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NanoPDF64

program manual

v.1.1 (2016)

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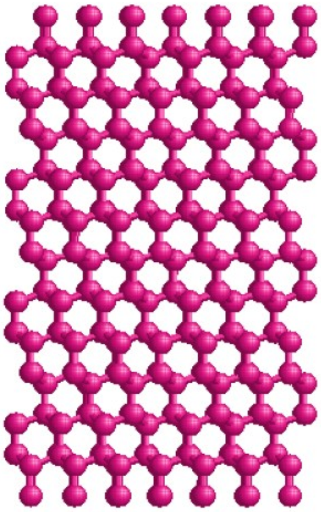
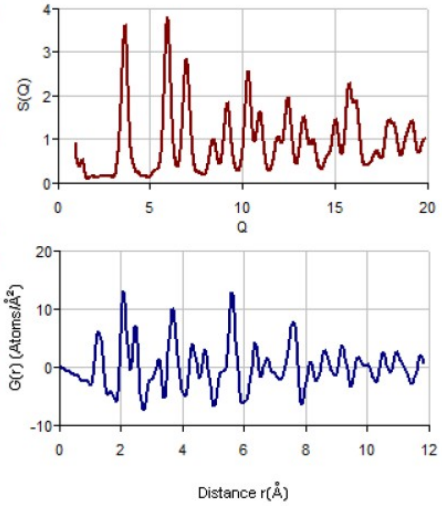




http://www.unipress.waw.pl/soft/crystallography/nanopdf/

Abstract

NanoPDF64 Software package is to support structural analysis of nanocrystals performed with application of real space powder diffraction method, PDF. In particular it is dedicated to elaboration and interpretation of experimental G(r) functions of nanocrystals. This is realized through building atomistic models of nanocrystals with non-uniform internal structure, calculation of theoretical G(r) functions and quantitative description of differences between G(r)'s of a parent perfect crystal lattice and this lattice after introduction of density modulation.

The program serves for:

- modeling of spherical, cube or cylindrical grains with diameter up to about ten nanometers
- modeling of grains with implemented density waves, (x), with spherical or radial symmetry
- calculation of pair distribution histograms (PDH)
- calculation of x-ray diffraction patterns, I(Q) and S(Q)
- calculation of G(r) (PDF) from powder diffraction data for models with a perfect crystal lattice and for models with density modulation waves
- calculation of $\delta(r) = \Delta r/r$ plot: function presents differences between inter-atomic distances (IDs) in nanograins with a perfect (undeformed) crystal lattice and IDs in this grain after introduction of density modulation

Currently NanoPDF64 includes modeling and calculations only for cubic and hcp-type structures:

- Monoatomic lattices: primitive cubic (P), bcc (I), fcc (F), diamond and hexagonal close packed (hcp) lattices with an arbitrarily chosen ABC layer stackings,
- Biatomic lattices: cubic zinc-blende and hcp structures with an arbitrarily chosen ABC layer stacking.

The homepage address of the NanoPDF64 package:
/http://www.unipress.waw.pl/soft/crystallography/nanopdf/

Flowchart of the program is shown in Fig.0-1

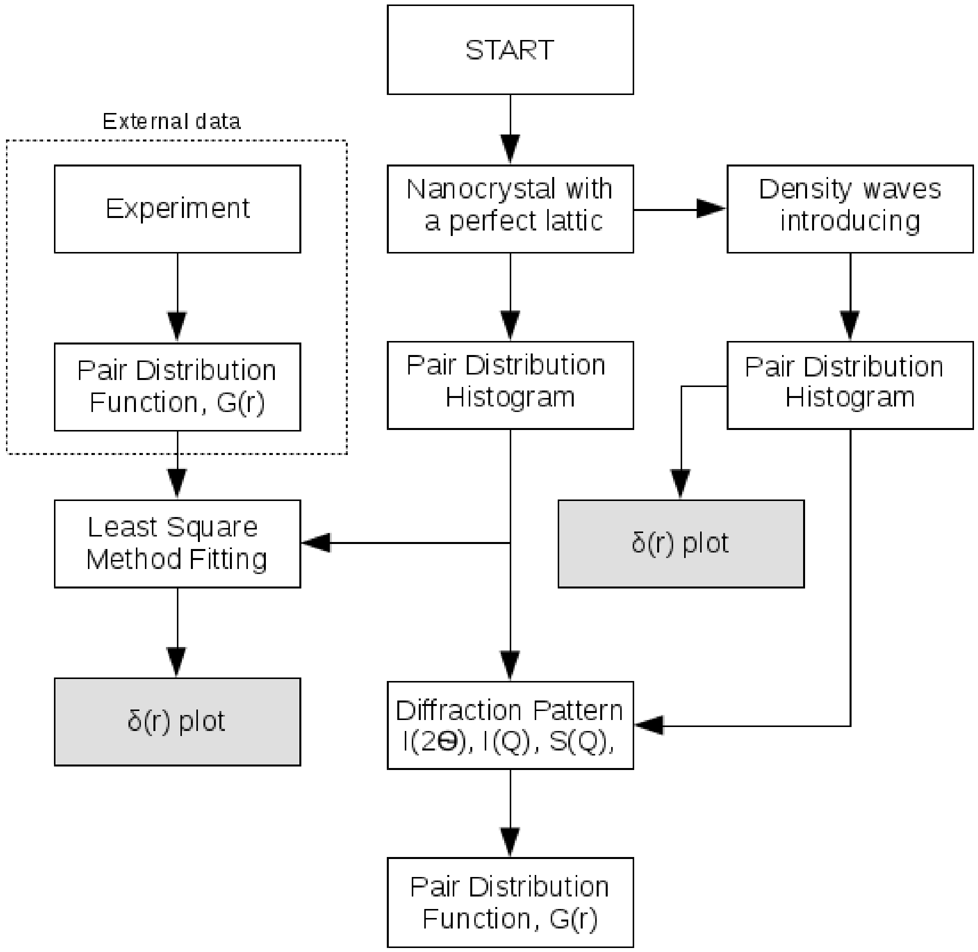


Fig. 0-1. Flowchart of the NanoPDF64.exe program

1. Introduction

1.1.Technical details

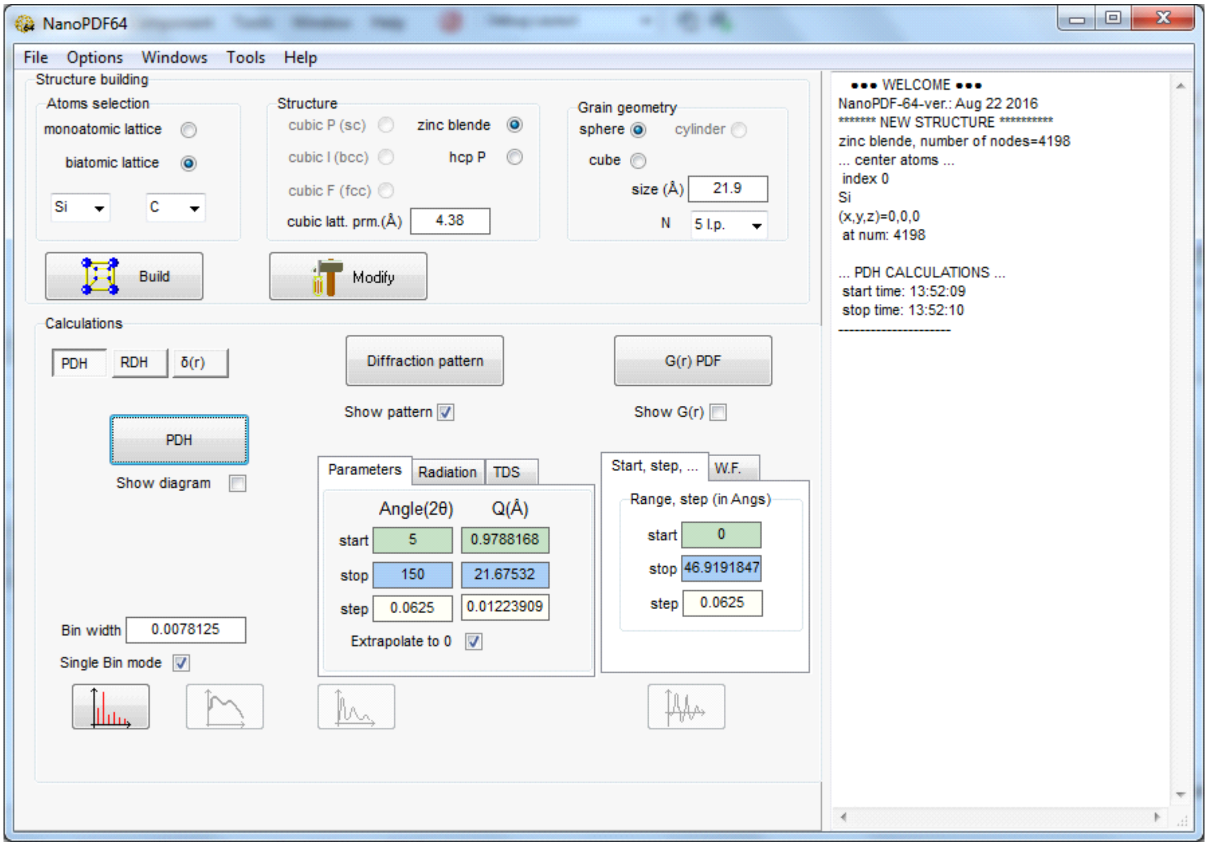
The NanoPDF64.exe program was written in C++ Builder XE 4 as a handy tool for nanograins modeling and structural analysis of real nanocrystalline materials based on experimental powder diffraction data. Program is 64 bits application and runs under the Windows environment; it is equipped with graphical user interface (GUI) and allows for rapid results evaluation using graphic routines. The program cooperates with other applications: diffdatafit for data fitting purposes (included to NanoPDF64 package) and with the Rastop (homepage: www.geneinfinity.org/rastop/) for visualization the 3D models of nanograins (Rastop is optional and may be changed to another application capable to read the XYZ files).
Both NanoPDF64 and diffdatafit do not make any modification to the Windows registry. The NanoPDF64 uses its own "*ini*" file where all configuration data are stored; the "ini" file is placed in the same directory like the NanoPDF64.

Installation of NanoPDF64 package on the Windows platform requires unziping it and copying to an arbitrary folder; it consists of:

- "diffdatafit.exe" console application; more about it in Chapter 4
- a "scfact.scf" file; it stores the coefficients for analytical approximation of X – Ray scattering factors values and is **necessary** for the NanoPDF64 operation; if missing the NanoPDF64 will inform the user about the issue and terminate
- a script file "rms.scr"; it consists of a set of Rastop commands which may be modified by the user to obtain better personalization of 3D images.

After the first run of NanoPDF64 a "NanoPDF64.ini" file is created. It is used to store the parameters utilized inside application and transfer them from one run to another. It is updated when the program is closed by the user and read-in when the program is invoked again. The "NanoPDF64.ini" file should not be edited by hand.

NanoPDF64 was tested under 64 bits Windows platform and under the Linux/Fedora v. 21÷24. Linux users may run the program after the installation of the Wine emulator. A standard PC class computers equipped with 2.53 GHz processor and 4.0 GB of RAM memory allows to do the calculations for nanograins with about 35 thousands atoms in less than 150 s. The current version (v.1.1-2016) of the software does not perform parallel computing but there is a limited version (and under the construction) of NanoPDF64 with the parallel computing based on the OpenMP library for the Linux system. It allows to greatly speed up some kinds of calculations.



monoatomic lattice ○
biatomic lattice ●
Si C
cubic P (sc) ○ zinc blende ●
cubic I (bcc) ○ hcp P ○
cubic F (fcc) ○
cubic latt. prm.(Å) 4.38
sphere ● cylinder ○
cube ○
size (Å) 21.9
N 5 l.p.
Show pattern ☑
Show G(r) ☐
Show diagram ☐
Bin width 0.0078125
Single Bin mode ☑

	Angle(2θ)	Q(Å)
start	5	0.9788168
stop	150	21.67532
step	0.0625	0.01223909

Extrapolate to 0 ☑

Range, step (in Angs)
start 0
stop 46.9191847
step 0.0625

```
   ●●● WELCOME ●●●
NanoPDF-64-ver.: Aug 22 2016
******* NEW STRUCTURE **********
zinc blende, number of nodes=4198
... center atoms ...
 index 0
Si
(x,y,z)=0,0,0
 at num: 4198

... PDH CALCULATIONS ...
 start time: 13:52:09
 stop time: 13:52:10
--------------------
```

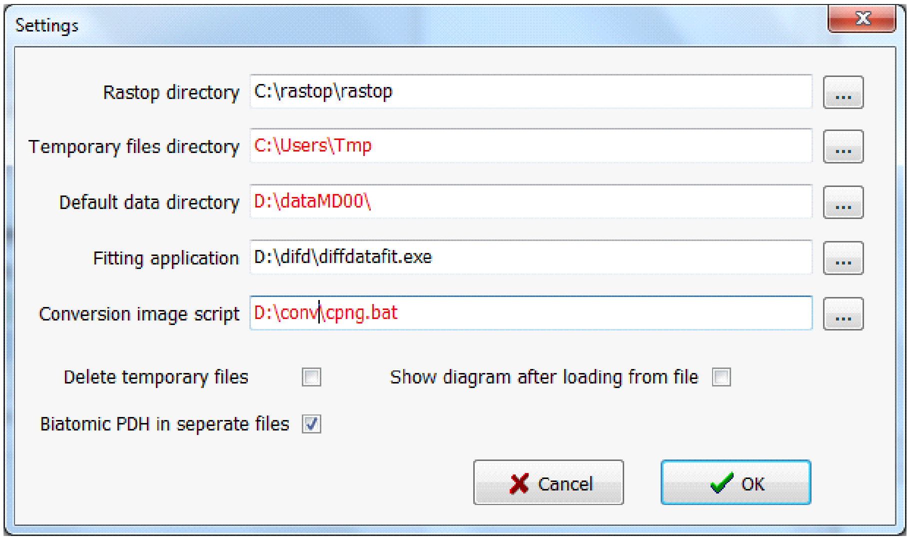
Fig.1-1. Main menu window of the NanoPDF64.exe program

1.2. Configuration

Configuration of NANOPDF64 is accessible through the **"Options → Settings"** submenu. The **"Settings"** menu opens a window (Fig. 1-2) where one can select:

- directory of the Rastop application
- directory for temporary data storage
- default(current) working directory
- path to the *diffdatafit* application
- path to the *.bat file where commands for image conversion are stored

Other options apply to control: the behavior of temporary files, the format of file(s) with PDH data, and the application behavior after loading data from files.
Paths can be set by hand or by calling the **“Choose directory”** dialog by a button placed on the right side of an edit window. After modification of directory or path the new value is displayed using the red fonts.



Rastop directory C:\rastop\rastop

Temporary files directory C:\Users\Tmp

Default data directory D:\dataMD00\

Fitting application D:\difd\diffdatafit.exe

Conversion image script D:\conv\cpng.bat

Delete temporary files ☐ Show diagram after loading from file ☐

Biatomic PDH in seperate files ☑

Fig. 1-2. The "Settings" menu window

1.3. Browsing the atomic scattering factors file

The atomic scattering factors (ASF) are computed based on coefficients placed in file “scfact.sft”. The values of coefficients are taken from International Table for X – Ray Crystallography IV. They can be browsed in the **“Atom properties”** window located in the **“Options → Element Properties F8”** submenu.

The scattering factors curves for selected element, i.e. *f(sinθ/λ)* are plotted after the “Plot” button click.

One can plot ASF curves in separated windows or using the **“Drag & Drop”** mechanism (to start and processing the **“Drag & Drop”** the “Shift” key must be pressed) can be replaced to a single window.

