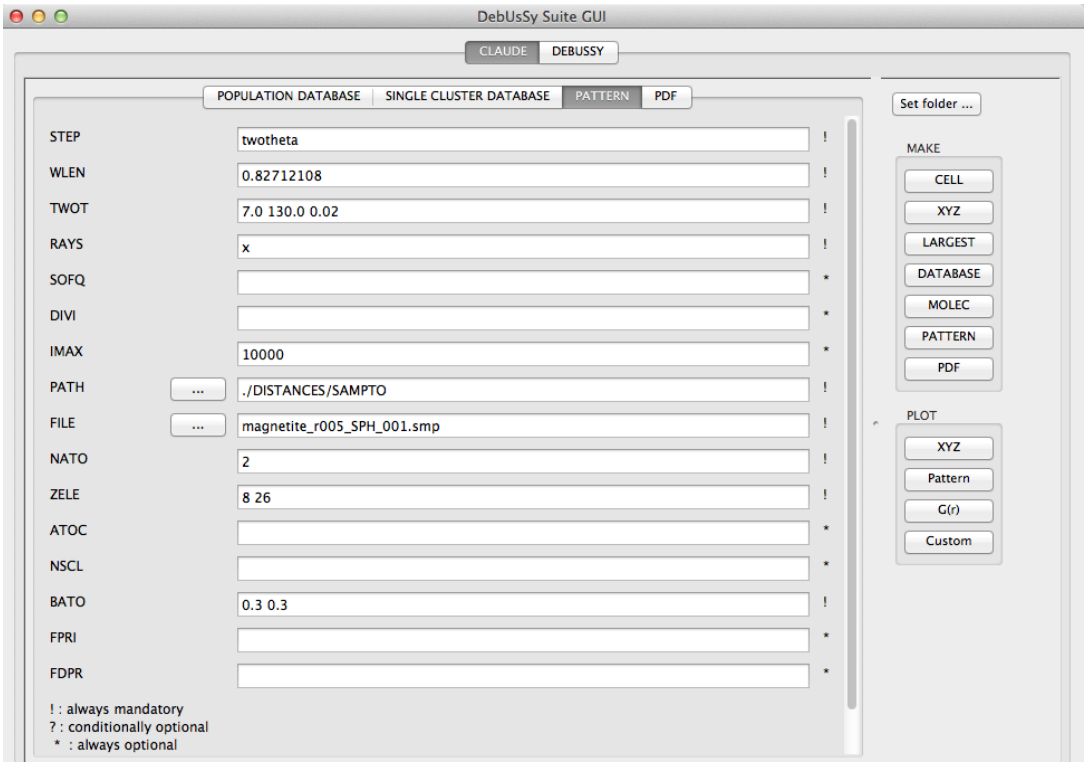
Move to the *CLAUDE_GUI* tab and by clicking on **Set Folder** select **./CLAUDE-Utilities/PATTERN/** working folder.
Select the **SINGLE CLUSTER DATABASE** tab and fill it by loading the *magnetite_r005_SPH.xyz* file from the working folder and giving some additional information about the cluster (reduced minimal distance, density and sampling information), as displayed below:



Once the **SINGLE CLUSTER DATABASE** tab is filled, use the **SAVE** button in order to save all the information in the *magnetite_sc.ddb* file (the file has the same extension but a slightly different content compared to the file used for building the database in the Example 1).

Once this file is created, it is possible to load it anytime (if required), by clicking on **LOAD .ddb.**, further modify and upload it through the **SAVE** button.
A single *.smp*/*.smp_INFO* couple of files is created by clicking on the **MOLEC** button of the **MAKE** vertical menu. An X-term is automatically opened and used by the GUI for displaying messages and output information.
The end of the single cluster database run is indicated by the following message ** JOB SMP SINGLE CLUSTER DONE! ** on the X-term. A new folder (**./DISTANCES/SAMPTO180A/**) is created, storing the files *magnetite_r005_SPH_001.smp* (containing the multiplicities of the sampled interatomic distances) and the associated *magnetite_r005_SPH_001.smp_INFO*.

