Automated fitting of G(r) in multiple finite size ranges

Example1

Determination of $\Delta r/r$ and fwhm(r) from experimental G(r).

The idea behind the procedure is the following. If the crystal lattice of a nanocrystal is not ideally periodic, and we believe it is not, peaks in G(r) will be slightly shifted from "ideal" positions. Also the peak widths will vary. In a typical G(r) only a few peaks at the very beginning may be resolved. Others heavily overlap and neither their widths nor positions cannot be individually determined. In order to overcome this limitation we divide the available data span into narrow ranges and fit G(r) in every range separately to get an average lattice parameter – *apparent lattice parameter* – *alp* – and an average peak width inside each range. From such data we try to learn about the actual atomic structure of nanocrystals.

We assume that you have already familiarized yourself with the fitting part by going through the first example. If certain parts of the procedure are not explicitly mentioned they "default" to what you have already done. Now let us begin with the main program window:

0	1 6	/			
🚱 NanoPDF64			-		×
File Options Windows Tools H	lelp				
monoatomic lattice biatomic lattice	ructure cubic P (sc) diamond like cubic I (bcc) hcp P cubic F (fcc) cubic latt. prm.(Å) 3.5667	Grain geometry sphere cylinder cube Size (Å) 80 N 22.43 L V	••• WELCOME ••• NanoPDF-64-ver:: Nov 29 2016 ******* NEW STRUCTURE ******** diamond like, number of nodes=378 center atoms index 0 C (x,y,z)=0,0,0 RDH CALCULATIONS start time: 2:59:02 PM stop time: 2:59:02 PM	146	^
Calculations					
PDH RDH δ(r)	Diffraction pattern	G(r) PDF			
RDH 3	Show pattern	Show G(r)			
	Parameters Radiation TDS	Start, step, W.F.			
Always search center	Angle(2θ) Q(1/Å) start 5 0.9788168 stop 150 21.67532	Range, step (in Angs) start 0 stop 162.930275 step 0.01			
Bin width 0.001 4 One Bin mode 🔽	step 0.1 0.01958255 Extrapolate to 0	Step 0.01			
	1 min				

Build 1 diamond sphere of 80A radius 2 and calculate RDF 3 for it. Make sure the "bin width" is small – try 0.0001 – and check that you are in "One bin mode" 4. Than go to **Tools** \rightarrow **Fitting**.

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eneral settings	Peak parameters		G		
max iter 1e1 max conv. 0	Initial positions of peaks	peak shape	Gaussian const area 🔍 🗸		START
ile Data constraints Residual weights	PDH/RDH from buffer PDH/RDH from file	Gauss (PDH)	Poly*Gauss (RDH)		
Dpen experiment file	Open PDH/RDH file	gaussian	9	î	Î.A.A.
::\Users\sg\Desktop\nppackage\DIA-UD280S.dat	Show	scale factor	0.00413631127		l. û.e
		a/a。	1.00021582 🗸 🗸		
Baseline settings	Reference model	peak width	0.140695897		δ(r)=∆(r)/r
Off Sphere Poly 7	** Thermal vibration model is ** PDH calculation parameter	· .			
slope factor -0.000162472666 Fittable	atoms: 378146	pw. fratio			Preview
	bin width: 0.001 monoatomic: 1	polynomial	- 7		
	bin mode: 1	p1	0 0		
From prev. fit From curr. fit Reset	< > ×	p2			
Show baseline 9					.
Show baseline		p3 _	0		<u>C</u> lose
		p4	•	~	

Load experimental G(r) 1, choose "Gaussian const. area" 2 and "Poly*Gauss(RDH)" 3. Set "scale factor", "a/a₀", "peak width" 4 and "slope factor" 5 to something reasonable and make those parameters fittable. Also set "D/2" to 40 but don't let it vary 6. Set to zero all the remaining parameters and don't let those to vary 7. If in doubt consult the picture above. Run a fit 8 to get some reasonable starting parameters. Remember to update the parameters by clicking on <u>two</u> "From curr. fit" 9 buttons.