The “scfact.sft” file contains also information on:

- cubic lattice parameter for selected elements
- element mass (not used by NanoPDF64)
- Debye temperature for selected elements (not used by NanoPDF64)

Each value can be edited after the click of selected cell. After modification the data can be saved (right mouse button click calls the popup menu with the **“Save”** submenu). New items can be added; to do this the “scfact.sft” must be opened by the external editor (e.g. **“Notepad”**) and three actions should be done:

- increase by one the “num” entry in the “gen” section (this record gives information about the number of items)
- a new record “numX=<the name of item>” should be added in the “gen” section, where X is a consecutive number (in general it is equal to the number of items); the name and the number of item shouldn’t interfere with previous names and numbers
- a new section “[<the name of item>]” should be added at the end of file; the best way is to copy the existing section and change the selected values

After modification and saving the “scfact.sft” the new value should be visible in the ASF browser and the “atoms selection” combo boxes (the NanoPDF64 must be reopened).

2. Modeling

2.1. General description of modeling

Currently NanoPDF64 includes modeling and calculations only for cubic and hcp-type structures:

- Monoatomic lattices: primitive cubic (P), bcc (I), fcc (F), diamond and hcp structures with an arbitrarily chosen ABC layer stackings
- Biatomic lattices: cubic zinc-blende and hcp structures with an arbitrarily chosen ABC layer stacking.

Five parameters for models with a perfect crystal lattice can be chosen:

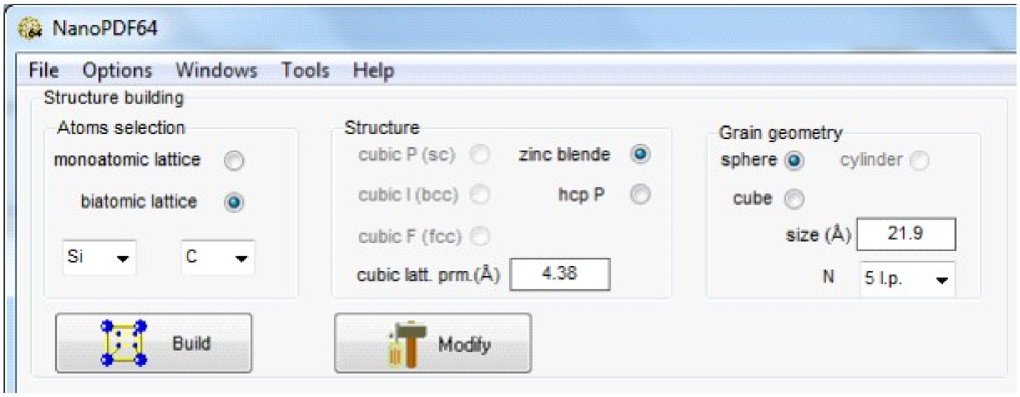
- chemical composition (here: one or two kinds of atoms)
- lattice type (Bravais lattice)
- lattice parameter (here: only one parameter, see Section 2.2.6)
- grain shape (sphere, cube or cylinder)
- size (sphere or cylinder radius, cube edge, cylinder height)

All dimensions are given in angstroms. The structure which has been built can be saved in an expanded xyz format file with ndl extension, which stores all information needed to recreate the settings after loading the file.

The NanoPDF64 program can read atom positions from a file selected by user. The preferred format is „ndl”. Reading other formats is possible but doesn't allow to restoration the structure parameters of saved atom positions (e.g. lattice parameter, grain geometry, etc.). The model can be displayed with RasTop by the **„Tools → Rastop → Ideal”** or **„Tools → Rastop → Model”** submenus.

2.2. Building structure with a perfect lattice

The parameters which need to be defined to build a model are grouped in three boxes (Fig.2-1):



Structure building

Atoms selection
monoatomic lattice ○
biatomic lattice ●
Si
C

Structure
cubic P (sc) ○
cubic I (bcc) ○
cubic F (fcc) ○
zinc blende ●
hcp P ○
cubic latt. prm.(Å) 4.38

Grain geometry
sphere ●
cylinder ○
cube ○
size (Å) 21.9
N 5 l.p.

Fig.2-1. **"Structure building"** menu window

Box 1: **"Atoms selection"**:
- chemical composition (here: one or two kinds of atoms)

Box 2: **"Structure"**:
- lattice type (cubic, diamond/zinc blende or hcp)
- lattice parameter (here: a for cubic lattices, EClp for hcp structures, see Section2.2.6)

Box 3**: "Grain geometry"**:
- grain shape (sphere, cube or cylinder)
- size (radius of sphere or cylinder or length of cube edge)

N- radius expressed in number of lattice parameters of corresponding unit cell - a for cubic, EClp for hcp structures.

2.2.1 Box 1 – Atoms selection

The group Box 1 consists of two radio buttons:

- monoatomic lattice
- biatomic lattice

and two combo boxes where elements forming the lattice are chosen. Each combo box has a list of names of atoms loaded from the "scft.scf" file. The whole list is available after mouse click or by typing the name of element.
After selection of monoatomic structure of a given element, the available types of lattices appear in Box.2; for some most common cubic polymorphs also value of lattice parameter appear in Box.2.

2.2.2 Box 2 - Structure (Bravais lattice)

Currently there are 5 structure types implemented in NanoPDF64 program which one chooses with use of five radio buttons. First three radio buttons correspond to monoatomic cubic structures with three different Bravai's lattices: (P) primitive, (F) fcc and (I) bcc. Fourth button defines alternately diamond-like or zinc-blende-like lattices for mono- and bi-atomic structures, correspondingly. With the fifth button one chooses a group of hexagonal close packed structures, hcp, for which one has to define ABC layer stacking, *c/a* ration and *u*-parameter – see Section 2.2.6.

2.2.3 Box 2 - Lattice parameter

The lattice parameter which is required to enter in Box 2 is that of a cubic unit cell, a_{cubic}. This parameter defines fully monoatomic cubic structures P, I and F, diamond and zinc blende structures. The initial values of trigonal lattice parameters (TLP) required for description of hcp structures and appearing in Box 3, $a_{0,trigonal}$ and $c_{0,trigonal}$, are calculated with reference to lattice parameter *a* of its cubic polytype (diamond or zinc blende = sphalerite).

For hcp structures the lattice parameter defined in Box.2 has a meaning of Equivalent Cubic lattice parameter, EClp. The as-calculated initial parameters $a_{0,trigonal}$ and $c_{0,trigonal}$ can be changed in next steps of building hcp type models, what may result in changing the initial value of EClp c.f. Sections 2.2.4 -2.2.6.

2.2.4 hcp structures

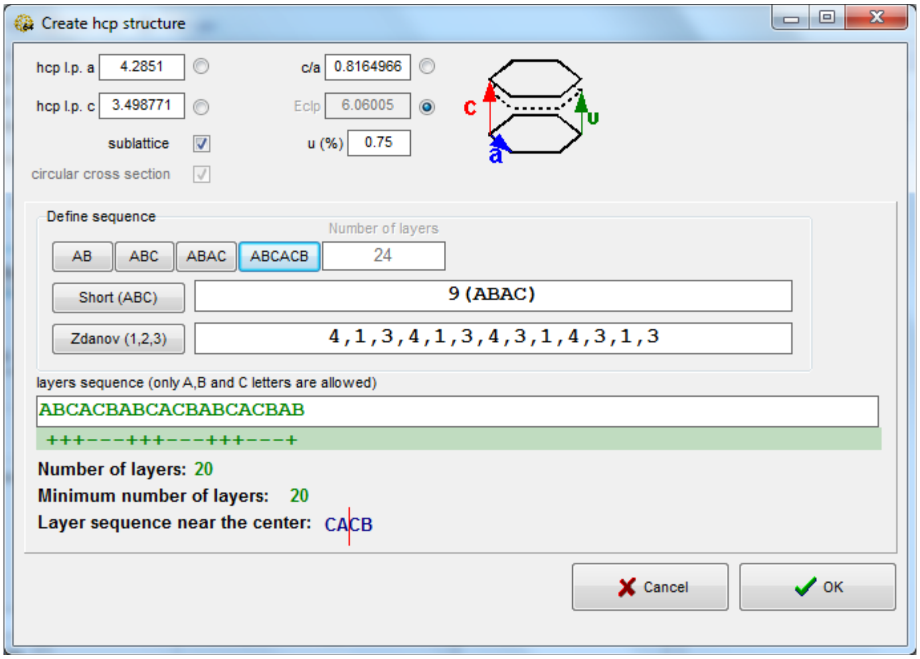
The hcp option serves for building close packed structures layer-by-layer, both for mono- and bi-atomic structures. When hcp-type structure is selected the "**Create hcp structure**" window (HCPW) is displayed (see Fig.2-2) after pressing the "**Build**" button. The hcp option is restricted to spherical or cylindrical shape of grains.
During the first run of HCPW window the initial trigonal lattice parameters are set according to rules presented in the Section 2.2.6. The TLP parameters are displayed in the edit windows connected to their own radio buttons. If the radio button is checked the modification of respective edit window is disabled (color changes to grey).
One can modify the cross section (limited to cylindrical shape grains) and enable or disable the sublattice checkbutton. The position of sublattice is determined by **"u"** parameter (see more in the Section 2.2.6).
Next run of HCPW recalls the parameters of the previous run.

One has several options to create the required layer stacking along the whole grain in the **"Define sequence"** box:

- using templates to choose among most common polytypes 2H (AB), 3C (ABC), 4H (ABAC) and 6H (ABCACB); full ABC sequence across the grain will appear in the

”layers sequence” window with total number of layers required to build the grain with a given size defined by the **“Numbers of layers”** edit window (the required number of layers is calculated for spherical grain from radius defined in main window)

- write an own template named **“Short ABC”** by hand typing any ABC sequence; the rules of notation are given in Section 2.2.5
- define complete layer stacking through Zhdanov notation with the required number of individual layers
- define by hand by typing one by one the A,B,C letters in the **“layers sequence”** edit window.



hcp l.p. a 4.2851 ○

hcp l.p. c 3.498771 ○

sublattice ☑

circular cross section ☑

c/a 0.8164966 ○

Eclp 6.06005 ●

u (%) 0.75

Number of layers 24

9 (ABAC)

4,1,3,4,1,3,4,3,1,4,3,1,3

layers sequence (only A,B and C letters are allowed)

ABCACBABCACBABCACBAB

+++---+++---+++---+

Number of layers: 20

Minimum number of layers: 20

Layer sequence near the center: CACB

Fig. 2-2. ”**Create hcp structure**” window (HCPW)

Below **”layers sequence”** edit window, on the green strip, the ”ABC” code is converted to a sequence of signs ”+”, ”-” (so called Hagg notation) where ”+” sign corresponds to the layer order ”AB”, ”BC” and ”CA”, ”-” corresponds to ”CA”, ”BA” and ”AC” stackings. In this notation 2H structure is described as $(+-)_{n}$., 4H polytype is $(++--)_{n}$, 6H - $(+++---)_{n}$, 3C $(++++)_{n}$ or $(----)_{n}$. Since in hcp structure same layers cannot occur one after another (AA, BB, CC are forbidden), appearance of an error in the created sequence is denoted by ”0”. The same procedure applies to mono- and bi-atomic structures. One should notice that in biatomic lattices A, B and C letters represent two hexagonal layers one above another separated by $u{*}c_0$ where c_0 is interlayer distance. In bi-atomic structures like ZnS or CdSe the neighboring layers form two identical sublattices from different atoms, e.g. Zn and S or Cd and Se, respectively, Fig.2-3. In mono-atomic diamond-like hcp structures, like diamond or Si, the double layers/two sublattices are formed from same atoms.

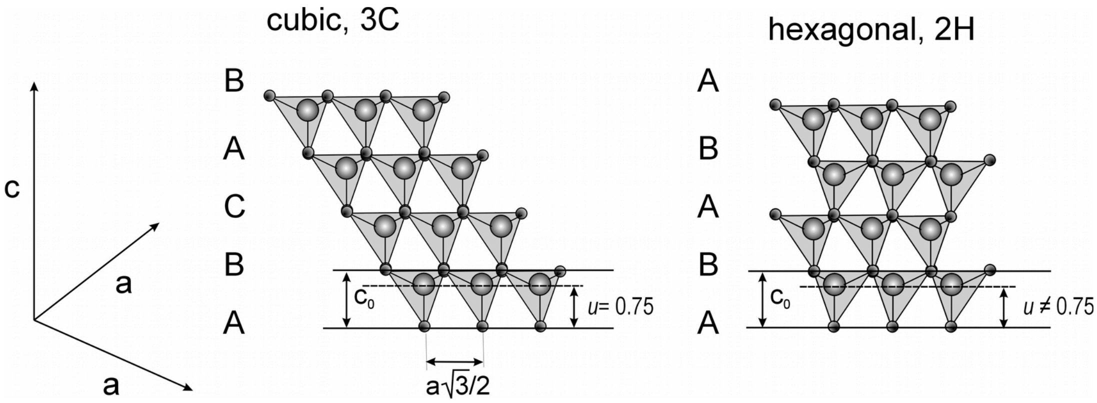


Fig.2-3. Layer stacking of 3C and 2H structures of bi-atomic hcp lattice

2.2.5 Building ABC sequence

For spherical grains the font in the **"layers sequence"** edit window will be changing colors depending on the length of the sequence. The required number of layers across the grain diameter given in Box 3 is calculated by dividing diameter by the-inter-layer distance c_0 of a given structure. The minimum number of layers is displayed by the **"Minimum number of layers"** label.

There are three colors which may appear in the editing window:

- black - sequence too short
- green - proper/sufficient length of sequence
- red - sequence too long

When cylindrical grain shape is chosen the font color is always black. Here, the number of layers defines the height of the cylinder/wire - its dimension in the direction perpendicular to the layer plane; note that in Box 3 only radius of the cylindrical grain model is specified.

Short (ABC) notation

The short notation was designed to make easier building very long sequences with stacking faults. Using this notation one creates a full layer stacking is combined from short ABC sequences using brackets and numbers which serve for repeating the short ABC sequences. For example (spaces have been added between subsequences for better visibility):

- 3(ABC) → ABC ABC ABC
- 2(AB)3(ABAC) → AB AB ABAC ABAC ABAC
- ABC2(AB) → ABC AB AB

Expressions can be arbitrary nested, for example:

- 2(A3(BC)) → A BC BC BC A BC BC BC
- A2(BC3(AC)) → A BC AC AC AC BC AC AC AC
- 9(AB2(CBAB2(ABAC4(AB)C)AB)ABC) → ABCBABABACABAB …

The expansion of nested expressions is based on recursion. The general rule for the expression creation is as follow:

expression→' number' or 'A B C letter' or '(expression)'

Zhdanov notation

The second case allows for rapid sequence building in Zhdanov notation which is sequence of numbers denoting sums of “+” or “— “ characters appearing one after another (Hagg notation) and separated by commas.

For example:

- 1, 2, 3 → + — — +++
- 3, 2 → — — — ++
- 6 → — — — — — —

Click on the “Template (1,2,3)” button reproduces complete ABC layer sequence.