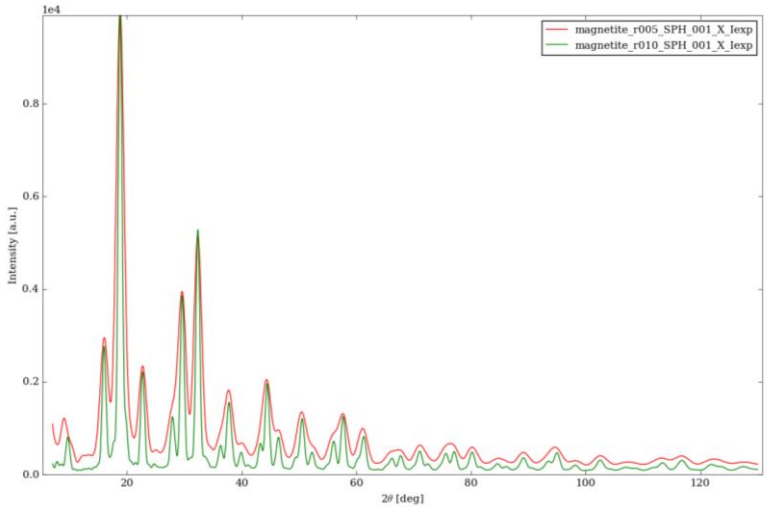
Select the **PATTERN** tab and use the **LOAD .inp** button for selecting the *diffractor.inp* file, provided in the current working folder. This file has ben already filled for this first example (*magnetite_r005_SPH*) and by loading it the following information are displayed on the **PATTERN** tab:



This *diffractor.inp file* can be loaded and modified if the user wants to run the other *.xyz* files. Once modified, the file has to be saved through the **SAVE** button.
The single DSE pattern calculation is computed by clicking on the **PATTERN** button of the **MAKE** vertical menu. An X-term is automatically opened and used by the GUI for displaying messages and output information.
The end of the run is indicated by the following message ** JOB PATTERN DONE! ** on the X-term and the *magnetite_r005_SPH_001_X_Iexp.tqi* file is created.

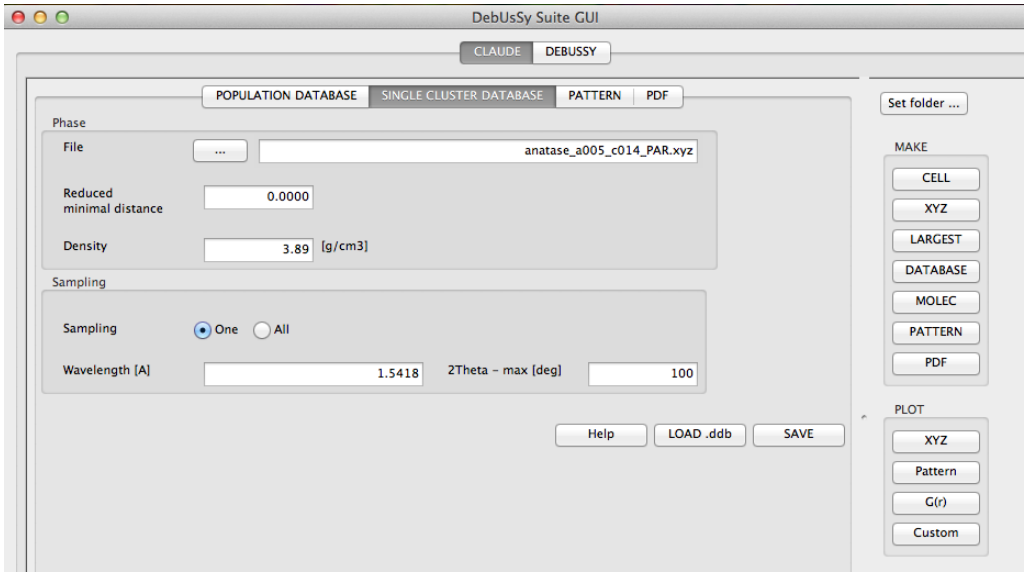
The same sequence of operations can be carried on in order to compute the X-ray powder pattern of the other supplied magnetite cluster. Firstly, select the *magnetite_r010_SPH.xyz* file in the **SINGLE CLUSTER DATABASE** tab, **SAVE** the edited *magnetite_sc.ddb* and run the **MOLEC** option of the **MAKE** vertical menu. Then, select the *magnetite_r010_SPH_001.smp* file in the **PATTERN** tab, **SAVE** the edited *diffractor.inp* file and run the **PATTERN** option of the **MAKE** vertical menu.