Fitting File Tools Windows			– 🗆 ×
File Tools Windows Fitting Additional settings			
Actions of diffdatafit.exe program		Additional fitting parameters	
show diffdatafit window ignore fitting errors		eps. abs 1e-3	START
show results in console window after calculations show diagonal of co	ovariance matrix	eps. rel 1e-3	
show data using embedded diagram 💿 always 🔘 in case of fit failure	;		
hold visible console after calculations until keyboard hit		method LM 🗸	I.A.A.s
save results to file resfile.txt		Jacobian Numerical 🗸	
Default actions before calculations			δ(r)=∆(r)/r
Show script Don't start fitting Default actions after calculations			0(1)-2(1)/1
show diagram after fitting	short beep after t	fitting	Preview
✓ add original data to diagram	show full informa	ation about results	
plot error curve subplot separate window	update starting pa	arameters after fitting	
✓ add baseline data to diagram	δ(r) correction	0	
add peaks position to diagram	points per unit	51	<u>C</u> lose

Now we have to decide what to display during the fitting procedure. We are going to make several tens of quick fitting runs in a row and displaying all those console windows makes no sense. Therefore we want to clear the "show diffdatafit window" checkbox. 1 If you leave "show diagram after fitting" 2 checked graphical result of every fit will show up and you'll have to close all those windows one by one. On the other hand it'll give you a chance to examine the fit quality. If unchecked, you'll only see numbers. Both situations are described further down in the text.

Now select **Tools**→**Region fitting:**

Fitting					- 🗆 ×
Fin Region fitting Ctrl+F					
General settings	Peak parameters				
max iter 1er max conv. 0	Initial positions of peaks	peak shape	Gaussian const area 🗸 🗸		START
File Data constraints Residual weights	PDH/RDH from buffer	Gauss (PDH)	Poly*Gauss (RDH)		
Upen experiment file	PDH/RDH from file	gaussian		^	Î.A.A.s.
C:\Users\sg\Desktop\nppackage\DIA-UD280S.dat	Show	scale factor	0.00413631127 🗹 🗹		1.0.
		a/a。	1.00021582		
Baseline settings	Reference model	peak width	0.140695897		δ(r)=∆(r)/r
Off Sphere Poly 7	** Thermal vibration model is ** PDH calculation parameter	pw. fratio			
slope factor -0.000162472666 V fittable	atoms: 378146				Preview
D/2 40	bin width: 0.001 monoatomic: 1	polynomial			
	bin mode: 1	p1	•		
From prev. fit From curr. fit Reset	< >	p2	0		
Show baseline		р3 [0		<u>C</u> lose
		p4	•	~	
		Release s.f.	, p.w. 🔶		
			From curr. fit Reset		

A window appears to define ranges within which the fits we be executed automatically. They may be defined manually by using "Add row" 1 and defining "Xmin" 2 and "Xmax" 3 but we will do it in an organized manner.

File Tools Windov Fitting Additional set	WS							
Fitting Additional set								
	tings							
General settings			Deak narametere					
max iter 🍪 Fitlist	-	_					- 0	X ST
File	2 2 δ	(r) 232	<x> 1</x>					
	Xmin	Xmax	Xave	alp	alp/a₀-1	p.w.	Conv	
C:\User 1	0	79.992						
Baseline Off slop From pre	lelete row	Add row	Scanning list from 1 to 65	step 		8 rows	START	(r)/r w

Set the data limits: from 1 4 to 65Å 5. There are no peaks below 1, and peaks above 65 are so week that least squares get unstable. Now divide all data into a series of ranges 3Å long 6 shifted by 1Å 7 with respect to each other. Finally press "Add rows" 8 to execute.