2.2.6 Setting structural parameters of hcp model: Equivalent Cubic lattice parameter, EClp, (c/a) ratio and u

For both spherical and cylindrical shaped grains the initial values of trigonal lattice parameters $a_{trigonal}$ and $c_{0,trigonal}$ are calculated from the “Lattice parameter” given in Box 2. For hcp structures this parameter has a meaning of Equivalent Cubic lattice parameter, EClp:

$$EClp = \left(2\sqrt{3}a_{trig}^{2}c_{0,trig}\right)^{1/3} \tag{2.1}$$

In the **”Create hcp structure”** Box there appear initial values of trigonal lattice parameters $a_{trigonal}$ and $c_{0,trigonal}$ which are calculated assuming that relationship between inter-layer $c_{0,trigonal}$ distance and in-plane inter-atomic distance $a_{trigonal}$, is that of a perfect cubic hcp-structure,

$c_{0,trigonal}/a_{trigonal}$ =0.8165. The parameters appearing in the **”Create hcp structure”** Box are:

$$a_{trig} = EClp/\sqrt{2} \qquad c_{0,trig} = EClp/\sqrt{3} \tag{2.2}$$

In general case, in hcp non-cubic structures, the (c_0/a) is not constant but it deviates from the value 0.8165. Therefore, for given ABC sequence in the ”**Create hcp structure**” Box one can freely set a new (c_0/a) ratio and recalculate individual parameters $a_{trigonal}$ and $c_{0,trigonal}$ for EClp given in Box 2.

There are also options to set $a_{trigonal}$ or $c_{0,trigonal}$ and recalculate (c_0/a) ratio for EClp given in Box 2 or, recalculate EClp for given (c_0/a) ratio.

An additional free parameter which defines hcp lattice with given ABC layer sequence and given (c_0/a) ratio is ”u” which defines the distance between two sub-lattices forming bi-atomic hcp structures and diamond lattice in the direction normal to the layer plane. For a perfect cubic lattice with ABC sequence u = 3/4 but in real materials it can be either smaller or larger than that, Fig. 2-3. For calculations of atomic positions in the model the default values is u = 0.75, and it can be changed in the **”Create hcp structure”** Box.

2.2.7 Box 3 – Grain shape (spherical or cylinder)

Two radio buttons: ”sphere” and ”cylinder” are for shape definition. The ”sphere” radio button enables all possible unit cell types listed in Box 2 **”Lattice type”**. The ”cylinder” button is limited only to hcp-type structures.

2.2.8 Box 3 – Dimension (radius)

Radius of the grain can be set directly in the “radius” edit window in Å or, as multiplicity of lattice parameter (l.p.) in the “N” combo box:

$$R = \text{l.p.} \times N$$

where: R is the radius, l.p. is the lattice parameter and N is a value chosen or entered by user in the combo box; for “radius” given in Å in N box value of R/l.p. appears.

For spherical grains the dimension is defined uniquely through grain radius. For cylindrical grains, in Box 3 one defines cylinder radius only. The third dimension, perpendicular to the hexagonal layers, is calculated as multiplicity of inter-planar spacing c_0, c.f. Section 2.2.5. For hexagonal prism R is the distance between opposite side planes.

2.2.9 Thermal vibration

This part is under construction.

2.2.10 Building initial model – summary and visualization

After setting all structural and geometrical parameters defining model of the nano-grains after click on **”Build”** button, the NanoPDF64 calculates atoms positions, saves them into the computer’s memory and activates three buttons inside the **”Calculation”** group box.

Nanograin structure can be displayed using submenu ”Tools→Rastop→Ideal” or ”Tools→Rastop→Model”. These options require the correctly set paths to the Rastop program and the “temporary files directory” in the settings window.

2.3 Building structure with density modulation

2.3.1 Introducing density modulation

Models with a non-homogenous internal structure are build by modifying the initial model with a perfect crystal lattice (see Section 2.2). We expect that in real nanocrystal lattice parameter changes across the grain and, thus, we subdivide the grain volume into parts to which we associate “local lattice parameters.” In a perfect crystal the lattice parameter defines uniquely all interatomic distances within given “local volume”. For description of models of nanocrystals we define a set of "local lattice parameters" for selected volume parts and we use them for further calculation of coordinates of individual atoms in the whole grain volume.

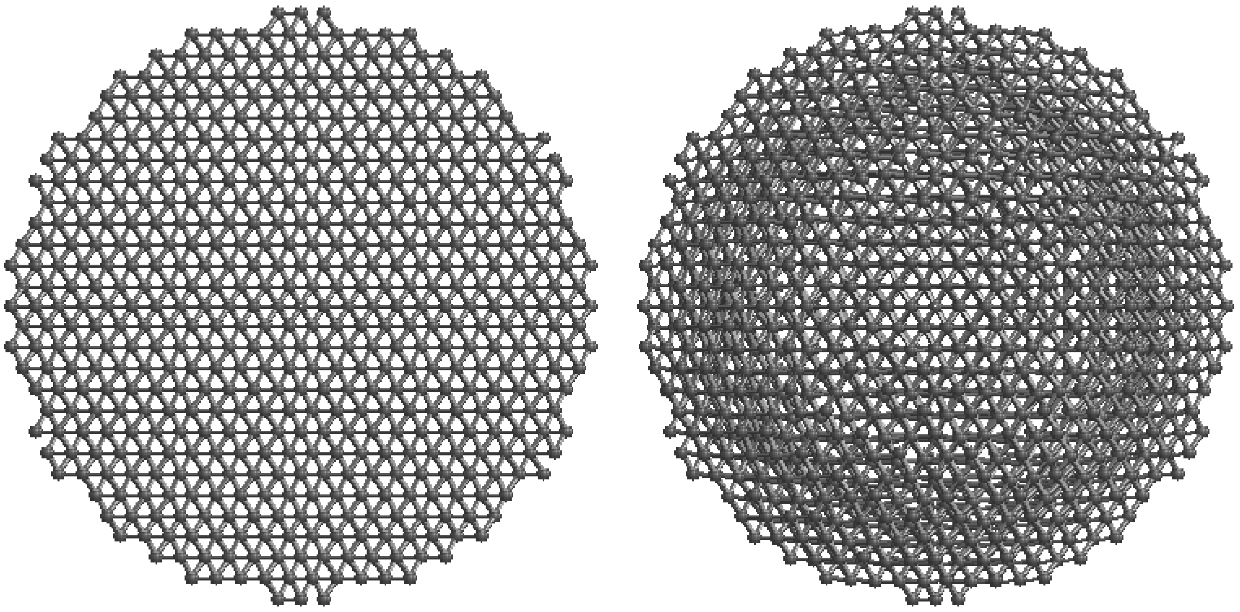


Fig. 2-4. The perfect structure and structure with density modulation wave of diamond nanograin. The Rastop program was used for visualization

To build model of a spherical nanocrystal with density waves the space within the volume of the grain is subdivided by concentric spherical surfaces, Fig.2-5, where the first spherical surface, rs_0, defines the inner grain core. The spaces between each two subsequent concentric spherical surfaces form shells surrounding the grain core (between rs_0 and rs_1, rs_1 and rs_2, etc.). The largest shell terminating the model we name the surface shell. For given shell "i" the positions of all atoms in the shell are shifted from their original positions along the radii by the constant deviation parameter $\varepsilon_i = (a_i/a_0-1)$, where a_i is local and a_0 is reference lattice parameter. The total radial shift η_{tot} of an atom placed in N-th shell from the position of a perfect lattice is given by the formula:

$$\eta_{tot} = r_m - r_p = \sum_{i=0}^{N-1} w_i \cdot (1+\varepsilon_i) + (r_p - rs_{N-1}) \cdot (1+\varepsilon_N) - r_p \qquad (2.3)$$

where: r_p - atom's distance to the center of a perfect lattice; r_m – atom's distance to the center after modification; w – width of a shell; ε – deviation parameter; rs – radius of a shell.

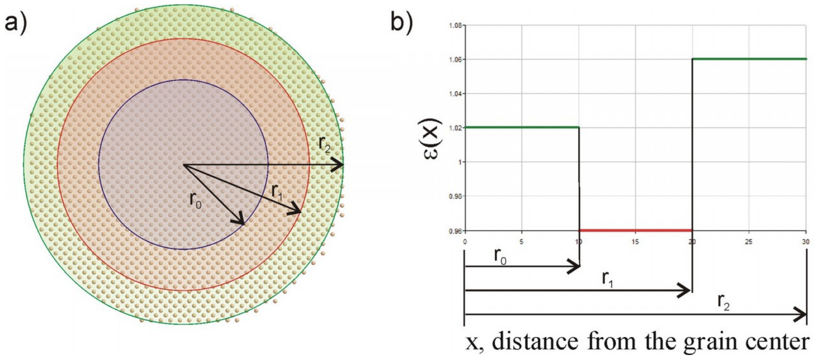


Fig. 2-5. a) Cross section of sphere (or cylinder) subdivided into core, shell 1 and surface. b) Corresponding ε(x) diagram presenting shortening (shell1) and elongation (core and surface) of interatomic distances in radial direction

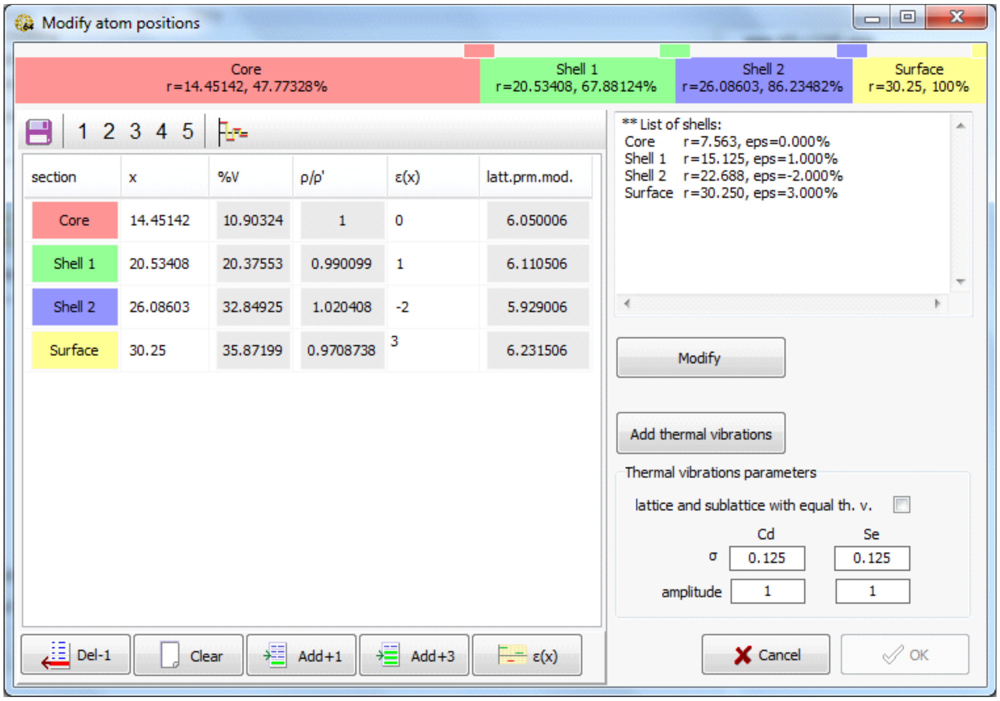
The density waves are presented in a form of ε(x) diagrams which quantify, in %, the deviation of inter-atomic distances r_i within every shell from the corresponding distances in the parent perfect structure, $r_{i,0}$; x is the distance from the grain center, Figure 2-5.

2.3.2 Parameters defining density waves

(<u>Comment</u>: Density modulation, if present in a real nanocrystal, should be described by a continuous function. Experimentally, however, it would be practically impossible to determine the exact shape of such functions. For the sake of simplicity, in the present model the density changes stepwise between sequent shells.)

A window for creation of a multishell model (with density waves) is activated by clicking on **”Modify”** button, Fig.2-6. On the left side of this window appears a table which serves for setting parameters of multi-shell models. Each row defines one shell of nanograin. The first shell is named ”core”, the last is ”surface”. After opening the table there appear only one row defining ”core” of the grain. To add (or remove) rows in the table there are ”+” (and ”-”) buttons placed underneath the table. The first row is always named ”core” the last ”surface”, in between the core and surface there appear shells denoted by numbers 1, 2 etc. The number of rows (shells) in unlimited.

Parameters of each shell are characterized in 6 columns. Values of 2nd and 5th Columns are editable, those in Columns 3 and 4 are calculated from those set in Column 2, the values in Column 6 are calculated from those set in Column 5.



Core r=14.45142, 47.77328% | Shell 1 r=20.53408, 67.88124% | Shell 2 r=26.08603, 86.23482% | Surface r=30.25, 100%

section	x	%V	ρ/ρ'	ε(x)	latt.prm.mod.
Core	14.45142	10.90324	1	0	6.050006
Shell 1	20.53408	20.37553	0.990099	1	6.110506
Shell 2	26.08603	32.84925	1.020408	-2	5.929006
Surface	30.25	35.87199	0.9708738	3	6.231506

```
** List of shells:
Core     r=7.563, eps=0.000%
Shell 1  r=15.125, eps=1.000%
Shell 2  r=22.688, eps=-2.000%
Surface  r=30.250, eps=3.000%
```

Thermal vibrations parameters

lattice and sublattice with equal th. v. ☐

	Cd	Se
σ	0.125	0.125
amplitude	1	1

Fig.2-6. The view of the ”**Modify atoms positions** ” window

Graphical presentation of ε(x) function is displayed after clicking on “**ε(x)**” window, c.f. Fig.2-6.

Column	Symbol	Description
1	**name**	**name** of the shell: core, shell 1, shell 2,.... surface
2	**x**	**distance from the grain center** = radius of the spherical surfaces defining the radius at which the shell ends/begins; the first value is the core radius, x_1=r_0, which is, at the same time the inner radius of the next shell. The radius is given in angstroms
3	**%V**	ratio, in %, of **volume of given shell** to the whole grain volume: %V = V_{shell}/V_{grain}
4	**ρ/ρ_0**	**relative density** of given shell: $\rho_{shell}/\rho_{perfect\ crystal}$
5	**ε(x)**	**the deviation, in %, of inter-atomic distances** within given shell from the corresponding distances in the parent perfect structure, ($r_i - r_{i,0}$). The values of ε(x) are constant within given shell defined, $r_{i,min} < x < r_{i,max}$; core extends from x = 0 up to x = r_0, shell 1 from x = r_1 up to x = r_2, etc.,
6	**latt.prm. mod.**	**local lattice parameter** of given shell; **EClp**, corresponds to density of the shell.

