Tutorial 3 - Correlated Motion

Overview

In this tutorial we will think about the correlated motion of atoms, how it affects the PDF, and try a few different approaches to how me might model this phenomena.

Required Files

Filename	Description
XPDF_Si_Qmax38.xy	NIST 640 Silicon, collected on I15-1
XPDF_Si_Qmax20.xy	NIST 640 Silicon, collected on I15-1
SrTiO3_NOMAD_Rebinned.xy	SrTiO3 collected on NOMAD at the SNS
SrTiO3.cif	Structure of SrTiO3

Instrument Parameters

Data File	Instrument Parameters
XPDF_Si_Qmax38.xy	Qmax = 38 Å^{-1}
XPDF_Si_Qmax20.xy	Qmax = 20 Å^{-1}
SrTiO3_NOMAD_Rebinned.xy	Qmax = 27 Å^{-1} dQ = 0.0530

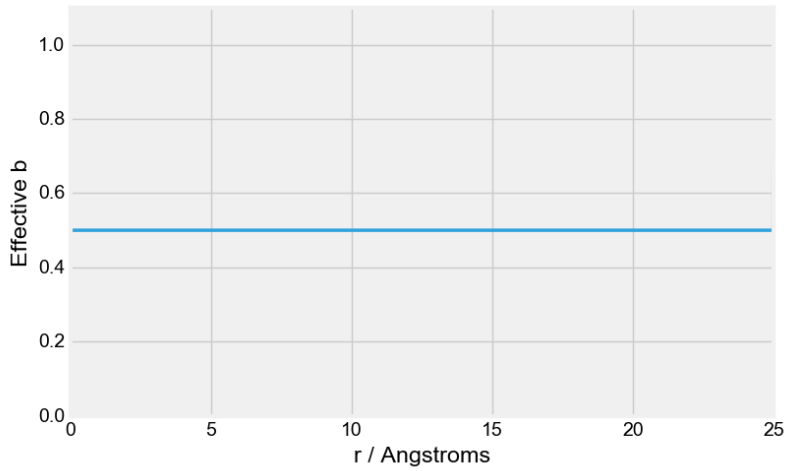
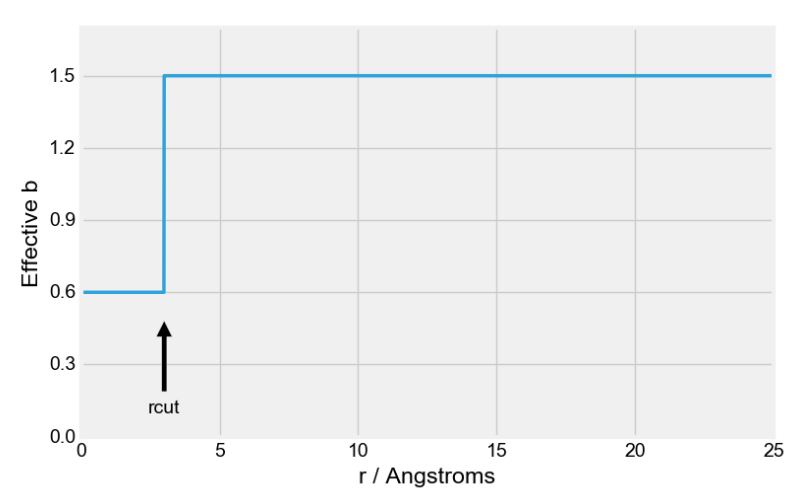
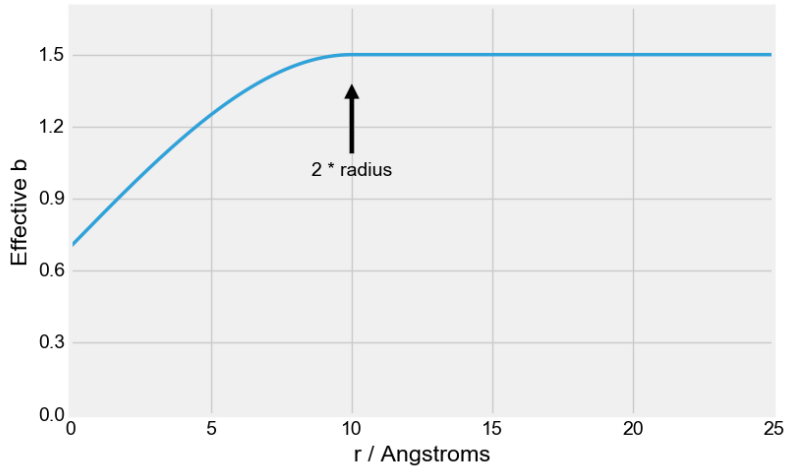
Tutorial Instructions

