NanoPDF64 fitting procedure example

Start with setting paths: Options->Settings

🚱 NanoPDF64	X	– 🗆 X
File Options Windows Tools	Help	
Stri Element properties	F8 Grain geometry	••• WELCOME ••• NanoPDF-64-ver: Nov 29 2016
m Settings	(sc) diamond like sphere cylinder	******* NEW STRUCTURE ********* diamond like number of nodes=378146
biatomic lattice	cubic I (bcc) O hcp P O cube O	center atoms
C 🗸 Se 🗸	cubic F (fcc) size (Å) 80 cubic latt. prm.(Å) 3.5667 N 22.43 l. v	C (x,y,z)=0,0,0 ideal grain
Euild Build	Settings	×
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RDH	Default data directory C:\Users\SG\Desktop\np64_11242	2016
	P. Experiment data directory C:\Users\SG\Desktop\np64_11242	2016
Always search center Fitting application C:\Users\SG\Desktop\np64_11242016\diffdatafit.exe		2016\diffdatafit.exe
ayor avor.	Image conversion script C:\Users\SG\Desktop\np64_11242	2016\cpng.bat
Bin width 0.0078125	Delete temporary files 🛛 Show diagram aft	ter loading from file 🔲
	Biatomic PDH in seperate files	
	×	Cancel 🗸 OK
		< ×

Now build your structure.

Choose: **monoatomic lattice**; Atom: **C**; **diamond like**; **sphere**; size **80Å** - actually this is the radius so the model is a 16nm sphere.

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File Options Windows Tools	Help		
Structure building			••• WELCOME •••
Atoms selection	Structure	Grain geometry	NanoPDF-64-ver.: Nov 29 2016
monoatomic lattice	cubic P (sc) 🔘 diamond like 🔘	sphere cylinder	diamond like number of noden=278146
biatomic lattice	cubic I (bcc) O hcp P O	cube 🔿	center atoms
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C 🗸 Se 🗸	cubic latt. prm (Å) 35667	N 22.421	(x,y,z)=0,0,0
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Calculations			C:\Users\SG\Desktop\np64_11292016\tmpFileRastr
			Rastop start
PDH RDH δ(r)	Diffraction pattern	G(r) PDF	
			RDH CALCULATIONS
	Show pattern	Show G(r)	stop time: 17:07:44
RDH			
	Parameters Radiation TDS	Start, step, W.F.	
	Angle(28) Q(1/Å)	Range, step (in Angs)	
Always search center	/ ligit(20) Q(1//)	start 0	
layer aver. 1	start 5 0.9788168	Start	
	stop 150 21.67532	stop 162.930275	
	step 0.1 0.01958255	step 0.01	
Bin width 0.001			
	Extrapolate to 0		
	Bo.	IAAA	

Click on **Build**. At this point you may already look at the model by choosing: **Tools->Rastop->Ideal**.

However, since the model contains over 370 000 atoms it will be quite a task for Rastop.

Switch to RDH tab.

🞲 NanoPDF64			— 🗆	×
File Options Windows Tools	Help			
Structure building Atoms selection monoatomic lattice	Structure cubic P (sc) O diamond like O s	rain geometry phere	••• WELCOME ••• NanoPDF-64-ver:: Nov 29 2016 ••••••• NEW STRUCTURE ••••••••• diamond like, number of nodes=378146	^
biatomic lattice	cubic I (bcc) O hcp P O	cube 🔾	center atoms	
	cubic F (fcc) 🔘	size (Å) 80	C	
	cubic latt. prm.(Å) 3.5667	N 22.43 I. 🗸	(x,y,z)=0,0,0	
Build	T Modify		RDH CALCULATIONS start time: 08:56:44 stop time: 08:56:44	
Calculations				
PDH RDH δ(r)	Diffraction pattern	G(r) PDF		
RDH	Show pattern	Show G(r)		
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Always search center	Angle(2θ) Q(1/Å)	Range, step (in Angs)		
	start 5 0.9788168	start 0		
layer aver.	stop 150 21.67532	stop 162.930275		
	step 0.1 0.01958255	step 0.01		
Bin width 0.001	Extrapolate to 0			
One Bin mode 🔽				
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Set **Bin width** to e.g. 0.001 – this is the accuracy of the interatomic distance calculation - and make sure that you are in the **One Bin mode**. Finally click on **RDH** button and press the **Plot** button to have a look at the histogram.