Tab. 2-1. Parameters defining density waves

2.4 Projection of density modulation waves - derivation of δ(r) plot

On G(r) an individual interatomic distance is represented by a peak with finite width and defined position.
Introduction of density modulation (through multi-shell model) leads to splitting of each single interatomic distance $r_{i,0}$ into a series of distances slightly different from the initial value. As a result, the peaks in *G(r)* move to "new" average positions $<r_i>$. The changes of $<r_i>$ distances caused by density modulation waves relative to those in the perfect lattice, $r_{i,0}$, can be presented in the form of δ(r) plots, equation (2.4):

$$\delta(r) = \Delta r_i/\mathrm{r}_{i,0}; \quad \Delta r_i = (<r_i> - \mathrm{r}_{i,0}) \tag{2.4}$$

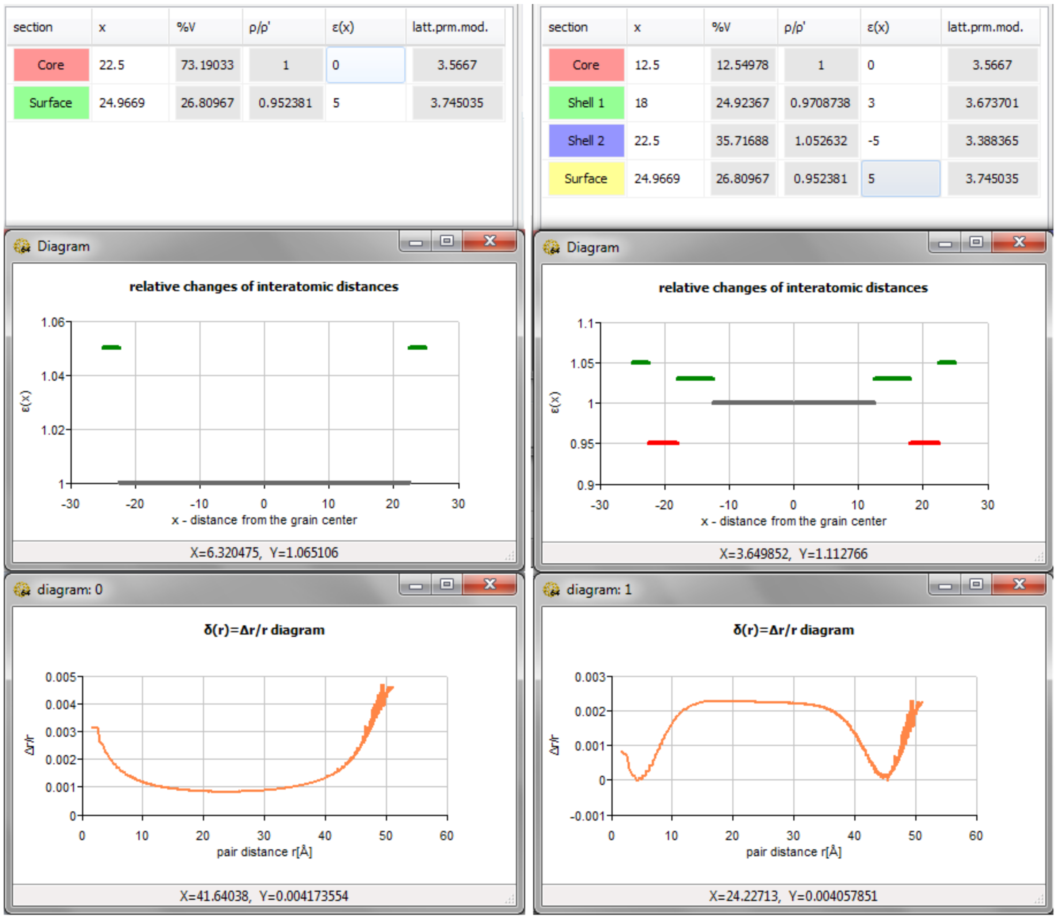
where $\Delta r_i = (<r_i> - r_{i,0})$ is the deviation of a given (volume averaged) inter-atomic distance $<r_i>$ from the corresponding $r_{i,0}$ distance in the perfect crystal lattice (in this text we use symbol r_i instead of $<r_i>$). The r_i values vary between the shortest inter-atomic bond in the grain, and the longest distance which, for spherical grains, is equal to the grain diameter 2R ($r_{1,0} \le r_i \le 2R$).

After implementation of density waves in a given model of a nanocrystal one gets δ(x) plot by clicking **δ(r) = Δr/r** button. Two examples of δ(r) plots corresponding to ε(x) functions are given below.

For the example given below the initial parameters of the nanograin are:

- diamond perfect lattice
- lattice parameter a = 3.5667 Å
- spherical grain radius R=25 Å

Density modulation waves parameters for two diamond models presented on Fig.2-7.



section	x	%V	ρ/ρ'	ε(x)	latt.prm.mod.
Core	22.5	73.19033	1	0	3.5667
Surface	24.9669	26.80967	0.952381	5	3.745035

section	x	%V	ρ/ρ'	ε(x)	latt.prm.mod.
Core	12.5	12.54978	1	0	3.5667
Shell 1	18	24.92367	0.9708738	3	3.673701
Shell 2	22.5	35.71688	1.052632	-5	3.388365
Surface	24.9669	26.80967	0.952381	5	3.745035

X=6.320475, Y=1.065106

X=3.649852, Y=1.112766

X=41.64038, Y=0.004173554

X=24.22713, Y=0.004057851

Fig.2-7. Parameters of ε(x) function of Models I and II, ε(x) diagrams and corresponding δ(r) diagrams

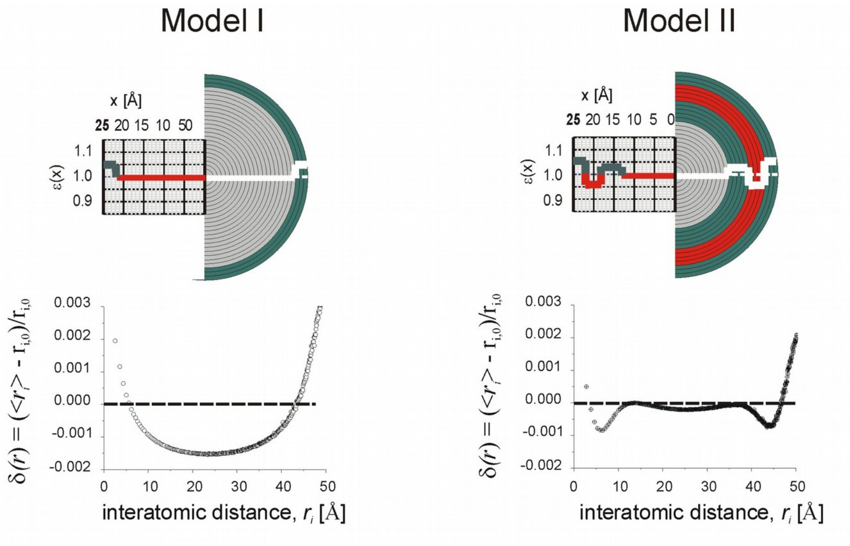


Fig. 2-8. Parameters of ε(x) plot defining Model I and Model II, its graphical presentation and corresponding δ(r) plots

Fig. 2-8 shows that the shape of $\delta(r)$ plots is closely correlated with ε(x) function, i.e. it depends on relative changes in interatomic distances along the grain diameter. The sequence of "waves" appearing in δ-diagrams is determined by a sequence of density waves emerging from the grain surface towards the grain center and described by ε(x) function: (i) The positions of "waves" appearing on δ-plots are correlated with distribution of density waves along the grain diameter and, (ii) The amplitude of the δ-waves is proportional to the magnitude of density variations about that of the reference parent structure.

There is a close correlation between $\delta(r)$ plot, which is determined for atomic models of nanocrystals and parameters which are measurable in a diffraction experiment, namely *apparent lattice parameters*, *alp(r)* values which are determined from experimental *G(r)* functions:

$$\delta(r) = \Delta r_i/r_{i,0} = [1 - alp(r_i)/a_0] \quad (2.5)$$

The lattice parameters "as refined" in routine diffraction data elaboration procedure either by application of Bragg scattering *I(Q)* and Rietveld-type programs, or by real space refinement methods applied to *G(r)* function (e.g. using PDFgui program), are volume average values. Since atomic structure of a nanocrystal is not uniform, average structural parameters, like "overall" lattice parameter have no unique/specific meaning and do not bring information on actual atomic structure of a nanocrystal. An alternative to calculation of one (overall) lattice parameter for the whole r-range of experimental *G(r)* function (what is routinely done e.g. with use of PDFgui program) is calculation of the lattice parameters for different intervals of the inter-atomic *r* distances. The set of values of such measured lattice parameters we call apparent lattice parameters, *alp(r)* (*B.Palosz, E.Grzanka, S.Gierlotka and S.Stelmakh, "Nanocrystals: breaking limitations of data analysis", Z. Kristallogr. 225 (2010) 588–598*).

Comparison of experimental $alp(r)/a_0$ with theoretical $\delta(r) = \Delta r_i/r_{i,0}$ plots was the basis of matching models with density waves to sample of nano-diamond and CdSe quantum, e.g. *"In Search for a Refinable Model of Nanocrystals", Bogdan Palosz ICCD, Denver X-ray Conference Proceedings, Advances in X-ray Analysis, vol.55 (2012), see also* http://www.unipress.waw.pl/soft/crystallography/nanopdf/

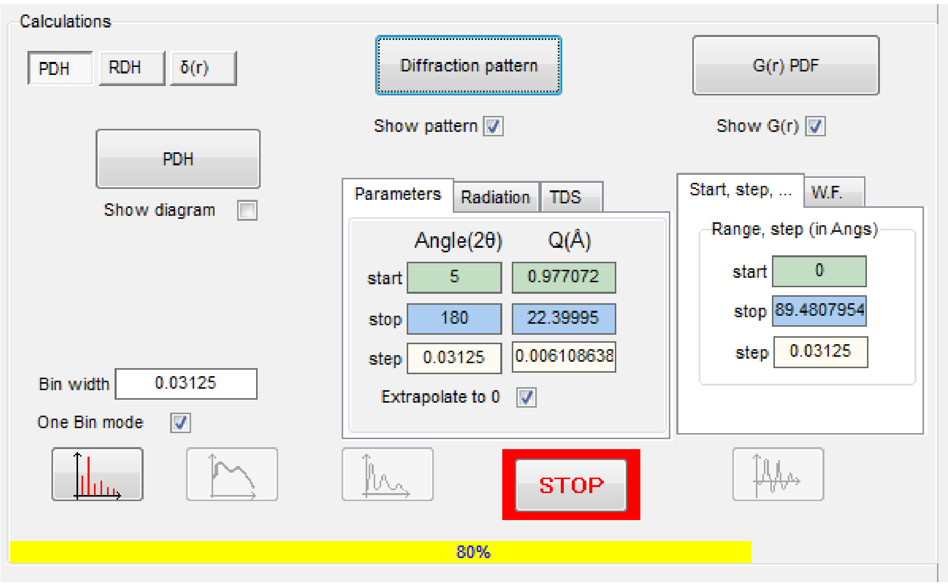
3. Calculations

3.1 General comments

Before starting calculations, one should check settings to avoid problems.
In general, all parameters are set automatically by the program (parameters are stored in the configuration file or are computed). In most cases one does not need to change them.
The parameters important for numerical calculations can be changed in the "**Calculations**" group box.

The "**Calculations**" group box consists of three groups:

- PDH/δ(r),
- diffraction pattern,
- PDF/G(r)



Show diagram ☐

Show pattern ☑

Show G(r) ☑

	Angle(2θ)	Q(Å)
start	5	0.977072
stop	180	22.39995
step	0.03125	0.006108638

Extrapolate to 0 ☑

Range, step (in Angs)

start 0

stop 89.4807954

step 0.03125

Bin width 0.03125

One Bin mode ☑

80%

Fig. 3-1. The "Calculations" group box of main view of the NanoPDF64 program

Computation progress is shown by yellow strip at the bottom of the "**Calculations**" group box.

Calculations can be canceled in any moment. To interrupt click on the **"STOP"** button. The **"STOP"** button is visible only during calculations at the bottom of the "**Calculations**" group box. The current information about the status of the program is given in the message window on the right side of the main window.

***Note:** If any changes are made in the model the calculations of PDH, I(Q),S(Q) and G(r) need to be repeated.*

3.2 PDH/δ(r)

Formally, the Pair Distribution Histogram (PDH) in the case of monoatomic lattices (or if chemical composition is irrelevant) is defined as follows

$$h(r)=\sum_{j,i}^{N}\delta\left(r-r_{ij}\right) \tag{3.1}$$

where r_{ij} is a distance between two atoms and δ is the Dirac function (DF), N – number of atoms.

In the case of non-monoatomic structures a separate histogram must be calculated for each combination of possible atom pairs. In general the number of separate histograms is $N_{sl}(N_{sl}+1)/2$ where N_{sl} is a number of monoatomic sublattices; e.g. for biatomic lattices AB $N_{sl}=2$ and the PDH consists of three distributions: A – A, A – B, B – B.
During computation of a histogram the DF function (which is infinitely narrow) must be approximated by a function (DFA) which gives a non zero value in a finite range called the width. The sum of values of a DFA function for a given distance and width is called a bin and the set of bins approximates a PDH distribution. It's assumed that all bins have the same width. The width is controlled by user.
The NanoPDF64 uses two algorithms of computation of PDH distribution.
The first one called the "one bin" mode (OBMode) allows for fast calculations but with lower accuracy. The DFA is given by formula:

$$\delta\left(r-r_{ij}\right) \approx \Delta_{apr}\left(r-r_{ij}\right) = \begin{cases} 1 & r-rij<BW \\ 0 & elsewhere \end{cases} \tag{3.2}$$

where: BW is a bin width.

Based on above definition the OBMode updates one bin in an array by value 1 at position given by formula:

$$BinPos = \left\lfloor \frac{distance \quad between \quad two\ atoms}{bin\ width} \right\rfloor \tag{3.3}$$

where brackets mean rounding down. The *BinPos* corresponds to distance between atoms.

The second one called the „two bins" mode (TBMode) distributes the contribution from a single interatomic distance between two adjacent bins in a proportion following from it's position relative to those bins. It takes more time but gives better accuracy and consumes less memory (the user can select a few times bigger bin width). For the first bin the DFA is defined as follow:

$$\delta\left(r-r_{ij}\right) \approx \Delta^{I}_{apr}\left(r-r_{ij}\right) = \begin{cases} 1-\alpha & r-rij<BW \\ 0 & elsewhere \end{cases} \tag{3.4}$$

and for the second bin:

$$\delta\left(r-r_{ij}\right)\approx\Delta_{apr}^{II}\left(r-r_{ij}\right)=\begin{cases}\alpha & r+BW-rij<BW\\ 0 & elsewhere\end{cases} \qquad (3.5)$$

where: $\alpha = frac\{r_{ij}/BW\}$, *frac* – is a fractional part of division.
The position of the first bin is given by the equation (3.3) as above and is increased by value 1-α. The position of the second bin is one more than the first bin and its value is increased by α (see Fig.3-2).
The comparison of results calculated for above algorithms is shown in Fig. 3-2.

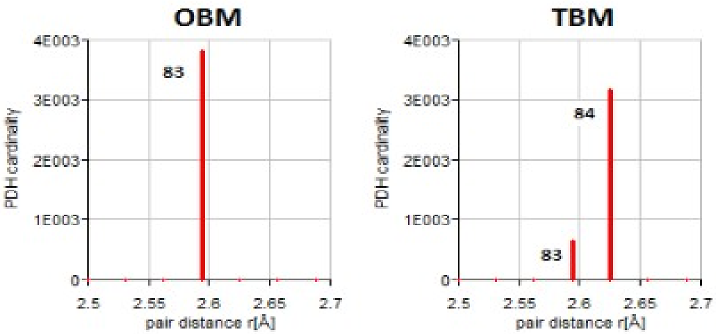


Fig.3-2. Excerpt of PDH calculated in the OBMode and TBMode regimes. The numbers near the bars are the bin positions in the array (assumed BW=1/32=0.031250)

The value of BW in some conditions has a great influence on results. In the case shown in Fig.3-3 the effect of quite small change of BW equal to *Δbw=1/1000-1/1024 = 2.534375e-5,* is very well visible. More accurate result for BW=1/1024 (green line) is the result of using in the computation a value which is negative power of 2. Such solution helps to remove effects of the “round-off” errors during conversion from binary to decimal numbers. So, our general advice is to use the BW values which are negative powers of 2. To enter the BW value equal to: 1/8, ..., 1/1024, 1/16384 one can use the context mouse menu of the **“Bin width”** edit window.
The typical values of bin width in the case of OBM mode are about *1/128=0.0078125* and in the case of TBM mode *1/16=0.0625.*

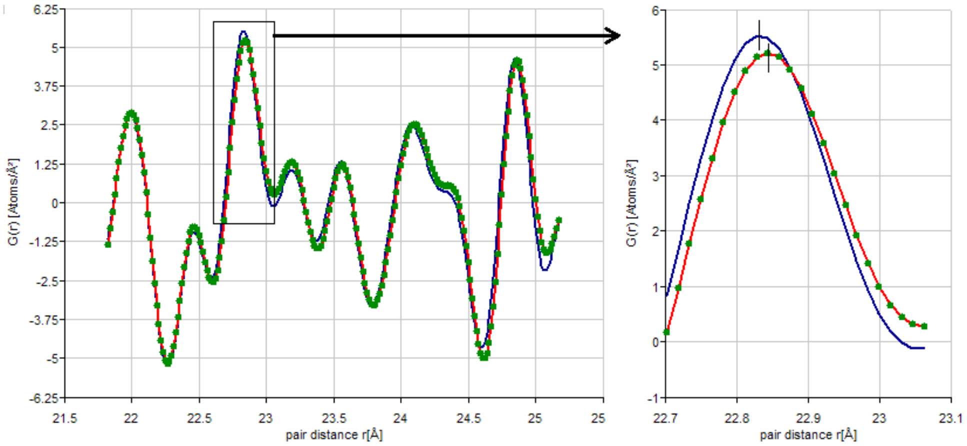


Fig. 3-3. The G(r) functions calculated for two values of BW: red line: BW= 1/1000, green line: BW= 1/1024)

The PDH calculations are activated after click on the **"PDH"** button, the δ(r) after click on the **"δ(r) =Δ(r)/r"** button. Results are stored in memory and can be presented after calculation either if the **"Show PDH"** check box is checked or after click on the button with diagram icon.