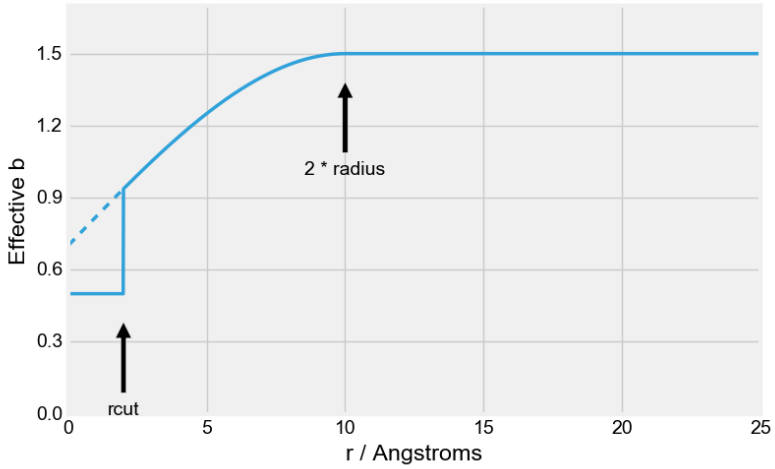
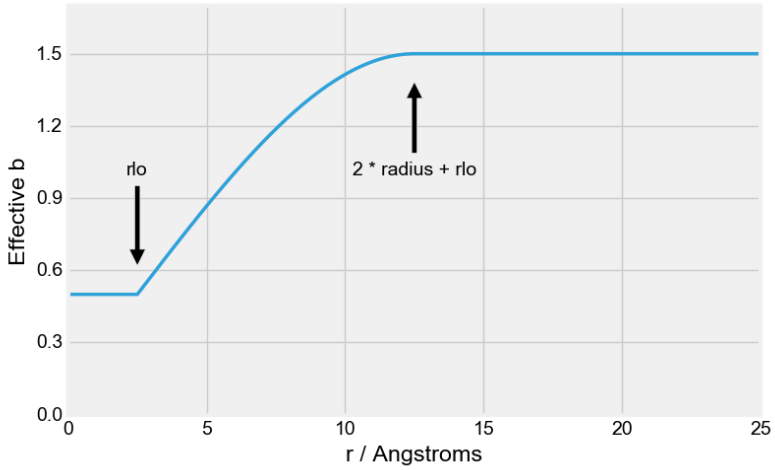
1. We'll start by looking at an X-ray PDF of Silicon, collected on I15-1. Create a new PDF refinement based on the above file XPDF_Si_Qmax38.xy. These are data collected to an extremely high Q, and therefore we can start to look at the peak widths and assume for the time being that they are sample-dominated rather than suffering from significant instrumental effects. Add `start_X 1` and `finish_X 50` to the **xdd** block, along with a `dQ_damping(dQ, 0.06)` starting guess for the dQ damping.
2. The silicon structure exhibits the space group $Fd\bar{3}m$, with a lattice parameter of 5.431144 Å, and consists of a single site at (0.125,0.125,0.125) in the second setting of the space group (hint: use `space_group Fd-3m:2`). We'll begin with an r-independent atomic displacement parameter **beq** as one would typically use in a topas Rietveld refinement:

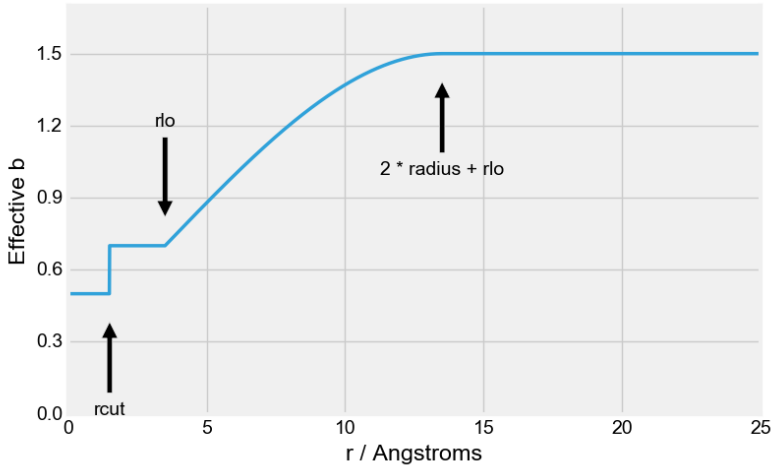
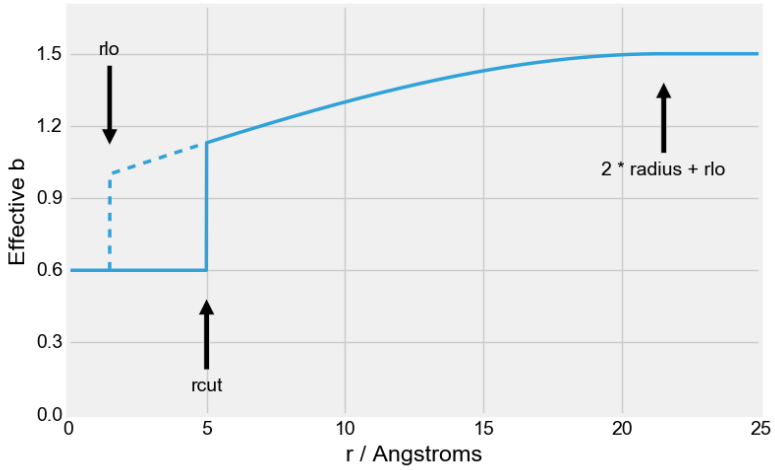
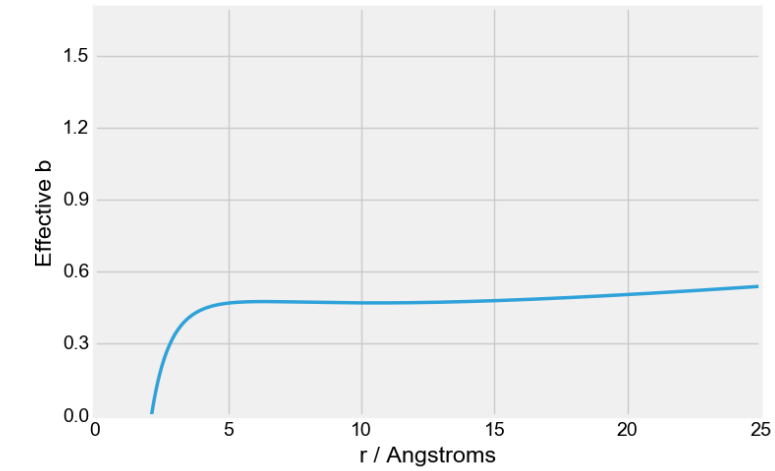
```
site Si    x 0.125    y 0.125      z 0.125      occ Si 1       beq @ 1
```

3. Send the file to topas and run the refinement. This instructs topas to calculate the width of every peak as if the distribution of correlation distances is independent of the correlation distance, and recall from the talks that this is therefore computed as $\mathrm{FWHM} = \sqrt{B_{iso,A} B_{iso,B} \ln(2)/\pi^2}$You should get a relatively poor fit; with the largest discrepancies at very low r; particularly on the peak at ~2.35 Å. The model you have refined has no ability to vary the peak width as a function of r, and therefore struggles when peaks are wider or narrower than others. Use the GUI to measure the widths of the first and second peaks in the PDF and confirm for yourself that this is the reason that the fit is poor in this region.
4. In the lectures, you were introduced to a number of functions that replace the `beq @ 1` section of the site. These functions then allow the effective **beq** to vary as a function of r. We will now try and estimate which of these functions we should apply and test our prediction.

Topas Function	Description	Image

`beq @ 0.5`	A flat beq that is independent of the distance. Familiar from Rietveld refinement. Not particularly good for refinements against PDF data.	
`beq_rcut(3,beqlo,0.6,beqhi,1.5)`	A step function with beq=beqlo below rcut, and beq=beqhi above. Good for materials which exhibit some specific local correlated motion, and no correlated motion over longer length scales. When using this function, rcut is not refinable.	
`beq_spherical(beqlo,0.7,beqhi,1.5,radius,5)`	A spherical function which starts at (r,beq)=(0,beqlo) and rises to (2*radius, beqhi). Good for materials which have some gradual dissipation of correlated motion as a function of r.	

`beq_rcut_spherical(!rcut,2,beqcut,0.5,beqlo,0.7,beqhi,1.5,radius,5)`	A spherical function as above, but with a special low-r region with a fixed (usually lower) effective beq. Good for materials that have some gradual dissipation of correlated motion, but have some low-r bonding which is particularly firm.	
`beq_rlo_spherical(!rlo,2.5,beqlo,0.5,beqhi,1.5,radius,5)`	A spherical function which begins at rlo, rather than at 0. Conceptually different to `beq_rcut_spherical` but often does not give similar result, as it allows a steeper $d\text{beq}/dr$ gradient for the same radius. Good for materials that have some longer-ranged gradual dissipation of correlated motion, such as molecular systems.	