We are now ready to analyze the experimental data. Choose **Tools** \rightarrow **Fitting** or press **Ctrl-F**. Start with loading G(r) to be analyzed – use "DIA-UD280S.dat" that comes inside the package. This experimental G(r) was obtained from neutron diffraction data of nanocrystalline diamond

File Tools Windows		
Fitting Additional settings		
General settings General settings max iter 5 max conv. 0 File Data constraints Residual weights	Peak parameters Initial positions of peaks PDH/RDH from buffer PDH/RDH from file Gauss (PDH) Poly*Gauss (RDH) gaussian scale factor 0.0009 a/a, 1	
Baseline settings Off Sphere Poly 7 slope factor -0.0003 r fittable D/2 40 r From prev. fit From curr. fit Reset Show baseline	Reference model ** Thermal vibration model is ** Thermal vi	$\delta(r) = \Delta(r)/r$ Preview Preview $\int \Box = \int \Box = \Box =$
num. of iterations: 5, convergence: 0.70928102731	Release s.f., p.w.	Reset

To make sure the data are OK double click on the file name to display the data graph. Now go to **Additional settings** tab:

Fitting File Tools Windows		- 🗆 X		
Fitting Additional settings				
Actions of diffdatafit.exe program	Additional fitting parameters			
show diffdatafit window	eps. abs 1e-3	START		
show results in console window after calculations show diagonal of covariance matrix	ens rel 1e-3			
snow data using embedded diagram O always O in case of ht failure	method I M	IAA.		
hold visible console after calculations until keyboard hit				
save results to file resfile.txt				
Default actions before calculations		8/22-4/22/12		
Show script Don't start fitting		$O(r) = \Delta(r)/r$		
Default actions after calculations		Draviaw		
show diagram after fitting	epatter fitting	Preview		
add original data to diagram	I information about results			
plot error curve subplot separate window update s	tarting parameters after fitting			
✓ add baseline data to diagram δ(r) correct				
add peaks position to diagram points per	unit 51	L <u>C</u> iose		
Experiment data loaded from file: C:\Users\SG\Desktop\np64_11292016\DIA-UD280S.dat				
		>		

At this point important setting are: show diffdatafit window; show diagram after fitting; add original data to diagram and add baseline data to diagram. Go back to **Fitting** tab.



Choose: **Poly7**; **Gaussian const area**; **Poly*Gauss(RDH)**; set **max iter** between 5 and 10. Now we set the initial parameters of theoretical $G(\mathbf{r})$. **Slope factor** controls the slope of the baseline near "0". It should be negative and small. **D**/2 is a half of the particle size. **Scale factor** controls the height of the peaks in $G(\mathbf{r})$. Usually it is quite small. **a**/**a**₀ adjusts the lattice parameter and **peak width** is self explaining. Use **Preview** button to see if the starting parameters make sense.



Experimenta data are plotted in **green**. Baseline is **blue**. With **slope factor** you change the baseline slope near "0". With **D**/2 you change the point where the G(r) vanishes at large distance. Remember: it is the half of this distance! Theoretical G(r) is **red**. It is the sum of the baseline and all the peaks taken from the RDH histogram you calculated before. The height of the peaks in G(r) is controlled by **scale factor**. Play with **slope factor** and **scale factor** to get the starting theoretical curve reasonably close to experimental one in terms of intensities. Also check the peak positions - a/a_0 - and widths!