The results can be stored to hard disk. The "PDH/δ(r)" data are saved in "*.his" or "*.dij" files respectively. To save data to disk one should use the submenu "Save PDH" or "Save delta(r)/r". Both submenus have keyboard shortcuts, F3 and F7.

3.3 Diffraction pattern

Diffraction pattern is computed based on the PDH distribution. Other parameters required for calculations are specified in the **"Parameters", "Radiation", "TDS"** boxes.

The **"Parameters"** box allows to set:

1. the range of calculations and resolution (i.e. start, step, stop);values are expressed in degrees (°); auxiliary all values are recalculated to reciprocal space units (Q); the "Q" values depend on the X – Ray wavelength selected in the **"Radiation"** box; the start value should be set greater than 0
2. if the "Extrapolate to 0" checkbox is checked, diffraction pattern in the range from 0 to the start value is padded with zeros; this is useful in G(r) calculations to remove artifacts at the beginning of G(r)

The **"Radiation"** box allows to control:

1. the X-Ray radiation wavelength; user can type a value of lambda (in angstroms) or select the known value of standard sources (i.e. Cu, Mo, Ag) from combo box
2. if the **"S(Q) with s.f."** checkbox is checked the scattering factors are taken in account during S(Q) calculations ; otherwise the chemical composition is ignored
3. others radio buttons control the data visualization if diagrams are to be displayed

The **“TDS”** box is currently inactive.

The diffraction pattern calculations are activated after pressing on the **"Diffraction pattern"** button.
The results can be stored in “*.diff” files (keyboard shortcut F4) or can be displayed.

3.3.1. Mathematical background of powder diffraction

Numerical simulations of the NanoPDF64.exe program are based on well known the Debye scattering equation for powder diffraction (*P. Debye, Ann. Phys., 46 (1915) 809 – 823*):

$$I(Q)=\sum_{i\neq j}^{N} f_i(Q)f_j(Q)\frac{\sin(Q\cdot r_{ij})}{Q\cdot r_{ij}}=\sum_{i}^{N} f_i^2(Q)+2\sum_{i=1}^{N-1}\sum_{j>i}^{N} f_i(Q)f_j(Q)\frac{\sin(Q\cdot r_{ij})}{Q\cdot r_{ij}} \qquad (3.6)$$

where: f_i, f_j are scattering factors, r_{ij} is the distance between atoms *i,* j.
The above formula is easy to implement into computer code but for large set of atoms (above a few hundreds) becomes useless. It is inefficient because it requires multiple evaluations of $sin(Qr_{ij})/Qr_{ij}$ (or in short $sinc(Qr_{ij})$) expression with the same argument. It is possible to avoid this problem and compute the *sinc* function only once for each distinct *Qr* value. This approach requires advance preparation of pair distance histogram *h(r)* according to rules shown in the previous section. The general formula taking into account the different types of atoms of crystal structure is given in e.g.: *E. Pantos et al, Journal of Molecular Structure 383 (1996) 303*; here the simplified formula for monoatomic is given.

$$I(Q)=f^2(Q)\left[N+2\sum_{i=1}^{Nb} h(r_i)\frac{\sin(Q\cdot r_i)}{Q\cdot r_i}\right] \qquad (3.7)$$

where: *Nb* is the number of bins, N is the number of atoms.

In the case of biatomic system with atoms belonging to sublattice A or sublattice B, three PDH distributions are needed: A – A, A – B, B – B equation takes the form:

$$\begin{aligned} I(Q)&=f_A^2(Q)N_A+f_B^2(Q)N_B+2f_A(Q)\sum_{i=1}^{NbA} h_A(r_i)\frac{\sin(Q\cdot r_i)}{Q\cdot r_i}+\\ &+2f_B(Q)\sum_{i=1}^{NbB} h_B(r_i)\frac{\sin(Q\cdot r_i)}{Q\cdot r_i}+4f_A(Q)f_B(Q)\sum_{i=1}^{NbAB} h_{AB}(r_i)\frac{\sin(Q\cdot r_i)}{Q\cdot r_i}\end{aligned} \qquad (3.8)$$

where: $f_A(Q)$, $f_B(Q)$ are scattering factors for atoms respectively A and B sublattices, h_A , h_{AB} , h_B are pair distributions for A-A, A-B and B-B atoms connections.
By dividing eq. (3.7) and eq.(3.8) by the structure function *S(Q)* is obtained:

$$S(Q) = \frac{I(Q)}{\sum_i^N f_i(Q)} \tag{3.9}$$

3.4 G(r)/PDF calculations

The last block is prepared for G(r)/PDF calculations. The G(r) function is the inverse Fourier transform of diffraction pattern, is closely related to the PDH distribution so it allows for data analysis in real space. The peak positions corresponds to pair wise distances, the peak amplitudes give relative probability of finding pairs. More details about *G(r)* analysis one can find in book *T. Egami, S. Bilinge, Underneath the Bragg Peaks, Structural Analysis of Complex Materials, 2012*.

The *G(r)* is defined by the following formula:

$$G(r) = \frac{2}{\pi}\int_0^\infty Q\left[S(Q)-1\right]\sin(Qr)\,dQ \tag{3.10}$$

where: *S(Q)* is a structure function given above in section 3.3.1, eq.(3.9).

It is a common practice to extend above definition with the windowing function *WF(Q)*:

$$G(r) = \frac{2}{\pi}\int_0^{Q_{\max}} Q\left[S(Q)-1\right]\sin(Qr)\; WF(Q)\,dQ \tag{3.11}$$

For diffraction data analysis the most common WF is the Lorch window function defined as follow:

$$WF(x) = \mathrm{sinc}\left(\frac{x\pi}{L}\right) \tag{3.14}$$

The windowing function helps to suppress the spurious ripples around a proper peak which result from the finite length of *S(Q)* data; the drawback is decreasing the resolution and amplitude suppressing. General rule is that the lower number of data points the stronger interference are observed (see e.g.: *Phys. Rev. B 73, 184113 2006*).

NanoPDF64 allows to skip ripples suppressing if WF=1; it is often called the Box Car Window. Both functions are accessible in the **“W.F.”** box.
One may set the range and step of *G(r)* function. Data can be stored in the “*.gr” file.

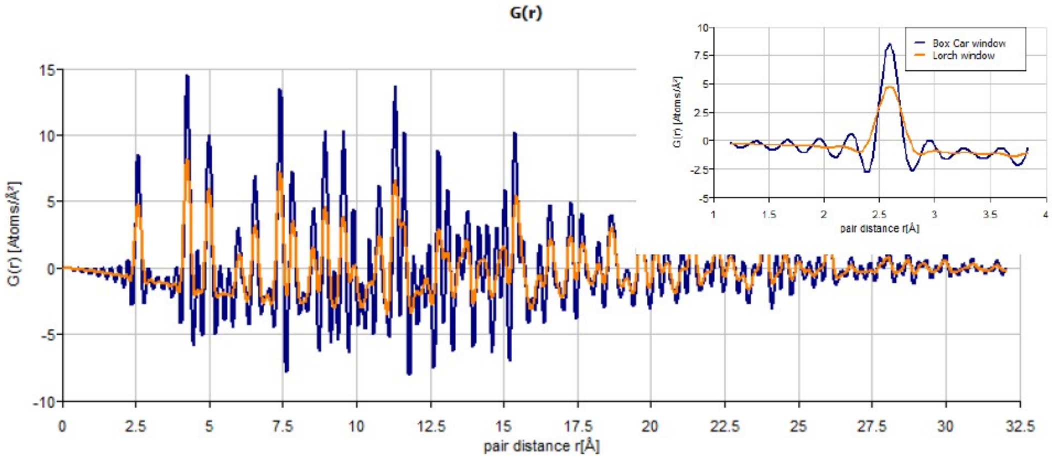


Fig.3-6. G(r) calculated with Box Car window (blue) and Lorch (window) orange

4. Data fitting

4.1. Short description

The data fitting procedures are designed to support the analysis of powder diffraction data based on X-Ray technique. On the contrary to the nowadays software which is mainly focused on elaboration of research results for grains with typical size more than 1 µm, the NanoPDF64 is prepared to work with diffraction data of nanoparticles. Nanoparticle crystal structures require a new approach to their analysis; in that case bulk structure is strongly influenced by surface. It manifests by deviations from perfect lattice structure dependent on size of grain and crystallographic directions. The classical analysis is often inadequate for structure determination of nanograins.

The NanoPDF64 fitting procedure is dedicated to real space analysis and quantitative examination of G(r) function.

4.2. Technical details

The fitting code have been placed in the separate console application *"diffdatafit.exe"*. In general the *diffdatafit* is called by the NanoPDF64 which is responsible for preparing input data and receiving the results of computations.
The input data are stored in the "conffit.txt" file. This is a text file created in the same directory as a file with diffraction pattern. The output data are sent by a named pipe; it's possible to create and save the results as a text file.
The fitting is based on the Levenberg–Marquardt (LM) algorithm (see e.g.: https://en.wikipedia.org/wiki/Levenberg%E2%80%93Marquardt_algorithm). This is a method prepared to solve non-linear least squares problems especially in least squares curve fitting. The LM algorithm must be supported by the properly selected function suited to a given problem. The function depends on a set of fittable parameters. To start a minimization, the user has to provide an initial guess. The LM algorithm needs derivatives of the fitting function as well; based on derivatives the Jacobian matrix is built. The JM

greatly speed up a convergence of curve fitting. In our case analytical derivatives are not a good solution as they are complex.

In the *diffdatafit.exe* the Jacobian matrix is calculated numerically without analytical approach. It allows to significantly save computation time with a slightly bigger fitting error.

The fitting routines of LM algorithms are supported by the GSL 1.16 library (homepage: https://www.gnu.org/software/gsl/) compiled for the MS Windows system with the Cygwin environment.

The *diffdatafit* has been created under the Qt Creator 5.1 environment.

5. How to fit data

Data fitting procedure is based on a model of perfect lattice generated by the user. The procedure of building was described in sections 2.2., 2.3. The next step is histogram creation. The user decides which distribution is suited to a given problem: the pair distribution histogram PDH or the radial distribution histogram RDH. The selected distribution is crucial for the next step; depending on the distribution PDH/RDH different types of functions are chosen for fitting. The flowchart of fitting is in Fig.5-1.

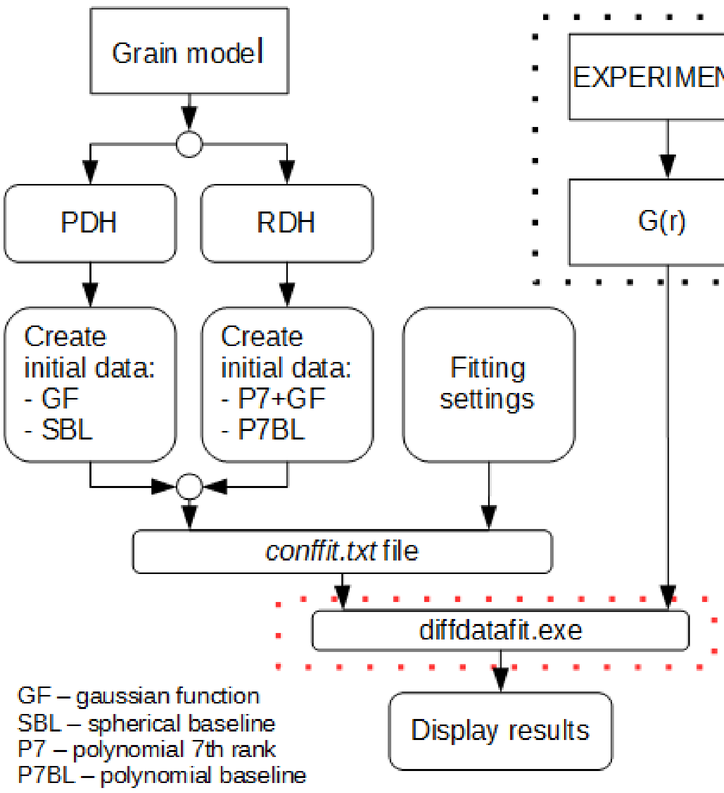


Fig.5-1. The flowchart of fitting routings

In the case of PDH it is assumed that the sample consists of spherical nanograins with the same size. In the other cases (non – uniform distribution of sizes, non – spherical shapes) the RDH should be used. It must be noted that to use PDH deviations from the spherical shape cannot be arbitrarily large.

