

Discus 3D- Δ PDF Tutorial

All examples presented here are based on 2D structures. This calculates faster and is easier to visualise for demonstration purposes but at the same time illustrates all the features that would also be observed in more complicated 3D structures.

Task 1: Thermal correlations

In this example we want to demonstrate what correlated thermal motion could look like in a diffuse scattering pattern and in the corresponding 2D- Δ PDF. A simple structure of 50x50 Cu atoms on a primitive lattice is build. By default, a B-value of 2.0 is assigned to each of the atoms.

The .cell file contains the structural information of the unit cell. Open the file crystal.cell in the folder 2DPDF_Thermal. You should see the following information:

```
title primitive cubic
spcgr Pm-3m
cell 5.00 5.00 5.00 90.00 90.00 90.00
atoms
cu 0.000 0.0000 0.0000 2.0
```

The first line specifies a title, in the second line the space group symbol is given. The third line specifies the lattice parameters (a, b, c, α , β , γ). For simplicity we have a cubic unit cell here with a lattice constant $a = 5 \text{ \AA}$. Line 4 specifies that now a list of atoms in the asymmetric unit will follow. Line 5 (and for more complex structures all the following lines) specify the atoms in the asymmetric unit. Here we have one Cu atom located on 0,0,0 with a thermal B-value of 2.0. Note that in the $Pm-3m$ space group this is a special position and there are no further symmetry equivalent atoms in the unit cell.

Open the file 2DPDF_Thermal.mac in an editor. This file contains all the commands that are given to discuss. First a bit of book-keeping and input checking is done. We will highlight the most important commands in the following:

In line 49 the read-menu is entered and the structure file is read.

In line 61 the command `therm 2d` is executed. Here a 2D displacement for each atom is calculated that corresponds to a thermal displacement. The atoms are shifted/wiggled from their average positions.

Next in line 69 we enter the Monte Carlo menu. In line 74 – 77 vectors between neighbouring atoms are set:

```
set vec, 1, 1, 1, 1, 0, 0
```

This command specifies to create **vector number 1** from **site 1** in the unit cell to **site 1** in the unit cell in unit-cells that are separated by the lattice vector **1,0,0**.

In line 78 the 4 vectors we created are grouped into a neighbourhood.

In line 79 we specify the target correlation. Here we set a spring potential from one Cu atom to another Cu. The minimum of the potential is if they are exactly separated by one lattice constant. The depth of the potential is given as an input-parameter for the macro.

Line 80 defines the move that we are allowed to make. Here atoms are allowed to swap their displacements.

In line 82 to 84 the parameters for the Monte Carlo simulation are set. We run 200*
#Atoms in the Crystal cycles and produce an output on the screen every 10*#Atoms in the
crystal cycles. The temperature is an input-parameter and specifies how many “bad” moves
we allow.

The Monte Carlo Simulation is started with the command run in line 87.

In line 91 we call the macro fourier.mac which calculates the Fourier transform and 3DPDF
for us.

All that is left in the macro is some structure analysis and the call of the sub-program kuplot
which plots the result.

To start the simulation and observe the diffuse scattering and the 2D- Δ PDFs start
discus_suite and navigate to the Tutorial folder. Then type

@2DPDF_Thermal.mac 100, 2.0

And hit enter. This starts the simulation. The parameters 100 specify the depth of the spring
potential and 2.0 specifies the temperature for the Monte Carlo simulation.

The final kuplot window will show you the diffuse scattering, the Cu-Cu bond length
distribution for the first neighbours and the 2D- Δ PDF. The Cu-Cu bond length in blue is
before sorting, red after the sorting for the structure that we calculated the Fourier
transform for.

Try changing the temperature and the depth of the potential and observe the changes to
the graphs that you see. In the 2D- Δ PDF pay special attention to the $\langle 1\ 0\ 0 \rangle$ neighbours.
What changes if you put a negative potential depth? What does this correspond to in terms
of interactions of neighbouring atoms?

Task 2: Occupation disorder

In this example we want to demonstrate what correlated occupation disorder could look like
in a diffuse scattering pattern and in the corresponding 2D- Δ PDF. A simple structure of
100x100 atoms on a primitive lattice is build. In contrast to task 1, now a certain percentage
of Cu atoms is exchanged for Au atoms.

Open 2DPDF_occ.mac. In this macro a lot of book-keeping is done. The structure is read in
line 63 in the same way as is done in the first example.

Then in line 65 part of the Cu atoms is replaced by Au atoms. The probability is one of the
input variables you can choose.

The Monte Carlo simulation is done in the macro sort.mac, which is called in line 66. When
you open this macro, you will see that in the Monte Carlo menu, vectors and neighbours are
specified in a similar fashion to the first example. The main difference here is the “mode”
and the targets. Mode specifies the move that the Monte Carlo simulation is allowed to do.
Here this is called “swchem”, which means switch the chemistry. In an attempted move the
chemistry of two atoms is swapped and evaluated whether the new correlations now better
comply with the specified targets. The targets that are specified here are chemical
correlations, indicated by the keyword “corr” in the target specification.

After the Monte Carlo simulation is finished the Fourier transform and the 2D-PDF are
calculated in the macro fourier.mac and the correlations are analysed.

To start the simulation and observe the diffuse scattering and the 2D- Δ PDFs start `discus_suite` and navigate to the Tutorial folder. Then type
`@2DPDF_occ.mac 0.50, -0.50, -0.50, 0.45, 0.45, 1.5`
 and hit enter. This starts the simulation. The parameters specify the composition (here 50 % Cu and 50 % Au), the correlations in $\langle 1\ 0\ 0 \rangle$, $\langle 0\ 1\ 0 \rangle$, $\langle 1\ 1\ 0 \rangle$ and $\langle -1\ 1\ 0 \rangle$ direction and the temperature (here 1.5) of the Monte Carlo simulation.
 The final `kuplot` window will show you the diffuse scattering, a visualisation of the structure and the 2D- Δ PDF.
 Try changing the temperature and correlations and observe the changes to the graphs that you see. In the 2D- Δ PDF pay special attention to the neighbours that are specified in the correlations. What changes if you change the sign of a certain correlation? What happens in the 2D- Δ PDF if you put certain correlations to 0?

Suggested parameter combinations are:

```
@2DPDF_occ.mac 0.50, 0.50, -0.50, -0.45, -0.45, 1.5      ! Stripes || x
@2DPDF_occ.mac 0.50, -0.50, 0.50, -0.45, -0.45, 1.5      ! Stripes || y
@2DPDF_occ.mac 0.50, -0.50, -0.50, 0.65, -0.65, 1.5      ! Stripes || [1 1 0]
@2DPDF_occ.mac 0.50, -0.50, -0.50, 0.45, 0.45, 1.5      ! Chessboard
@2DPDF_occ.mac 0.50, 0.50, 0.50, 0.45, 0.45, 1.5      ! Pure domains
@2DPDF_occ.mac 0.50, -0.30, 0.30, 0.25, -0.25, 1.5      ! Inclined stripes
@2DPDF_occ.mac 0.20, 0.80, 0.80, -0.90, -0.90, 1.5      ! Inclined stripes
```

Task 3: Atomic size effect

In the previous exercise we generated chemical short-range order in a structure. Most of the time this chemical short-range order will be accompanied by a size effect relaxation. “Larger” atoms will be separated by greater distances than “smaller” atoms.

In this example we want to demonstrate what the atomic size effect could look like in a diffuse scattering pattern and in the corresponding 2D- Δ PDF. A simple structure of 50x50 atoms on a primitive lattice is build. Similar to task 2 we can specify the first neighbour occupation correlation. For simplicity we only specify the $\langle 100 \rangle$ correlation. We can also specify a relative relaxation for the atomic displacements.

Open `2DPDF_sizee.mac`. As in the previous examples, first a lot of book-keeping is done. The structure is read in line 62 in the same way as is done in the first two examples. Then in line 65 part of the Cu atoms is replaced by Au atoms. For simplicity we fixed the probability here to 0.5.

In this example two Monte Carlo simulations are run. The menu is entered in line 82. First, we define interatomic vectors and neighbours in a similar fashion to the first example. The first cycle applies the “swchem” move and has as a target occupation correlations. (See lines 92 and 93).

After the first Monte Carlo simulation we reset all the previously set parameters (line 100) and setup a second simulation that has the same neighbours but now is allowed to move the atoms. Here the targets are set to Lennard-Jones potentials. As we want different bond length for Au-Au, Au-Cu and Cu-Cu pairs we need to specify three different targets: one for each bond length. This time the “mode” of the Monte Carlo simulation is “shift”. In every try

an atom is shifted by a small amount and then it is evaluated whether the targets for the bond lengths are better achieved.

After the Monte Carlo simulation is finished the Fourier transform and the 2D-PDF are calculated in the macro `fourier.mac` (line 126) and the correlations are analysed.

To start the simulation and observe the diffuse scattering and the 2D- Δ PDFs start `discus_suite` and navigate to the Tutorial folder. Then type

```
@2DPDF_size.mac 0.0, 0.05, 2.0
```

And hit enter. This starts the simulation. The parameter 0.0 specifies the occupation correlation (in the first try we want a random distribution, hence 0 correlation). The second parameter specifies the relative lattice relaxation, i.e. the target for the Cu-Cu bond length is $0.95 \cdot \text{lat}[1]$, while the target for the Au-Au bond length is $1.05 \cdot \text{lat}[1]$ and mixed bonds prefer the average $\text{lat}[1]$ distance. The last parameter again specifies the temperature of the Monte Carlo simulation.

The final `kuplot` window will show you the diffuse scattering, the Cu-Cu, Au-Au and Cu-Au bond length distributions for the first neighbours and the 2D- Δ PDF.

Try changing the relative relaxation from positive to negative and observe what changes in the diffuse scattering and in the 2D- Δ PDF? Try adding a chemical correlation, what changes, which of the two effects is the dominating effect, the relaxation or the chemical ordering?