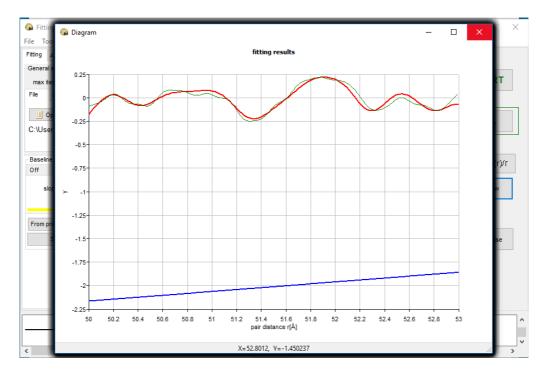
1								
🚳 Fitl	ist						_	×
8	δ 🔚 - 🖆	(r) 🔺 🗹						
No	Xmin	Xmax	Xave	alp	alp/a₀-′	1 p.w.	Conv	^
1	1	4	2.5					
2	2	5	3.5					
3	3	6	4.5					
4	4	7	5.5					
5	5	8	6.5					
6	6	9	7.5					
7	7	10	8.5					
8	8	11	9.5					
۹	٩	12	10.5					¥
			Scanning list				9	
4	Delete row	Add row	from 1	step	1	Add rows	START	
	Clear		to 65	width	3	Add fows	START	
	d		max. value					

The list gets filled as above. Start fitting **9**

Now depending on the choices you made in "Additional settings" you will either see the list getting filled by the fitted parameters:

Fitlis		δ(r) 🔺 📝	<x> 1</x>				- 0	×
No	Xmin	Xmax	Xave	alp	alp/a₀-1	p.w.	Conv	
В	15	18	16.5	3.56671E+0	2.8700E-6	1.4578E-1	7.3888E-2	
9	17	20	18.5	3.56739E+0	1.9220E-4	1.3669E-1	1.4767E-1	
10	19	22	20.5	3.56766E+0	2.6855E-4	1.4463E-1	8.0548E-2	
11	21	24	22.5	3.56738E+0	1.9174E-4	1.5347E-1	7.1365E-2	
12	23	26	24.5	3.56622E+0	-1.3372E-4	1.5629E-1	5.7823E-2	
13	25	28	26.5	3.56696E+0	7.2730E-5	1.5791E-1	1.9458E-2	
14	27	30	28.5	3.56780E+0	3.0930E-4	1.5833E-1	2.7589E-2	
15	29	32	30.5					
16	21	3/	32.5					
<u></u>	Delete row	Add row	Scanning list from 1 to 65 max, value	step	2 Add n	ows	ТОР	

or the graphs of the fitted curves appearing one after another:

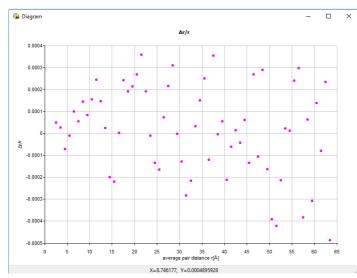


While closing all those windows – 62 in our case – you will have a chance to examine the fit quality.

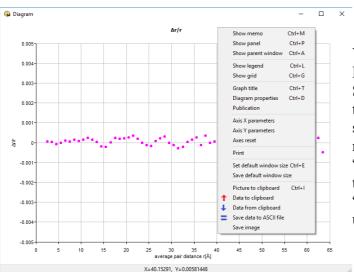
Underneath you will still find the fit results.