The PDH/RDH histogram gives values for fitting of peak positions (directly taken to fitting procedure) and their amplitudes. It must be noted that “PDH/RDH” histograms must be combined together before the fitting to yield proper initial values of fitting (see Fig.5-2). The detailed information about the role of PDH/RDH distribution and construction of the fittable functions are given in “*NanoPDF64 - A software for theoretical calculation and quantitative real space analysis of powder diffraction data of nanocrystals, K. Skrobas, S. Stelmakh, S. Gierlotka and B. Palosz, Computer Physics Communications - in preparation.*

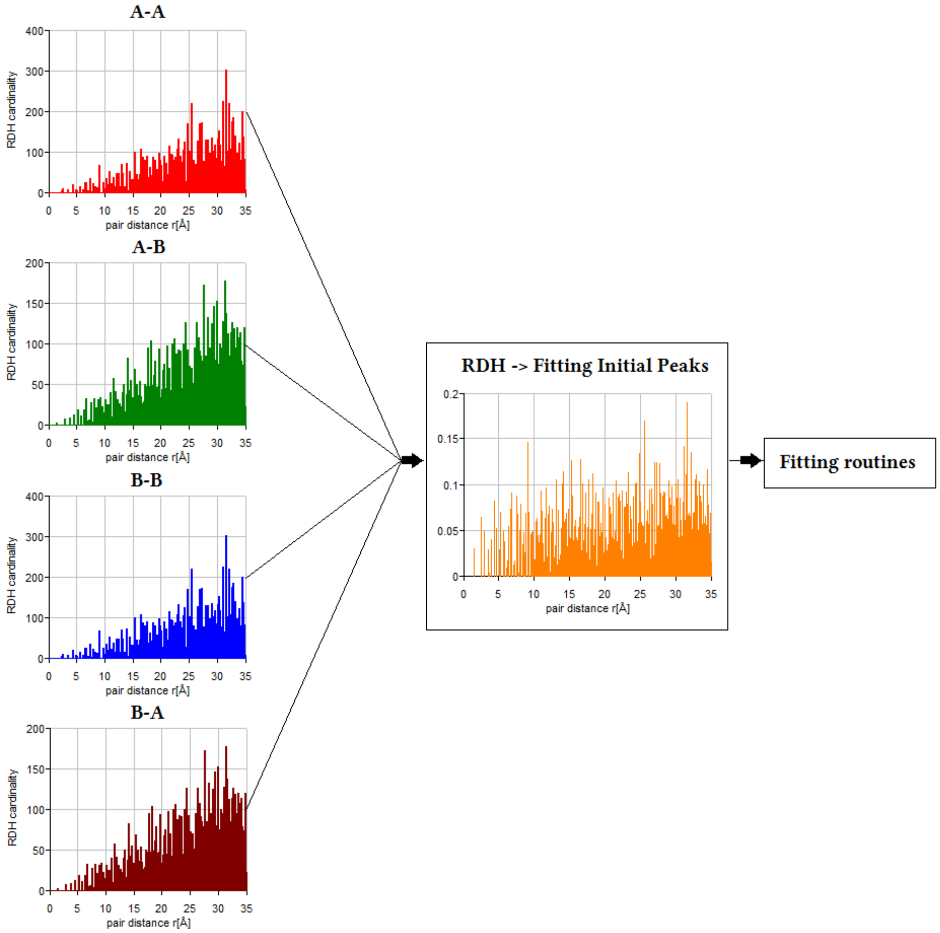
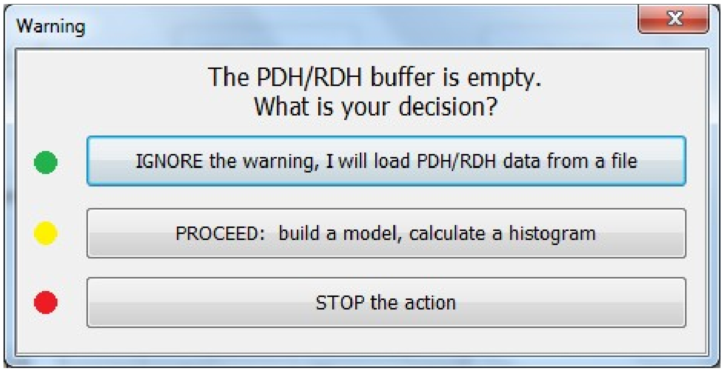


Fig.5-2. Partial histograms calculated for spherical grain and combined RDH distribution recalculated to met the conditions required by fitting routines.

The fitting option of NanoPDF64 is accessible after click the “Tools →Fitting” submenu. If PDH/RDH distribution was not computed the warning dialog (Fig.5-3.) appears. The one should make decision to do PDH calculations in background by press the “OK” button (it is assumed that the model is created), stop action by press the “Cancel” button or to proceed by press the “Ignore” button. In the latter case the distribution should be load from a file (the “Open PDH/RDH file” button).

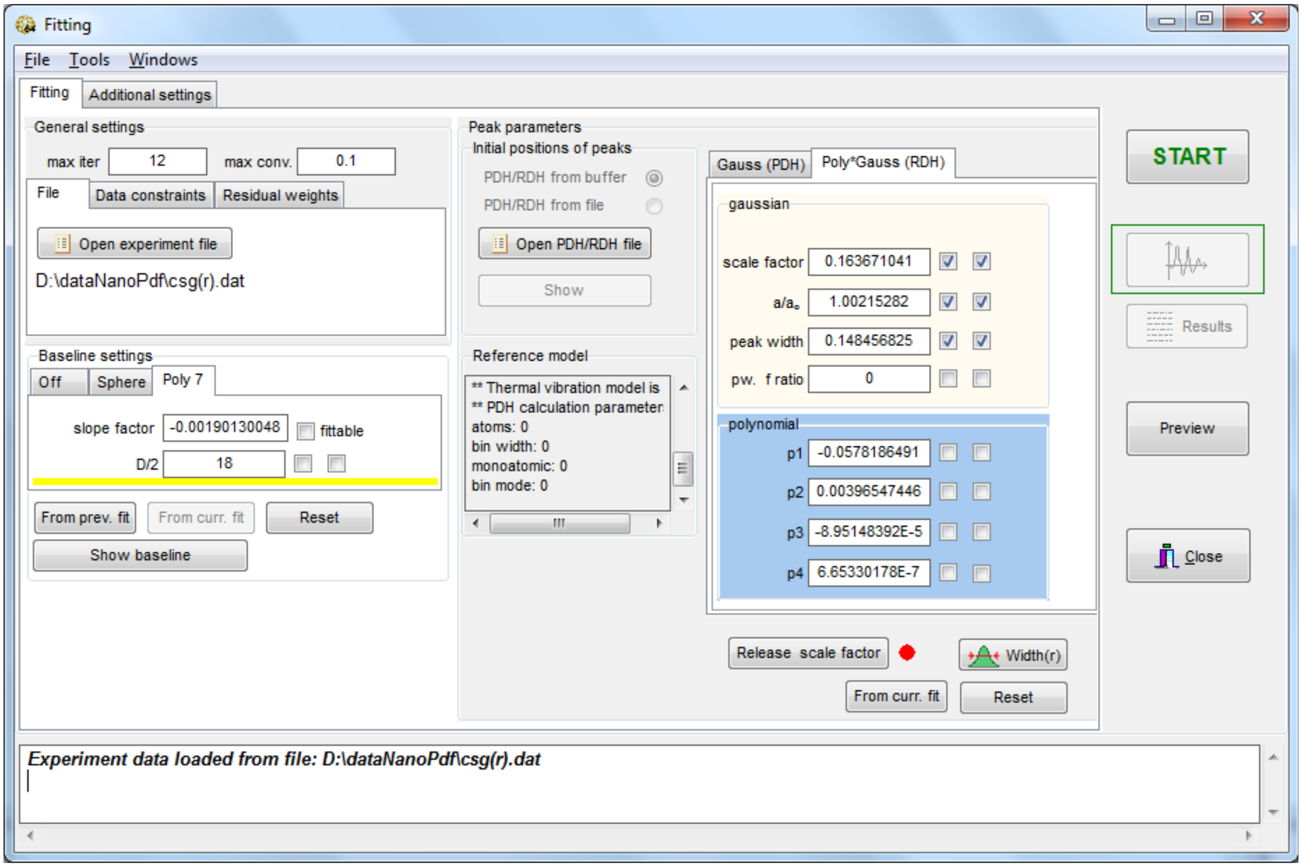
Other way to support the fitting software with PDH/RDH distribution is loading a file where data are stored. More about it is in subsection 5.2.



The PDH/RDH buffer is empty.
What is your decision?

Fig.5-3. The "Warning" dialog is shown if histogram buffer is empty

The “Fitting” window is shown in Fig.5-4. Generally it consists of two pages: “Fitting” and “Additional settings”.
The most important settings are placed on the “Fitting” page. The typical way to start fitting operations is described below in a few steps.



max iter: 12
max conv.: 0.1

D:\dataNanoPdf\csg(r).dat

slope factor: -0.00190130048 ☐ fittable
D/2: 18 ☐ ☐

● PDH/RDH from buffer
○ PDH/RDH from file

** Thermal vibration model is
** PDH calculation parameter
atoms: 0
bin width: 0
monoatomic: 0
bin mode: 0

scale factor: 0.163671041 ☑ ☑
a/a₀: 1.00215282 ☑ ☑
peak width: 0.148456825 ☑ ☑
pw. f ratio: 0 ☐ ☐

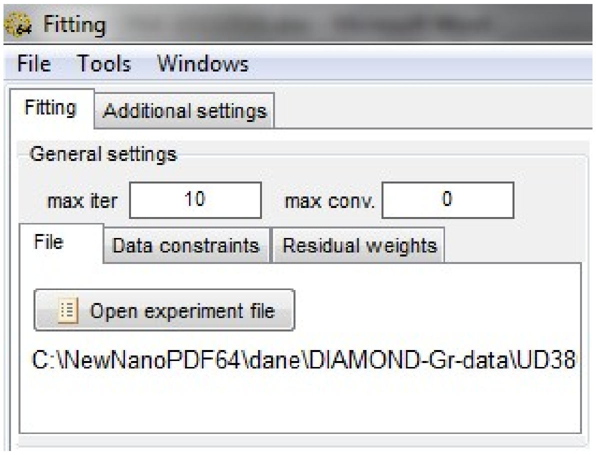
p1: -0.0578186491 ☐ ☐
p2: 0.00396547446 ☐ ☐
p3: -8.95148392E-5 ☐ ☐
p4: 6.65330178E-7 ☐ ☐

Experiment data loaded from file: D:\dataNanoPdf\csg(r).dat

Fig.5-4. The "Fitting" window interface

5.1. Loading experimental data

The experimental data to be fitted during the first run must be loaded from file. The next runs call the value from the previous one. The input file operations are placed on the "File" page in the "General settings" box (Fig.5-5.).



max iter 10
max conv. 0
C:\NewNanoPDF64\dane\DIAMOND-Gr-data\UD38

Fig.5-5. The view of "File" page after opening experimental data file

The user should click on the "Open experiment file" and select a "*.dat" file. The format of "dat" file should consists of X-Y data placed in two columns.

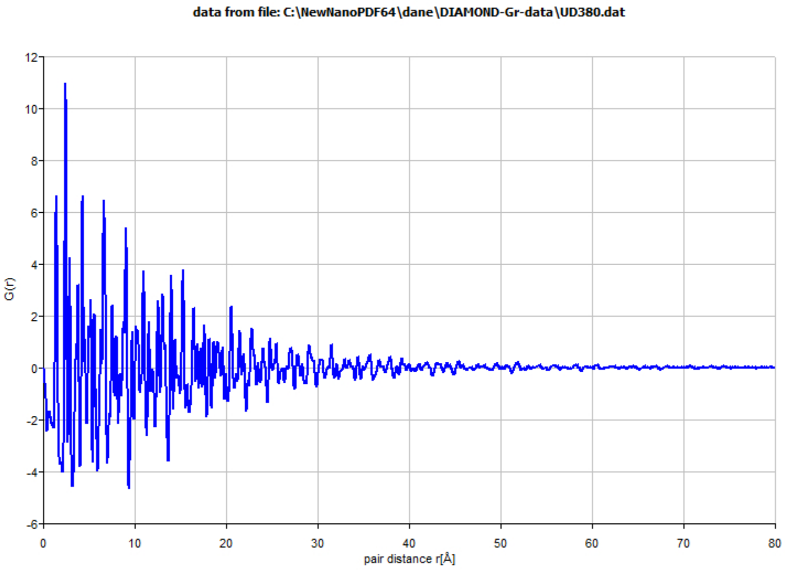
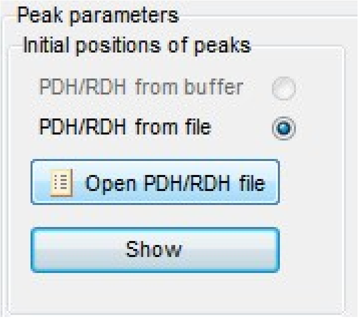


Fig.5-6. An example of experimental G(r) data

If loading is successful the path to the selected file is displayed on the label placed below the button. The user can double click on the label to see the graphic representation of data (Fig.5-6).

5.2. PDH/RDH data file

If PDH/RDH data is loaded from a file the user must find and click the “Open PDH/RDH file” button placed in the “Initial positions of peaks” box (Fig.5-7). The “Initial “ block allows to select between the PDH/RDH buffer and file if buffer was written by computations of PDH in the Main window. The data can be shown after click on the “Show” button.



Peak parameters

Initial positions of peaks

PDH/RDH from buffer ○

PDH/RDH from file ●

Fig.5-7. The view of "Initial positions of peaks" box.

5.3. Preview

Before fitting use of preview operation is recommended. The preview operation displays a graph with a function controlled by parameters and graphs according to settings placed on the “Additional Settings” page.

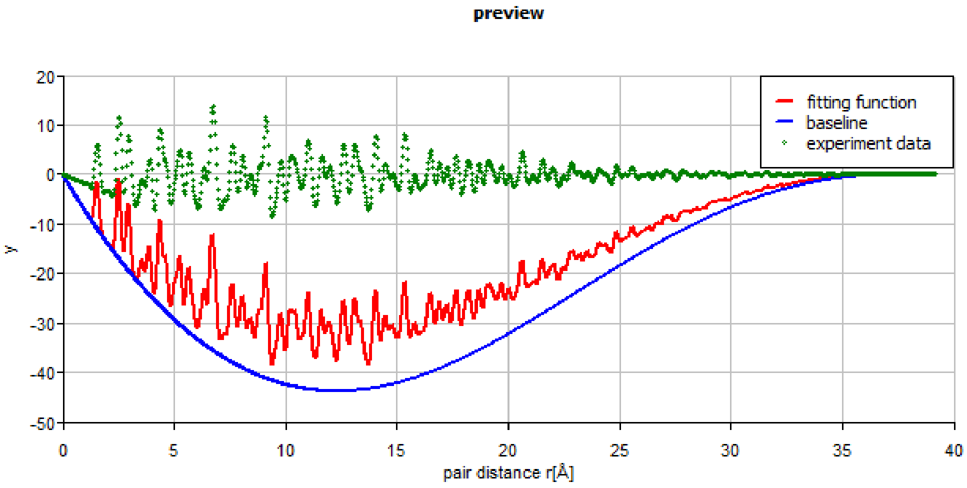
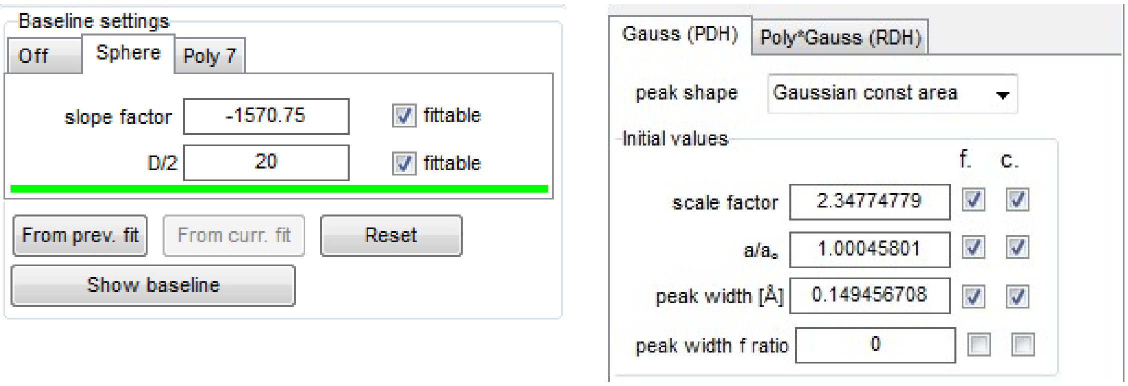


Fig.5-8. The preview of data points before fitting

5.4. Adjusting initial parameters

Each parameter besides the name and value has two checkboxes (Fig.5-9). The checkbox placed on the left controls if the parameter if fittable (checked) or not (unchecked). The checkbox on the right tells if the parameter is coupled for all fitting functions in ensemble (checked) or not (unchecked). In most cases the parameters should be coupled.


(a)

(b)

Baseline settings: Sphere

slope factor -1570.75 ☑ fittable

D/2 20 ☑ fittable

Gauss (PDH)

peak shape: Gaussian const area

Initial values

		f.	c.
scale factor	2.34774779	☑	☑
a/a_0	1.00045801	☑	☑
peak width [Å]	0.149456708	☑	☑
peak width f ratio	0	☐	☐

Fig.5.9. Initial parameters box for baseline (a) and for gaussian type functions (b)

The fitting parameters are grouped in two boxes:

1. Baseline settings
2. Peak parameters

Baseline functions are closely related to autocorrelation functions, see “*NanoPDF64 - A software for theoretical calculation and quantitative real space analysis of powder diffraction data of nanocrystals, K. Skrobas, S. Stelmakh, S. Gierlotka and B. Palosz, Computer Physics Communications - in preparation,*.