The two DSE patterns (*magnetite_r005_SPH_001_X_Iexp.tqi* and *magnetite_r010_SPH_001_X_Iexp.tqi*) can be simultaneously selected and visualized trough the **PATTERN** button of the **PLOT** vertical menu (see the picture below):



DSE simulation of a single anatase cluster

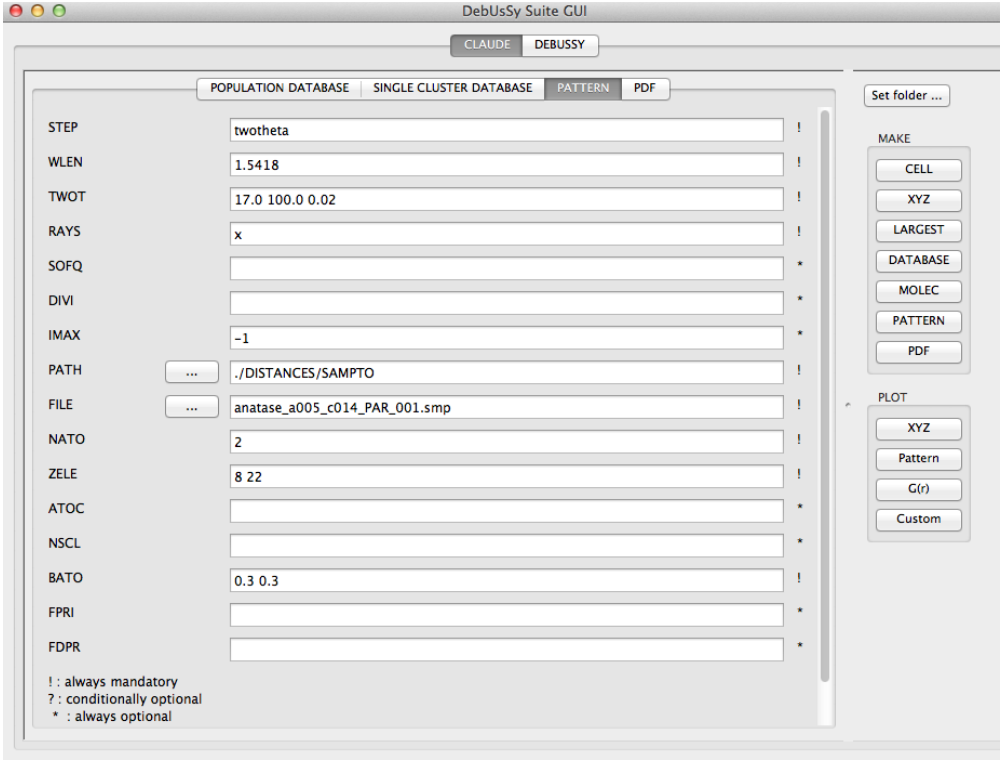
Move to the *CLAUDE_GUI* tab and by clicking on **Set Folder** select **./CLAUDE-Utilities/PATTERN/** working folder.
Select the **SINGLE CLUSTER DATABASE** tab and fill it by loading the *anatase_a005_c014_PAR.xyz* file from the working folder and giving some additional information about the cluster (reduced minimal distance, density and sampling information), as displayed below:



Once the **SINGLE CLUSTER DATABASE** tab is filled, use the **SAVE** button in order to save all the information in the *anatase_sc.ddb* file.