🚳 Fit	list						- 0	×
8	Έ - 🗄 δ	(r) 📥 🗹 🛛 <	x> 1					
No	Xmin	Xmax	Xave	alp	alp/a₀-1	p.w.	Conv	^
55	55	58	56.5	3.56776E+0	2.9758E-4	2.1052E-1	5.3345E-4	
56	56	59	57.5	3.56533E+0	-3.8323E-4	2.0387E-1	5.5026E-4	
57	57	60	58.5	3.56693E+0	6.3260E-5	2.3841E-1	5.9632E-4	
58	58	61	59.5	3.56560E+0	-3.0790E-4	2.2998E-1	7.8017E-4	
59	59	62	60.5	3.56720E+0	1.3905E-4	2.1797E-1	1.0942E-3	
60	60	63	61.5	3.56642E+0	-7.8850E-5	2.2770E-1	8.2380E-4	
61	61	64	62.5	3.56754E+0	2.3446E-4	2.3954E-1	4.8245E-4	
62	62	65	63.5	3.56496E+0	-4.8709E-4	2.3532E-1	3.6464E-4	
								~
<u> </u>	Delete row	Add row	Scanning list from 1 to 65 max. value	stepwidth	1 Add ro	ws ST	ART	

Press $\delta(r)$ 1 button to see the how the fitted lattice parameters deviate from the initial value.

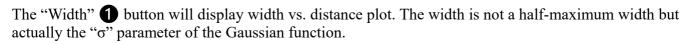


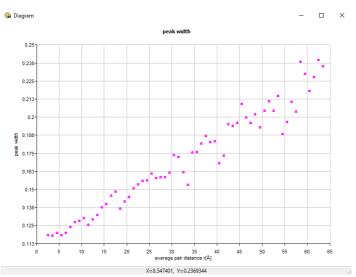
The values look quite scattered but the scatter is actually below 0.1%. It's just statistical noise.



You may change the Y-scale to see it better. Click Righ mouse button on the graph. A menu appears. Select "Axis Y parameters", and change the limits to: min: -0.005 max: 0.005 step : 0.001. Now you see that the line is essentially flat. Other useful menu items are: "Data to clipboard" and "Save data to ASCII". This is the way to export the data from the plot to external file. "Save image" and "Picture to clipboard" let you use the graph as-is.

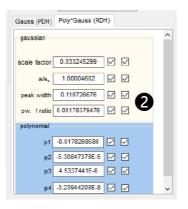






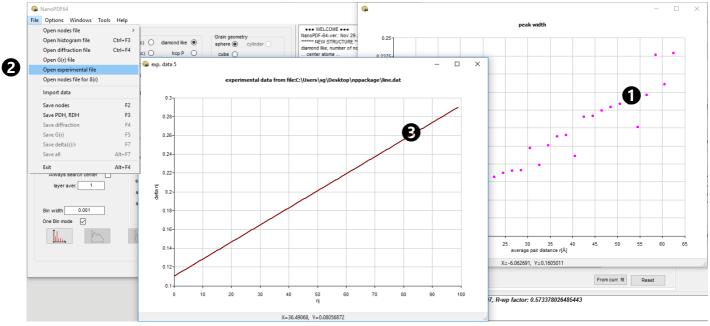
The dependence looks linear.

We may now compare it to what was obtained in the first fitting example during fitting the entire G(r) curve at once:

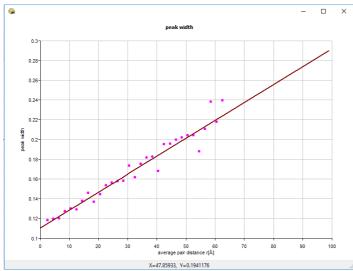


The procedure gave linear dependence with intercept 0.1107 and slope 0.001838 A data file with exactly such line: "line.dat" is placed inside the NanoPDF64 directory. In order to overlay it on top of the fit results do the following:

Move the plot of "peak width" ① aside, but don't close it. Don't close other windows either. Move them away to dig out the main window of NanoPDF64. Select File \rightarrow Open experimental file ② and load "line.dat".



Plot of the line appears. Press and hold Shift on the keyboard. Pick the line **3** with the mouse, drag it to plot **1** and drop it there. A combined plot appears:



This operation actually copies the data, not just the line!!!

The results of the complete G(r) fitting and of the scanning of G(r) by small ranges appear to be quite similar!