Zoom works by dragging the mouse with **Left** mouse button and **Ctrl** keyboard button pressed. Enlarged graph opens in a new window. You actually only zoom the X-axis. Y–scale is set automatically. If you want to change it press **Right** mouse button on the graph and select the appropriate option from the menu that appears.

Now close the graph windows and go back to Fitting window.

Fitting File Tools Windows		- 🗆 ×
Fitting Additional settings		
General settings max iter 5 max conv. 0 File Data constraints Residual weights from 1 to 79.992 max. value: 79.992 Reset Baseline settings Off Sphere Poly 7 slope factor -0.0003 rfttable D/2 40 From prev. fit From curr. fit Reset Show baseline	Peak parameters htial positions of peaks PDH/RDH from buffer PDH/RDH from file Show Reference model ** Thermal vibration model is ** POH calculation parameter atoms: 378146 bin width: 0.001 monoatomic: 1 bin mode: 1 <	START $ \begin{array}{c} \downarrow $
num. of iterations: 5, convergence: 0.7092810273	Release s.f., p.w. From curr. fit Reset	^ ~
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At this point it makes sense to switch to **Data constrains** and limit the range of the analyzed data e.g. disregard the data oscillations at the beginning.

Make the following parameters variable: **slope factor**, **scale factor**, **a/a**, **peak width**. It is done by checking **the boxes** next to the parameters' values. Make sure all other boxes are **unchecked**. Doubled boxes near some parameters have special meaning. If you clear the second box, a given parameter is decoupled for all peaks in G(r). If you e.g. decouple intensities, the relative heights of the peaks will not follow the structure geometry (actual distance multiplicity) but will be fitted independently. Usually the fitting procedure goes nuts with such setting. Make sure both boxes are checked for parameters to be varied.

In order to start least squares fitting click on "START".

The **console window** will appear showing the calculation progress. When it is over the result will be displayed in the **graph**.



At this point there exist two sets of parameters: those initially set and those calculated by least squares. The **Preview** button if pressed will still display the graph of the initial state, and the **Plot** button will display curves as fitted.

If you are happy with the result of the fit you may update the starting parameters by clicking two **From curr. fit** buttons:



It is important to remember that our software does not update parameters automatically. Other fitting programs do, which may confuse persons who frequently do least squares. **Don't forget to update parameters after each successful run!** If you work with demo data do it now! The button on the left updates just the **slope factor**, the one on the right all the rest, including **D**/2 which we don't fit at the moment.

The next step for the demo data is allowing the peak width to vary with distance in a linear manner. You do that by releasing the **pw.f.ratio**. Start fitting again. The match between the model and the data becomes better, but the shape of the baseline remains as that for a sphere. This is not the case for the demo data. Now you should release polynomial parameters **p1** to **p4** one by one, and each time do the fitting run and <u>update parameters!</u> If the result looks weird:



it's time to apply variable data weights.

The "peaks" at the end of G(r) are quite small and the least squares procedure basically ignores them. **Residual weights** if activated change the data weights in a linear manner, in the demo case from 1 at the data beginning to 1.8 at the data end.



The values are to be chosen by trial-and-error method. At the very last try to release **D**/2 parameter. The final fit should look like:



Zoom-in into the large distances part of the curve to check the fit quality.



In our case the analytical G(r) is composed of 1976 heavily overlapping Gaussian peaks. You may set the **add peaks position to diagram** checkbox in the **Additional setting** tab to see where they are:



This shows that what appears to be peaks in G(r) are actually just data oscillations which are quite nicely reproduced by analytical G(r).

Note the shape of the baseline! It does not look like that for a sphere which we begun with, but rather suggests elongated shapes – plenty of long interatomic distances with similarly low abundance. However TEM microscopy shows basically regular grains:



The reason for such discrepancy is still unclear for us.

The final fit parameters are shown in the image below.