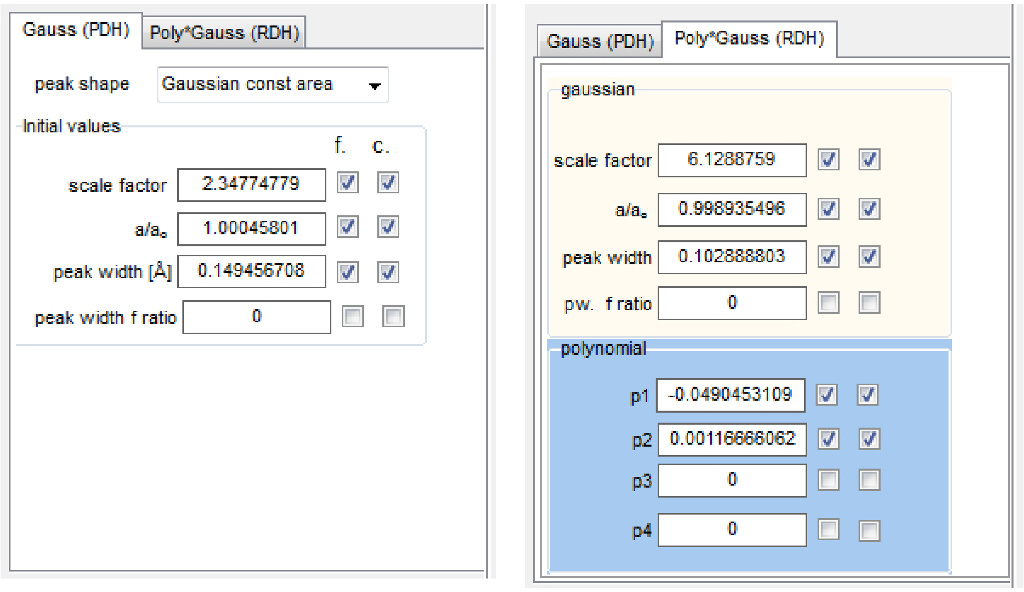
The user can select three modes of baseline:

1. Off (Disabled)
2. Sphere
3. Poly7

The “Off” mode generally is not recommended; it allows only to fit the position of peaks. The second case was designed for G(r) of spherical shape nanograins. Two initial parameters are adjustable: the slope factor and radius (D/2), Fig.5.9a. The slope factor scales the entire baseline. It’s name reflects the fact that it is equal to the slope of BL near the (0,0) point.

The “Poly7” baseline was designed to control the behavior of peaks in the case of G(r) for non – spherical shape nanograins..
The peak parameters are placed in two groups (Fig.5-10):

1. Gauss (PDH)
2. Poly*Gauss (RDH)



(a)

peak shape: Gaussian const area
Initial values (f. c.)
scale factor: 2.34774779 ☑ ☑
a/a₀: 1.00045801 ☑ ☑
peak width [Å]: 0.149456708 ☑ ☑
peak width f ratio: 0 ☐ ☐

(b)

gaussian
scale factor: 6.1288759 ☑ ☑
a/a₀: 0.998935496 ☑ ☑
peak width: 0.102888803 ☑ ☑
pw. f ratio: 0 ☐ ☐

polynomial
p1: -0.0490453109 ☑ ☑
p2: 0.00116666062 ☑ ☑
p3: 0 ☐ ☐
p4: 0 ☐ ☐

Fig.5-10. The view of "Gauss" (a) and "Poly*Gauss" (b) pages

To select a group one should click the button “Gauss” or “Poly*Gauss” (PG). The “Gauss” group works well for nanograins with spherical shape. In that case two shapes of peak can be selected: *Gaussian* and *Gausian const area* (GCA) from the “peak shape” combo box. The first case assumes gaussian peak according to (simplified) formula:

$$gauss(x)_i = scf \cdot pdh(r_i) \cdot \exp\left(-\left(\frac{x - \frac{a}{a_o} \cdot r_i}{pw + r_i \cdot f} \right)^2 \right) \qquad (5.1)$$

where: *scf* – the scale factor, *a/a*$_o$ – the ratio: peak position after fitting to initial peak position, *pw, f* –parameters controlling the peak width, *pdh(i)* – i – th value taken from the pair distribution histogram
The GCA shape is given by:

$$y = \sqrt{\frac{\ln(2)}{\pi}} \frac{a_0}{a_2} \left[-\ln(2) \left(\frac{x - a_1}{a_2} \right)^2 \right] \qquad (5.2)$$

The “Poly*Gauss” group is based on fitting function that combines Gaussian and polynomial of 7–th order:

$$pg(x)_i = \left[(x-D) \cdot \left(\sum_{j=0}^{5} p_j \cdot (x^j - D^j) \right) \right] \cdot scf \cdot \exp\left(-\left(\frac{x - \frac{a}{a_o} \cdot pdh(i)}{pw + pdh(i) \cdot f} \right)^2 \right) \quad (5.3)$$

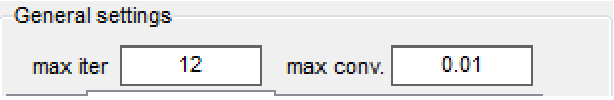
where: $p_0=1$, D – the diameter parameter, $p_1 \ldots p_5$ – other parameters of polynomial. The PolyGauss works well for non – spherical nanograins. The PolyGauss fitting function and its derivative is equal 0 when $x=D$.
In both cases i.e. the Gauss and PolyGauss ensembles, it is assumed that fitting functions are equal 0 if $x>D$.

5.5. Fitting interruption conditions

Before fitting one can set the values which control the conditions of computing interruption. There are three cases:

1. Maximum number of iterations
2. Convergence
3. Errors: absolute and relative

If any of above conditions are met *diffdatafit.exe* finishes computations and sends error status and the final data if : fitting was successful or error signalization was disabled. The user has a possibility to ignore the fitting errors if the “ignore fitting errors” checkbox (placed on the “Additional settings → Actions …” box) is checked.
The “number of iterations” and “convergence” edit windows are placed in the “General settings” box (Fig.5-11).



General settings

max iter 12

max conv. 0.01

Fig.5-11. The "max iter" and "max conv." edit windows view

The *diffdatafit.exe* interrupts the fitting if the reached convergence is below the value indicated by the user. The convergence test is based on chi – squared test. For each step program calculates the sum according to the formula:

$$\delta = \frac{\sum_i (y_{ic} - y_{ip})^2}{N - N_p} \tag{5.4}$$

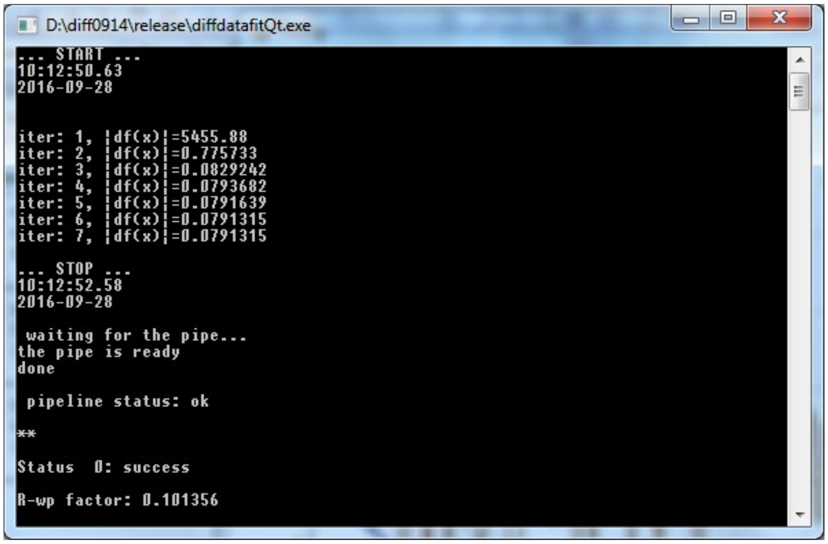
where: y_c stands for current fit, y_p – the previous fit, N – number of experimental data, N_p – number of parameters. The $\delta<1$ indicates good fit.
The absolute and relative errors are placed in the “Additional settings → Additional fitting parameters” group. The meaning of errors is explained in the GSL 1-16 manual (page 424):

> *“... function tests for the convergence of the sequence by comparing the last step dx with the absolute error epsabs and relative error epsrel to the current position x. The test returns GSL_SUCCESS if the following condition is achieved,* $|dx_i| < epsabs + epsrel\,|x_i|$ *for each component of x and returns GSL_CONTINUE otherwise”*

where x is returns the current vector with the fit parameters.
The more details about the GSL fitting routines one can find in the manual placed on the internet site: https://www.gnu.org/software/gsl/manual/html_node/

5.6. *Fitting (the first run)*

The fitting operation begins after the click the “START” button.



```
... START ...
10:12:50.63
2016-09-28


iter: 1, ¦df(x)¦=5455.88
iter: 2, ¦df(x)¦=0.775733
iter: 3, ¦df(x)¦=0.0829242
iter: 4, ¦df(x)¦=0.0793682
iter: 5, ¦df(x)¦=0.0791639
iter: 6, ¦df(x)¦=0.0791315
iter: 7, ¦df(x)¦=0.0791315

... STOP ...
10:12:52.58
2016-09-28

 waiting for the pipe...
the pipe is ready
done

 pipeline status: ok

**

Status  0: success

R-wp factor: 0.101356
```

Fig.5-12. The *diffdatafit* console window during run presents partial results of fitting and status after finished calculations

To observe the status of computations (Fig.5-12) the “show datafit.exe window” checkbox should be checked. The checkbox has been placed in the Additional settings → Actions …” box. During calculations the NanoPDF64 is waiting for finalization of fitting task. It’s signalized by the change of the “START” button to the “STOP” button with the blinking red rectangle.

During fitting computations the number of iterations and convergence value are shown. After fitting the “R-wp” factor is calculated based on formula:

$$RWP = \frac{\sum_i (y_i - y_{ie})^2}{\sum_i y_{ie}^2} \tag{5.5}$$

where y_{ie} – experimental data point. The RWP factor about 0.1÷ 0.2 indicates very good fit.

Computations can be stopped by the user at any moment by closing the *diffdatafit* console window or clicking the “STOP” button.

5.7. *After fitting*

After successful fitting the results are sent back to NanoPDF64. The program enables buttons serving for results presentation. i.e.: the “results, graphical mode” and “results, text mode” buttons (see Fig.5-13).

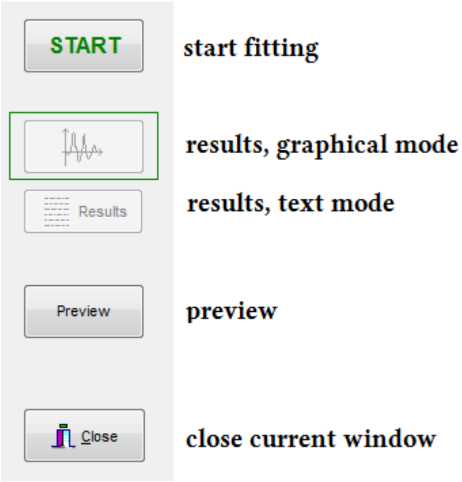
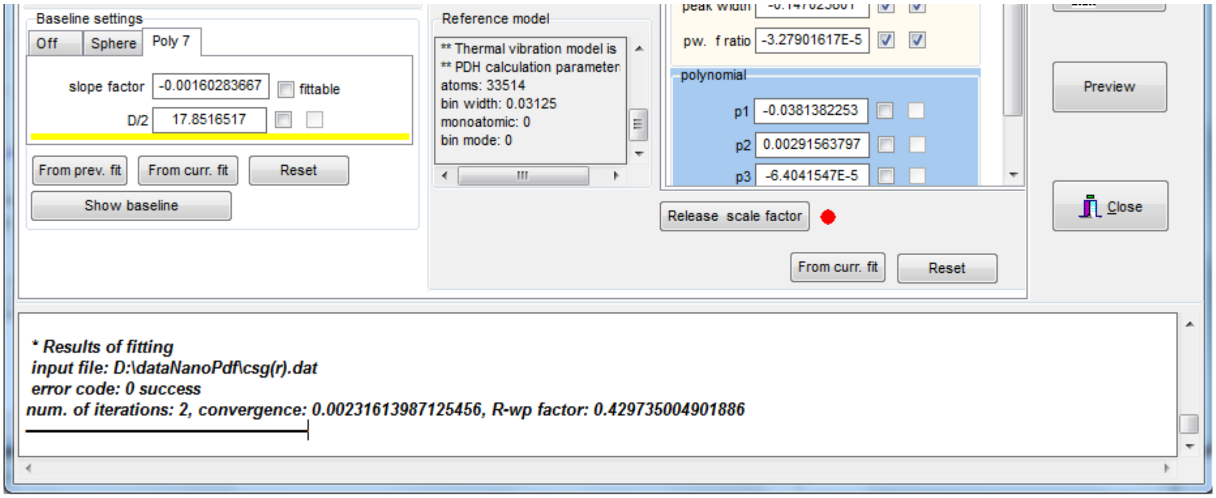


Fig.5-13. The control panel of "Fitting" window

The status of fitting is displayed in the “Memo” box placed at the bottom of the “Fitting” window (Fig.5-14).



slope factor -0.00160283667 ☐ fittable

D/2 17.8516517 ☐ ☐

```
** Thermal vibration model is
** PDH calculation parameter
atoms: 33514
bin width: 0.03125
monoatomic: 0
bin mode: 0
```

pw. f ratio -3.27901617E-5 ☑ ☑

p1 -0.0381382253 ☐ ☐

p2 0.00291563797 ☐ ☐

p3 -6.4041547E-5 ☐ ☐

```
* Results of fitting
input file: D:\dataNanoPdf\csg(r).dat
error code: 0 success
num. of iterations: 2, convergence: 0.00231613987125456, R-wp factor: 0.429735004901886
```

Fig.5-14. Status of fitting after run shown in the "Memo" box

The user can display the results by clicking the “results, graphical mode” button. There is also an option to begin the graphical presentation (Fig.5-15) without clicking if the “show diagram after fitting” checkbox is checked. The checkbox has been placed on the “Additional Settings → Default actions after calculations” group box. There are also settings to control displaying other useful information, e.g.: experimental data points, error curve or peaks position.

