

8. Nanostructures - C60 Refinement

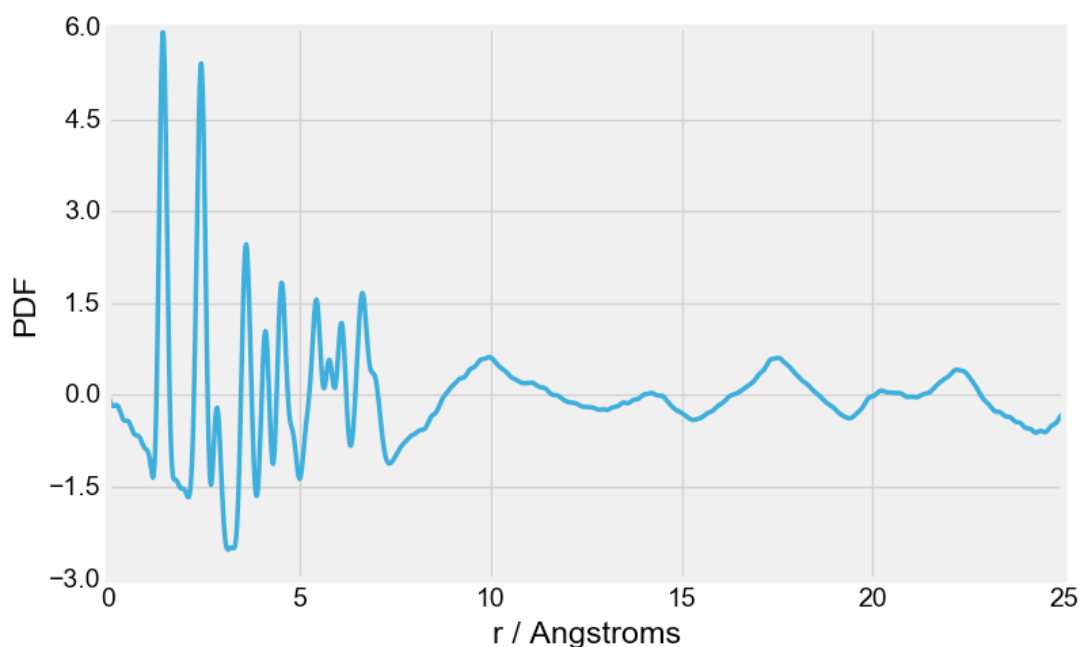
Overview

In this tutorial we will look more closely at some of the ways of fitting nanostructured materials, in this case we will be looking at the refinement of a model of C60.

Required Files

File	Description
XPDF_C60.xy	PDF of C60 collected on I15-1 at room temperature
C60_Fm-3.cif	Rough starting point for Fm-3 ordered structure of C60

Tutorial Instructions



1. Above is an image of the PDF of buckminsterfullerene, C60. It is often held up as an excellent example of what a PDF looks like, as it comes from a material that most scientists can picture, and contains some interesting features. It can roughly be described as consisting of a low-r region with sharp peaks from the intramolecular correlations; and a high-r region with broader features from the intermolecular correlations. The high-r region is broader because the balls undergo a tumbling disorder which removes any sharp correlations.
2. Open C60_Fm-3.cif in Vesta, and confirm that this *nearly* the ordered structure of C60: you should see that the arrangement of atoms is not quite right but the general connectivity is familiar.
3. Create a new refinement input file using "XPDF_C60.xy", refine it over the range 1 to 50 Å and add a refining dQ_damping.
 - a. Import the structure from C60_Fm-3.cif; refine some standard `beq` atomic displacement parameters along with the lattice parameter and atomic coordinates and a scale factor; and add a `view_structure` keyword

- b. Output the refined structure using 3.Phase information > outputs > output .CIF file `Out_CIF_STR(C60_Fm-3_refined.cif)` to save the refined structure into a new CIF file. Note, this CIF file will be updated with the refined structure, regardless of whether you update the input file.
- Run the refinement, and click yes when prompted to update the input file. The fit should be underwhelming, because we're not giving topas any information about the disorder, and not allowing it any scope for introducing any itself. However, although the fit would indicate we have not got the correct model, if we compare the starting and refined structures in Vesta, you should see that this refinement has significantly improved the look of the structure.
 - Since we have a PDF which seems to show some r-dependent broadening, lets try and employ some of our r-dependent `beq` function (beq spherical with low r cutoff) we used in the tutorial on correlated motion.
Use `beq_rcut_rlo_spherical(!rcut,2,beqcut,0.5,rlo,3.5,beqlo,0.7,beqhi,1.5,radius,5)` for all three sites: there is no reason to allow the three sites to have different `beq` values since they are all structurally equivalent if not symmetrically so.
 - Run the refinement again - the fit should be a lot better. So is this a good model? Are there any discrepancies between the calculated and observed PDFs? What does the cumulative Chi2 show? What could be the issue with this model?
 - There is good agreement between the observed and calculated PDFs at very low-r and at high-r; but there are some discrepancies around ~6 Å. This is because this region of the PDF contains both intra- and inter-molecular correlations. Nothing in the model makes any distinction between these correlations, so in the calculated PDF they have the same width, even though in this region intra-molecular correlations should be sharp (because of the rigidity of the molecular unit); and the inter-molecular correlations should be broadened (because of the tumbling motion of the balls). We need to build this distinction into our model to enable us to model these effects correctly. We do this by combining two models: one to represent the inter-molecular correlations; and a separate model of an isolated bucky ball to give us the intra-molecular correlations.
 - We'll use the existing model we have for the inter-molecular structure model. Revert the structure to simple `beq` atomic displacement parameters, and give the phase a sensible name.
 - To build an isolated bucky ball, we'll need to take the existing structure we have and remove the symmetry which creates the neighbouring molecules.
 - Load the refined cif into Vesta.
 - Remove the symmetry by clicking Edit > Edit Data > Unit Cell > Remove Symmetry. Once you click apply, there should be 240 atoms in the model in the Structure Parameters tab.
 - To make it easier to see what's happening, we'll also move a ball from the corner of the cell to the centre: under the Unit Cell tab click Transform and apply an origin shift of (0.5, 0.5, 0.5). You should now have a ball at the centre of the unit cell.
 - Hide all atoms which are not part of this central ball by selecting them using the select tool () and pressing backspace. Once you have only 60 atoms on display, export the coordinates of these sites to an .xtl file using File > Export Data.
 - In topas, create a new `str` by copying the long-range one from above. Give it a sensible name, change the space group to P1, force this `str` to have the same lattice parameter as the long-range structure, and remove the three existing sites. Open the xtl file in jEdit and copy just the coordinates into this new `str` block, and make them all sites by adding the necessary keywords (Hint: using Ctrl+Click and drag allows you to write across multiple lines simultaneously!)
 - All of these carbon atoms should have the same `beq` atomic displacement parameters. Make sure you use a different name from `beq` values for the long-range structure. - Topas will still find some correlations between this ball and the one at the centre of the neighbouring unit cell unless we force it not to. We do this by applying a `scale_phase_X` keyword to force the scale of this `str` to be 0 beyond a certain value:

```

1 prm !rC60 7.3
2
3     scale_phase_X =
4         IF X > rC60 THEN
5             0
6         ELSE
7             1
8         ENDEF;

```

- Run the refinement. You should immediately see there is a problem at low-r. What is the cause of this?

12. We have excluded inter-molecular interactions from our intra-molecular isolated bucky ball (by removing neighbouring molecules and applying the `scale_phase_X`), but we have not excluded intra-molecular correlations from our broadened inter-molecular `str`. You can confirm this by highlighting this phase in the topas GUI and seeing that there are correlations all the way down to $r=0$. We need to play a trick to remove these intra-molecular correlations because we cannot have a structure without a molecule:
 - a. we add in a third phase and calculate the intra-molecular correlations for an isolated molecule which has the very high `beq` values and subtract this phase from the total fit.
 - b. To do this, make a copy of the isolated bucky ball `str`, but give it the same scale factor and thermal parameters as the higher symmetry inter-molecular `str`.
 - c. Then modify the `scale_phase_X` keyword tell topas to subtract this `str` rather than add it.
13. Run this refinement: you should get a relatively good fit. There are some minor discrepancies, and probably a displeasing discontinuity. Why does this step in the model appear? Can you get rid of it? What approximations have we made in constructing this model?
14. Although this fit is quite good given the approximations we have made, we have so far not refined the structure of the isolated molecule because of the way we quickly used Vesta to create it.
 - a. Let's be knowingly reckless and try refining the molecular structure by throwing an `@` in front of the atomic coordinates of all but one of the atoms in the intra-molecular isolated molecule `str` (leave the negative correction `str` as it is, this needs to reflect the structure from the inter-molecular model).
 - b. Run this refinement, and you should see that this is not a useful way of refining the structure since the molecular structure explodes and yields a measurably worse fit to the data.
 - c. Obviously, do not press "yes" when prompted if you want this updated into your input file!
15. We proceed by generating the list of atoms using the symmetry operations explicitly, rather than by using the existing xtl input from Vesta. This way, we will define the location of one atom within the P1 structure, and ourselves utilise the symmetry operations of the space group to only produce the atoms located in the molecular unit we are interested in.
 - a. Start by identifying the Wyckoff positions of the three sites in the `Fm-3` phase. (Hint: use a similar methodology to tutorial 7)
 - b. Change the space group to P1, and then for each of the three carbons in the asymmetric unit, create a list of sites with the `x`, `y`, and `z` parameters defined as functions of the coordinates of the parent carbon in the broad inter-molecular `str`.
 - c. Rerun the refinement.