Once this file is created, it is possible to load it anytime (if required), by clicking on **LOAD .ddb.**, further modify and upload it through the **SAVE** button.
Clicking on the **MOLEC** button of the **MAKE** vertical menu; once the message ** JOB SMP SINGLE CLUSTER DONE! ** on the X-term is displayed, the new folder (**./DISTANCES/SAMPTO390A/**) has been created, storing the files *anatase_a005_c014_PAR_001.smp* (containing the multiplicities of the sampled interatomic distances) and the associated *anatase_a005_c014_PAR_001.smp_INFO*.

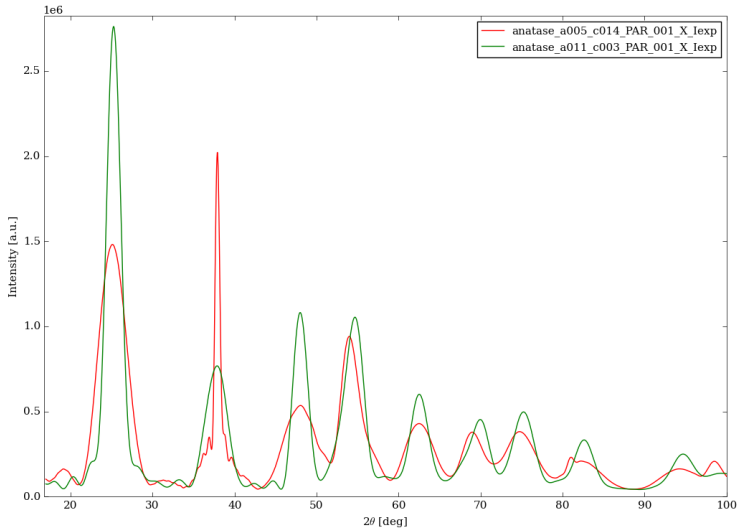
Select the **PATTERN** tab and use the **LOAD .inp** button for selecting the existing *diffractor.inp* file (the one already used for the previous magnetite examples). Edit the **PATTERN** tab in order to provide the information for the new examples, as displayed below



Once filled, this file can be saved through the **SAVE** button.
The single DSE pattern calculation can be computed by clicking on the **PATTERN** button of the **MAKE** vertical menu. The end of the run is indicated by the following message ** JOB PATTERN DONE! ** on the X-term and the *anatase_a005_c014_PAR_001_X_Iexp.tqi* file is created.

The same sequence of operations can be carried on in order to compute the X-ray powder pattern of the other supplied anatase cluster. Firstly, select the *anatase_a011_c003_PAR.xyz* file in the **SINGLE CLUSTER DATABASE** tab, **SAVE** the edited *anatase_sc.ddb* and run the **MOLEC** option of the **MAKE** vertical menu. Then, select the *anatase_a011_c003_PAR_001.smp* file in the **PATTERN** tab, **SAVE** the edited *diffractor.inp* file and run the **PATTERN** option of the **MAKE** vertical menu.

The two DSE patterns (*anatase_a005_c014_PAR_001_X_Iexp.tqi* and anatase_*a011_c003_PAR_001_X_Iexp.tqi*) can be simultaneously selected and visualized trough the **PATTERN** button of the **PLOT** vertical menu, as shown in the picture below:



EXAMPLE 4: *G(r)* calculation

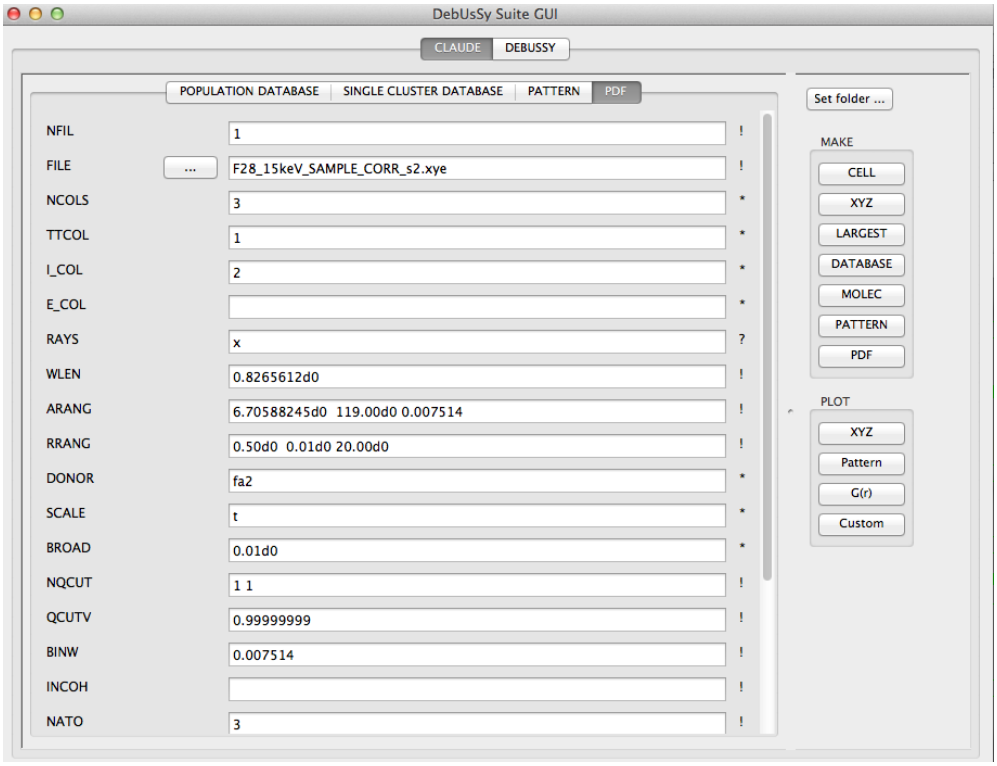
(working folder: ./**TUTORIAL/CLAUDE-Utilities/PDF**)

Overview

The aim of this example is computing the reduced *G(r)* function of the of synchrotron data collected on the two samples used for the Example 1 of this tutorial: *F28_15keV_SAMPLE_CORR_s2.xye* and (the iron oxy-hydroxide) *F23_15keV_SAMPLE_CORR_s2.xye*.

Pair Correlation Function calculation

Move to the *CLAUDE_GUI* tab and by clicking on **Set Folder** select **./CLAUDE-Utilities/PDF/** working folder.
Select the **PDF** tab and use the **LOAD .inp** button for loading the *dopdf.inp* input file from the current working folder; this file contains the necessary information for computing the reduced *G(r)* of the provided data, as displayed below:



The *G(r)* calculation is computed by clicking on the **PDF** button of the **MAKE** vertical menu. An X-term is automatically opened and used by the GUI for displaying messages and output information.
The end of the run is indicated by the following message ** JOB PAIR CORRELATION DISTRIBUTION DONE! ** on the X-term and the *F28_15keV_SAMPLE_CORR_s2.rpdfn* file is created.
The same operations can be carried on in order to compute the reduced *G(r)* of the iron oxy-hydroxide experimental pattern (*F23_15keV_SAMPLE_CORR_s2.xye*), by selecting the new file in the **PDF** tab, saving the edited *dopdf.inp* using the **SAVE** button and launching again the same calculation.
The two *G(r)'s* (*F28_15keV_SAMPLE_CORR_s2.rpdfn* and *F23_15keV_SAMPLE_CORR_s2.rpdfn*) can be simultaneously selected and visualized trough the **G(r)** button of the **PLOT** vertical menu, as shown below: