Rietveld Refinement

Tuesday, January 12, 2016   10:32 PM

pyGSAS (also called GSAS 2 or GSAS II)

Before doing refinement:
1. Download and install pyGSAS at https://advancedphotonsource.github.io/GSAS-II-tutorials/
2. (optional) Watch a few tutorials on that website
3. Make sure your XRD data has been saved in a format GSAS can read. Most work fine but I usually make sure to save my data as .raw, .fxye, or .gsas
4. Run a calibration on your instrument using a well-known standard. Use this to generate accurate UVW profile parameters and an updated zero value for your instrument. Save this information into an updated instrument parameter file.

Steps for actual refinement:
1. Open a new project and save it with a new name. Multiple windows are used in pyGSAS. The most important one is labeled Data Tree. This is the window that controls what other windows are displayed and what information is displayed on them.
2. Select Import->Powder Data-> and then select the format and file of your diffraction data. In our example problem you will need to refine multiple temperatures. Start with 25C heating.
3. pyGSAS will then automatically prompt you to input an instrument parameter file, do so. Note: you can use the same instrument parameter file for all temperatures so I placed it in the root folder rather than the individual temperature folder. Once complete you will now have a new entry in your Data Tree window labeled "PWDR…" where … is the name of the histogram you entered.
4. Select Data Tree->PWDR->Sample Parameters and make sure the "Diffractometer Type" is selected to the correct value (Bragg-Brentano vs Debye-Scherrer, for example. In the characterization lab most users have Bragg-Brentano as the common setting). Go to Data Tree->Instrument Parameters and make sure the radiation wavelength is correct. For in class example you need to change it from Cu to Co k alpha.
5. Unclick the histogram scale factor box and type in the correct goniometer radius. Other values like the sample displacement or transparency will be adjusted here later, if necessary.
6. Select Import->Phase->from cif file and then one by one select each phase you want to refine. It's best to add and refine each phase incrementally unless you are sure that all the phases are actually there. In the in class example we know for sure that both rock salt CoO and spinel Co3O4 are present so add them both. The cif files are in the root folder. Make sure that you click the box to associate this new phase with the histogram of interest. In this case we want "PWDR CoO25C.RAW" Once complete you will now have another new entry in your Data Tree window labeled "Phases" with two entries; CoO and Co3O4

7. Select Data Tree->Phases->CoO and then you'll notice that one of the other windows now pops up with a lot of information about the CoO phase. This window is entitled "Phase Data for CoO" and it has many tabs. Select the "Data" tab and then click the Phase Fraction refinement box. This allows us to refine the intensity of this specific phase. We need to do this for all phases so that we can eventually determine the phase fraction of all phases present.

8. We are almost ready for first refinement. But first we need to go to Data Tree->Controls and from the drop down next to Max Cycles select 10. This means we will do 10 iterations of the Refinement each time. You can do less or more but 10 is generally a good number.

9. Select Data Tree->Calculate->Refine. The refinement will run and when complete it displays the Rw (weighted residual) value. For 25C I get ~17.57% which is pretty good for a first run. It can be much larger on first run. When it asks to load new results select OK. If you ever do a refinement and it gets much worse you can also reject the changes.

10. In the Data Tree window left click first on one of the phases and then on PWDR item. We do this to have another window pop up and show the histogram along with our newly fitted pattern. (if you don't click phase first then the legend showing each phase and the small colored ticks for where we expect hkl reflections will not appear) Go to this new window labeled "GSAS II plots" and at the bottom of the window select the magnifying glass icon which lets you zoom in on certain regions. Zoom in on some of the main peaks. You'll see blue plus marks (experimental data points), red line (background), green lines (calculated pattern), teal line (difference between experimental and calculated pattern) and vertical colored ticks (red, blue etc indicating expected peak position for different phases) We notice a few things: first off, some peaks are being fit more or less ok but the shape of the peaks isn't yet right (need to be broader) and we also see that some peaks aren't fit at all.

11. Select Data Tree-> PWDR->background and a new window opens up. If the general shape of the background (not individual missing peaks) is wrong then you can add more terms to the Chebyschev polynomial but rarely is this necessary. Usually 3 is fine unless you have lots of amorphous material in your xrd scan. However, in this window we can also select "Peaks in background" which will let us assign certain peaks as background. We only do this if we have good reason too. You should never for a pattern to fit a peak where you expect a peak for one of your phases. In this case these peaks come from our substrate and we don't know what that phase is, so we will assign them to background. There are ~10 peaks that we need to assign so from the dropdown box select 10 Peaks in Background.

12. Once we select >0 for Peaks in Background a peak list appears where we need to manually input where these peaks are at. There are four parameters: pos (position), int (intensity), sig and gam (relate to shape of peak). Using the GSAS II Plots window note the 2theta position and intensity of the peaks we want to assign as background. Type in position accurately as possible (note: hovering cursor on plot will produce x,y value on very bottom of window) and then put in the intensity doubled, leave sig alone, and make gam 8. Click

the refine button for intensity and gam only, not position or sig. Run refinement.

13. Once you have very close fits for these background peaks you can turn on refine box for positions of background peaks to get slight improvement. No need to turn on sig.

14. Looking at our plot we now see that largest error is from our peak shape and peak location. We can fix peak location first. Select Data Tree->Phases->CoO and in the phase window that appears select the refine unit cell box. Do same for Co3O4.

15. Now we need to fix shape. Go to Data Tree->PWDR->Instrument Parameters and click the U refine box. This refers to the variables U, V, and W which are just mathematical coefficients for peak shape. Click refine and we see that our fit is getting very good. Go back and click the W box, leave V alone for this example. We are down below 5% error which indicates a pretty good fit (always aim for at least <10%). We can continue to turn on other variables where justified. CAUTION: do not turn on variables without having good reason. The fit might improve but without physical basis yielding incorrect refinement.

16. One last variable we should refine is the sample height error. Go to Data Tree->PWDR->Sample Parameters and click the sample displacement refinement box.

17. For this in class example this refinement is now ~~finished~~ abandoned. We need to record the phase fraction of our two phases. To do so go to the folder where you file is saved and look for the file name but with the .LST file extension. Open in notepad and scroll down to the phases section and near the top of each phase will be listed the Weight Fraction (tip: just search for "Weight fraction") the value that follows is the weight fraction, so multiply by 100% to convert to weight percent of each phase. I find that we have 40.5wt% CoO and 59.5wt% Co3O4. Lots and lots of other useful info is found in this .LST file. Lattice parameters, sample displacement etc. Most of this can be seen and read from data tree window, but weight fraction can only be read here (that I know of).

18. Repeat for other temperature

When doing subsequent scans where you'd like to copy work from first scan (background peaks, for example, we don't want to input those again.)

1. Take your file from the last scan and do save as to save a new project in the next folder (350C, instead of 25C)

2. We need to add our new histogram corresponding to a higher temperature. Go to Import->Powder Data and add the 350C.RAW file. Add the instrument parameter again. You now have two different PWDR items in the data tree.

3. Go to the PWDR item for the higher temperature histogram and set diffractometer type to Bragg-Brentano and radiation wavelength to Co as we did before.

4. Go to Data Tree->PWDR for the old scan (25C) and select Background. In the background window that appears click Command->Copy params and then it lets you choose to copy background, instrument etc over to new histogram. Do so. Now you should have your background peaks etc.

5. Select Data Tree -> data-> delete tree items and delete the old histogram, we no longer

need it.

6. Before we try and refine this we should turn off a bunch of variables or refinement will diverge. Turn off all refinement boxes except phase fraction for CoO and Co3O4, chebyschev background, and background peak position. All else is turned off for now. Refine and I get Rw around 14%.

7. We know the sample was heated from 25C to 350C so thermal expansion should have caused lattice parameters to expand. We can try to turn on lattice refine but it's possible that the parameters are so shifted that the refinement software cannot determine new position without a little help. You can test this. Take a look at GSAS II plot window and see where tick marks of phases are and where calculated peaks are. If calculated peak overlaps actual peak partly then refinement should find it. If it's so far off that there is no overlap the refinement often fails and you should first manually change lattice parameter before checking refine unit cell box.

8. Begin to turn on other refinement variables one by one. Thermal expansion moved sample up so Sample Displacement will change with increasing temperature. It's safer to turn on variables slowly doing a few at a time. Too much freedom and refinement can diverge and ruin your work.

To create a beautiful XRD Rietveld refinement plot, follow these steps
1. Download the [GSAS to XRD Rietveld.py file](#) from the repo.
2. Export your histogram from GSAS
   a. Export -> Powder data as -> Histogram csv file
   b. Delete out header rows from histogram csv file. This may be the first ~34 or so rows. Keep the row with "x, y_obs, weight, y_calc, y_bkg, Q" columns, but delete everything above.
3. Export your list of hkl peaks for all phases
   a. Export -> Export HKLs…
   b. Convert the d spacing to a list of Q values where peaks occur by using formula Q=2*pi/d
4. Merge list of Q values to histogram csv file
   a. Name column phase 1 and paste Q values for phase 1. Remember to paste values, not formulae.
   b. Name column phase 2 and paste Q values for phase 2
   c. Repeat as needed for other phases
   d. The file should look like this when you are done

e.

x	y_obs	weight	y_calc	y_bkg	Q	phase 1	phase 2
10.0019	80	0.0125	108.407	108.407	0.71109	1.804383	2.003369
10.016	86	0.011628	108.399	108.399	0.712095	2.46161	3.271487
10.0302	88	0.011364	108.391	108.391	0.7131	2.638874	3.83617
10.0444	75	0.013333	108.383	108.383	0.714105	2.900195	4.00675
10.0585	84	0.011905	108.375	108.375	0.71511	3.011049	4.626589
10.0727	88	0.011364	108.368	108.368	0.716114	3.196785	5.041714
10.0869	102	0.009804	108.36	108.36	0.717119	3.608765	
10.1011	83	0.012048	108.352	108.352	0.718124	3.92106	
10.1152	85	0.011765	108.344	108.344	0.719129	4.059823	
10.1294	104	0.009615	108.335	108.335	0.720134	4.145265	
10.1436	104	0.009615	108.327	108.327	0.721138	4.156233	
10.1577	98	0.010204	108.319	108.319	0.722143	4.47065	
10.1719	102	0.009804	108.311	108.311	0.723148	4.570653	
10.1861	108	0.009259	108.303	108.303	0.724153	4.699958	
10.2002	92	0.01087	108.295	108.295	0.725157	4.9232	
10.2144	95	0.010526	108.287	108.287	0.726162	5.068066	
10.2286	94	0.010638	108.279	108.279	0.727167	5.088094	
10.2427	85	0.011765	108.271	108.271	0.728171	5.262784	
10.2569	114	0.008772	108.263	108.263	0.729176	5.27777	
10.2711	83	0.012048	108.255	108.255	0.730181		
10.2853	96	0.010417	108.247	108.247	0.731185		
10.2994	82	0.012195	108.239	108.239	0.73219		
10.3136	109	0.009174	108.231	108.231	0.733195		
10.3278	101	0.009901	108.223	108.223	0.734199		
10.3419	107	0.009346	108.215	108.215	0.735204		
10.3561	105	0.009524	108.207	108.207	0.736209		
10.3703	80	0.0125	108.199	108.199	0.737213		
10.3844	130	0.007692	108.191	108.191	0.738218		
10.3986	90	0.011111	108.183	108.183	0.739222		
10.4128	84	0.011905	108.175	108.175	0.740227		
10.427	98	0.010204	108.167	108.167	0.741231		
10.4411	106	0.009434	108.159	108.159	0.742236		
10.4553	105	0.009524	108.15	108.15	0.74324		
10.4695	90	0.011111	108.142	108.142	0.744245		
10.4836	86	0.011628	108.134	108.134	0.745249		
10.4978	95	0.010526	108.126	108.126	0.746253		
10.512	88	0.011364	108.118	108.118	0.747258		

5. Rename the Histogram file "refinement.csv"
6. Open the GSAS to XRD Rietveld.py file in your favorite python IDE software. I recommend visual code studio.
7. Set the filename (line 13) to the correct path for your data
8. Set the savefig destination (line 91)
9. Update the names of the phases, plot limits on x, y axis etc so that final product looks nice.