`beq_rcut_rlo_spherical(!rcut,2,beqcut,0.5,rlo,3.5,beqlo,0.7,beqhi,1.5,radius,5)`	The combination of the above two functions; a spherical function starting at r0, with an rcut as well. Be aware that this function does allow rlo to refine lower than cut, which gives you the second figure on the right.	 
`beq_empirical(@, 0.20365,@, 0.01026,@, 2.20848,@,-5.67262)`	An empirical function of the form $\mathrm{beq} = a + br + c/r + d/r^2$, which just allows topas to fit to the data as well as it can given a polynomial to refine. For use when you have no logical idea of what the behaviour will be, or when your material is behaving very strangely. Beware when using this function that it can easily return non-realistic effective b eqs. When using, it is recommended that you plot the function to check on the effective beqs topas is using.	

What do you know about silicon as a material? Which of these functions do you think is going to be best for the silicon data we are modelling?

5. Alter your input file to test all of these **beq** functions, which should replace the **beq** `@ 1` on the site line

```
site Si    x 0.125    y 0.125      z 0.125      occ Si 1     beq_rcut(3,beqlo,0.6,beqhi,1.5)
```

For each, try to fix any low-r distances that you can by inspecting the data. If your function introduces a step, where should that step be? Note down the r_wp for each model: which is the best?

6. You should find that `beq_rcut_spherical` and `beq_rcut_rlo_spherical` give similar r_wp values. Since `beq_rcut_spherical` is a special case of `beq_rcut_rlo_spherical` with rlo=0, this should indicate to you that in these data, there is nothing to indicate that rlo should be anything other than 0. In your refinement using the more complex `beq_rcut_rlo_spherical` function, look at the value and the esd of the rlo parameter. When a refined parameter looks like this, it is an indication that there is nothing in the data driving this value.

7. All of this work has been performed assuming that the only contribution to the peak width is the distribution of the atomic correlations. We will now test this hypothesis by comparing this data collected to a Qmax of 38 to the same data but only Fourier transformed to a Qmax of 20. Extend your input file to make it easy to switch between the existing **xdd** and a new one for the above XPDF_Si_Qmax20.xy data, by including the two **xdd** blocks within **#ifdef #endif.** We'll also now add in the effect of the maximum Q, so we need to include a named variable Qmax which we can calculate this from. Include a **#define** statement to select which **xdd** you'd like to work with - we don't want topas to be trying to refine both at once, so comment out the #**define** Qmax38.

```
'#define Qmax38
 #define Qmax20

#ifdef Qmax38   xdd  XPDF_Si_Qmax38.xy   prm !Qmax 38 #endif
#ifdef Qmax20   xdd  XPDF_Si_Qmax20.xy   prm !Qmax 20 #endif
```

   Make sure you're also using the beq_rcut_spherical to define the r-dependent **beq**.
8. Run the refinement for both **xdd** blocks, and note down the refined values of beqcut, beqlo, beqhi, and radius for both. You should see that they differ. This is because although we have told topas that there is a variable called Qmax, we don't actually use it anywhere. We include the effect of the limited maximum Q by including the convolute_Qmax_Sinc(, Qmax) macro at the **xdd** level - i.e. between the **#ifdef xdd** lines and the **str** line in the inp file (this is good practice for later examples, for this refinement you may actually notice that it makes no difference where the convolute_Qmax_Sinc(, Qmax) is placed)
9. Compare the refined values once more. You should now find that the values are comparable.
10. We'll now look at a slightly more interesting example. Create a new inp file for SrTiO3_NOMAD_Rebinned.xy, making sure to add in the **pdf_data** and **neutron_data** keywords, since this is neutron PDF data; and add a dQ_damping and convolute_sinc_Qmax with the above values, and add **weighting** 1 and **start_X** 1 if they are not already present.
11. Insert a structure from SrTiO3.cif, refine the lattice parameter and **beq** values, and note down the **r_wp**.
12. Investigate the best **beq** function, or combination of **beq** functions, for this system. Remember to keep the spherical radii equal for each site by using the same variable name in each function. You should find that it is not necessary to use the most complex **beq** functions for this case, and you should find that some atoms require less complexity than others.
13. Are there any limitations to this method of treating correlated motion? Would you expect the correlated motion between the strontium cation and a neighbouring oxygen to be the same as that between neighbouring oxygens?

Conclusion

When trying to refine a structural model against some PDF data, it is important to include some ability for the model to exhibit r-dependent peak broadening that would be unexpected from the perspective of typical Rietveld refinement. However, from our knowledge of chemistry and physics we know that atoms do not vibrate in isolation but rather under the influence of neighbouring atoms and local crystal fields. Using the beq function approach allows us to model the relative atomic displacement between pairs of atoms at different distances. In theory one could consider modelling the peak widths not using this phenomenological approach, but from a theoretical understanding of lattice dynamics and phonons, and some research has been performed in this area. However, it should be stressed that there are likely better ways to access phonon information than from modelling of peak widths in a PDF.

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