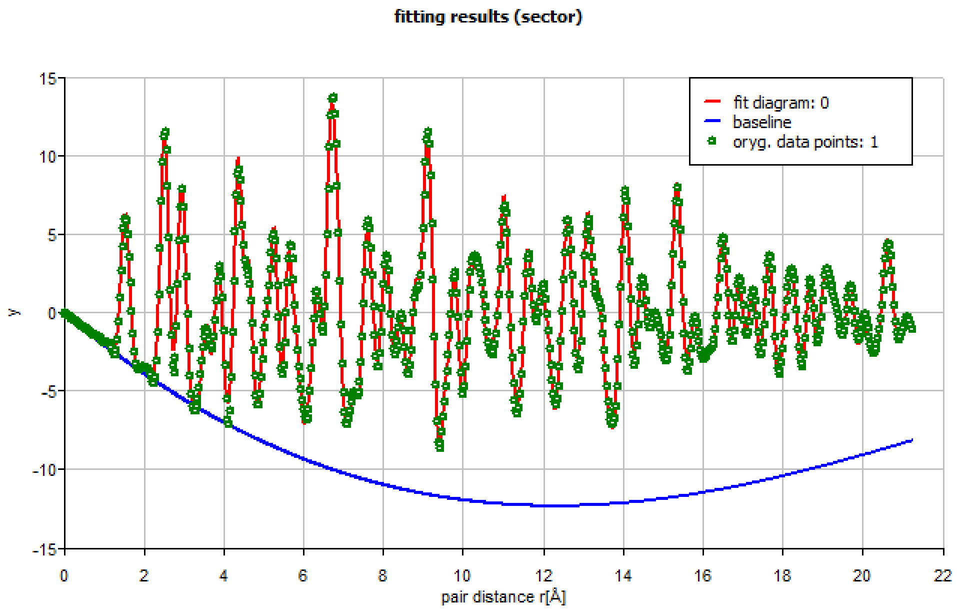


Fig.5-15. An example of successful fitting

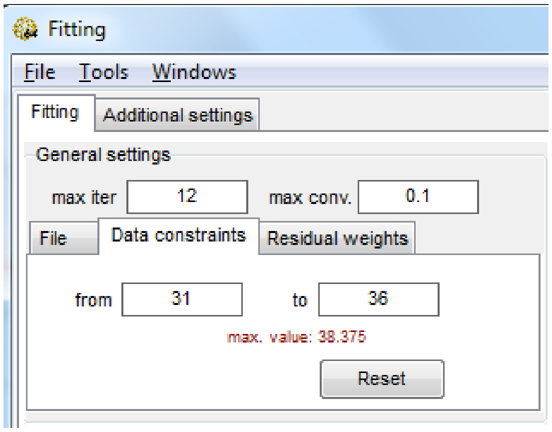
5.8. Fitting (the next runs)

If fitting is to be continued with parameters of the previous run the user should click on the “From curr. fitt” buttons. There are 2 buttons; the first one calls parameters for the “Baseline” function and the second one for the “Gauss” or “PolyGaussian” mode. There is also an option to enable the automatic parameters updating. The updates are enabled if the “update starting parameters after fitting” checkbox is checked; the component has been placed on the “Additional Settings → Default actions after calculations” group box.

5.9. Other fitting options

5.9.1. Experimental data constraints

By default, experimental data are taken to fitting in its full range but there is possible to limit the range. In that case the user should fill in the “from” and “to” edit windows placed on the “Data constraints” page (Fig.5-16). The page is placed on the “General settings” box.

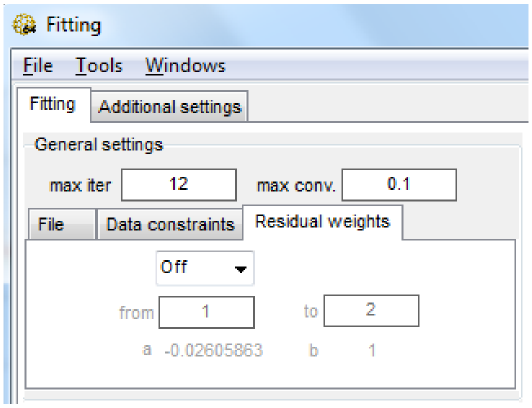


max iter: 12
max conv.: 0.1
from: 31
to: 36
max. value: 38.375

Fig.5-16. The view of "Data constraints" page

5.9.2. Residual weight

The “Residual weights” (RW) page (Fig.5-17) controls the influence of fitting local errors on total fitting error. It allows the fitting routines to apply higher weights to G(r) at larger distances. The local errors are depended on a peak position. By default the RW is off; it means that all errors are taken with the same weight (i.e. weight are equal 1). If option is enabled the values of the weights are controlled by the linear “ax+b” function. The user can set parameters of RW placed on the “from” and “to” edit windows. The “from” value refers to the beginning of the experimental data, the “end” value refers to the final part. The inner procedure based on the RW values and the “Data constraints” parameters calculates the “a” and “b” values of the linear function. Both values are shown under the “from/to” edit windows.



max iter 12
max conv. 0.1
Off
from 1 to 2
a -0.02605863 b 1

Fig.5-17. View of the "Residual weights" window

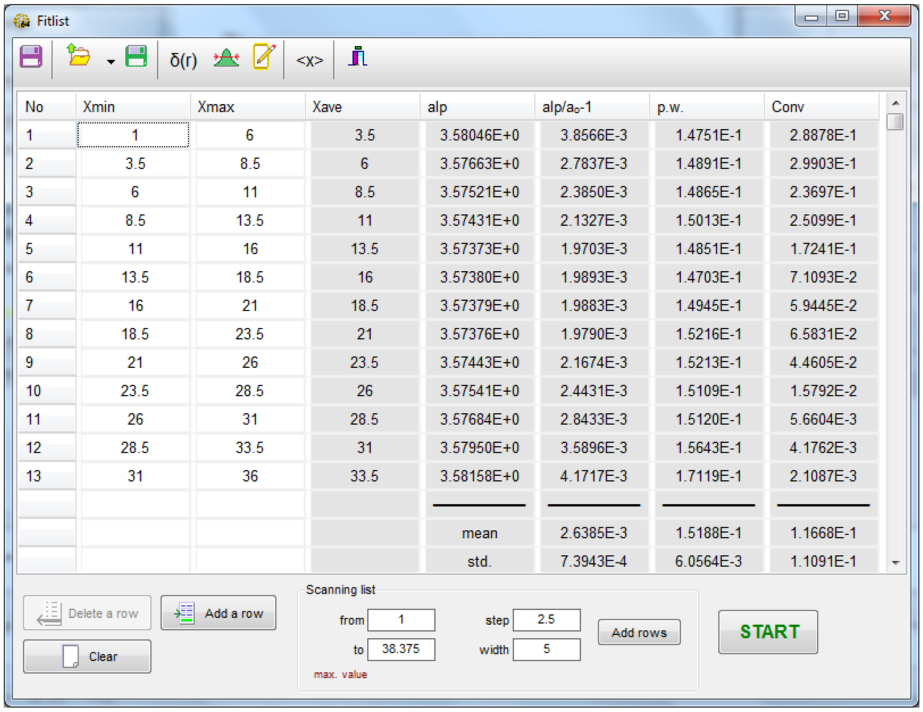
5.10. Region fitting

The “Region fitting” (RF) is a tool designed to allow (Fig.5-18) the user to divide the fitting region for subregions and fitting them separately. The RF is accessible by the “Tools→Region fitting” submenu.

During the first run the RF (Fig.5-16) opens a new window with an empty array. The empty array may be filled in by hand (white areas) or by the procedure started by the “Add rows” button placed on the “Scanning list” box. The “Xmin” and “Xmax” columns indicate the boundaries of a subregion. The another columns (grey areas) are filled in during fitting. The “Scanning list” box creates equal width subregions; the value of width is set by the “width” edit window. The distance between subregions is controlled by the value shown in the “step” edit window. It must be noted that subregions may overlap.

To start “fitting” the “Start” button must be pressed. The initial fitting parameters and fitting options are taken from the parent “Fitting” window except the boundaries of the fitting subregion.

After fitting the “delta(r)” and “p.w.” can be presented in graphical mode if a proper button from the main toolbar is pressed.



No	Xmin	Xmax	Xave	alp	alp/a$_0$-1	p.w.	Conv
1	1	6	3.5	3.58046E+0	3.8566E-3	1.4751E-1	2.8878E-1
2	3.5	8.5	6	3.57663E+0	2.7837E-3	1.4891E-1	2.9903E-1
3	6	11	8.5	3.57521E+0	2.3850E-3	1.4865E-1	2.3697E-1
4	8.5	13.5	11	3.57431E+0	2.1327E-3	1.5013E-1	2.5099E-1
5	11	16	13.5	3.57373E+0	1.9703E-3	1.4851E-1	1.7241E-1
6	13.5	18.5	16	3.57380E+0	1.9893E-3	1.4703E-1	7.1093E-2
7	16	21	18.5	3.57379E+0	1.9883E-3	1.4945E-1	5.9445E-2
8	18.5	23.5	21	3.57376E+0	1.9790E-3	1.5216E-1	6.5831E-2
9	21	26	23.5	3.57443E+0	2.1674E-3	1.5213E-1	4.4605E-2
10	23.5	28.5	26	3.57541E+0	2.4431E-3	1.5109E-1	1.5792E-2
11	26	31	28.5	3.57684E+0	2.8433E-3	1.5120E-1	5.6604E-3
12	28.5	33.5	31	3.57950E+0	3.5896E-3	1.5643E-1	4.1762E-3
13	31	36	33.5	3.58158E+0	4.1717E-3	1.7119E-1	2.1087E-3
				mean	2.6385E-3	1.5188E-1	1.1668E-1
				std.	7.3943E-4	6.0564E-3	1.1091E-1

Scanning list

from 1

to 38.375

max. value

step 2.5

width 5

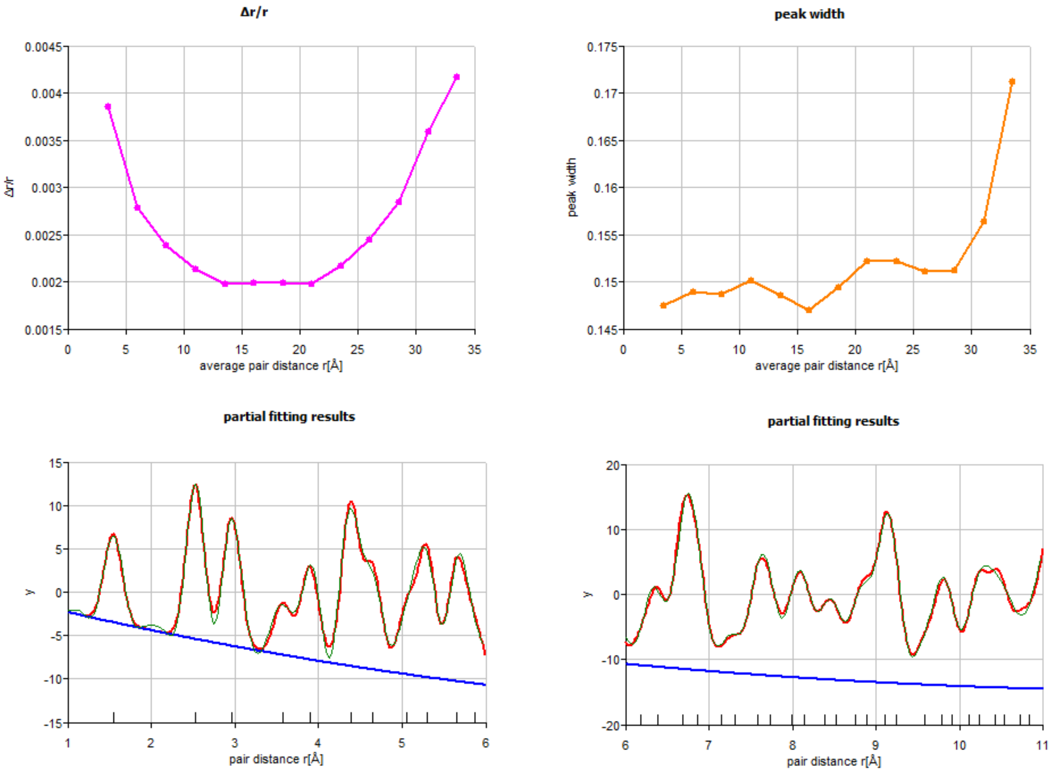


Fig.5-18. The "Fitlist" window and results of fitting for an example of G(r) function. The G(r) was calculated for a lattice distorted by introducing deviations based on Core – Shell model

5.11. Additional settings page

The “Additional settings page” (ASP) (Fig.5-19) allows to control the behavior of both applications: *diffdatafit* and NanoPDF64. The ASP has for boxes:

1. Actions of diffdatafit.exe program (ADP)
2. Additional fitting parameters (AFP)
3. Default actions before fitting (DAF)
4. Default actions after fitting (DAC)

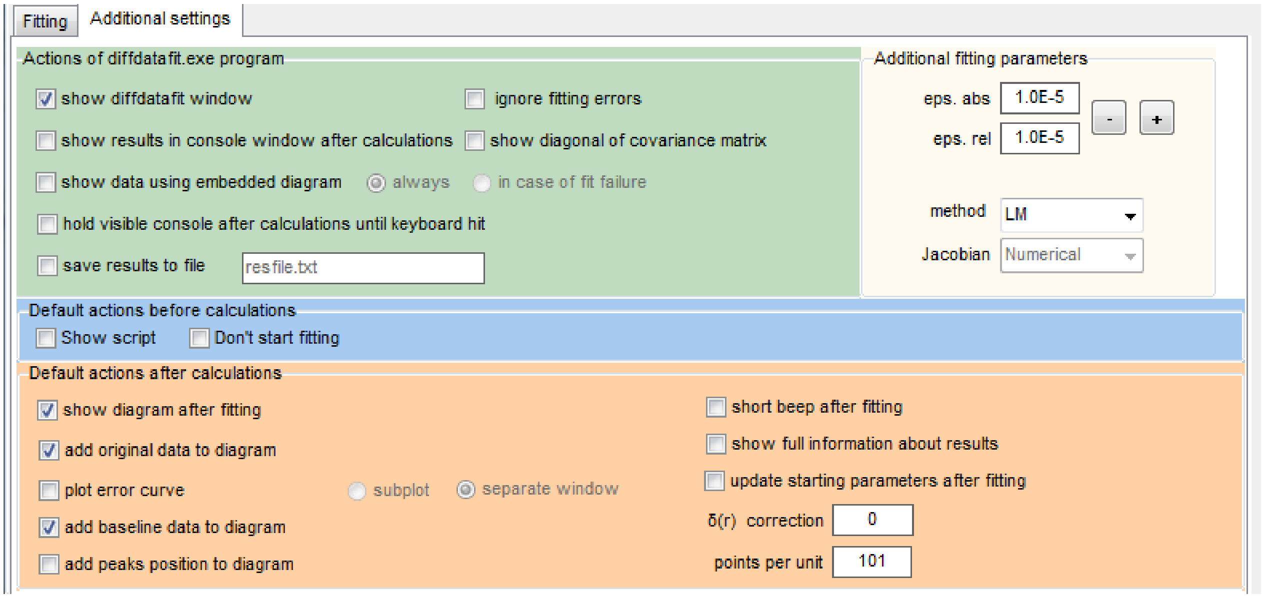
The name of actions are self explaining. From the ADP the most useful are the:

1. Show *diffdatafit* window – during fitting the console window of *diffdatafit* is kept visible; it allows to observe the progress of fitting
2. Ignore fitting errors – in the case of failure enforces *diffdatafit* to send back results; it’s useful in cases when the algorithm does not converge.

The AFP box allows to adjust the level of errors (see subsection 5.5) and select the fitting method: Levenber – Marquat or u LM. The ULM is not recommended; it gives very poor fit although is much faster than LM. The “Jacobian” combo box has informing character is limited to the “Numerical” option.

The DAF is only for testing purposes. The “show script” displays configuration file (conffit.txt) of fitting in the Memo window below ASP.

The DAC has options to control the graphical mode of data presentation (the first column) and some default actions to be done after fitting (the second column).



Actions of diffdatafit.exe program

☑ show diffdatafit window
☐ ignore fitting errors
☐ show results in console window after calculations
☐ show diagonal of covariance matrix
☐ show data using embedded diagram ● always ○ in case of fit failure
☐ hold visible console after calculations until keyboard hit
☐ save results to file resfile.txt

Additional fitting parameters

eps. abs 1.0E-5
eps. rel 1.0E-5
method LM
Jacobian Numerical

Default actions before calculations

☐ Show script
☐ Don't start fitting

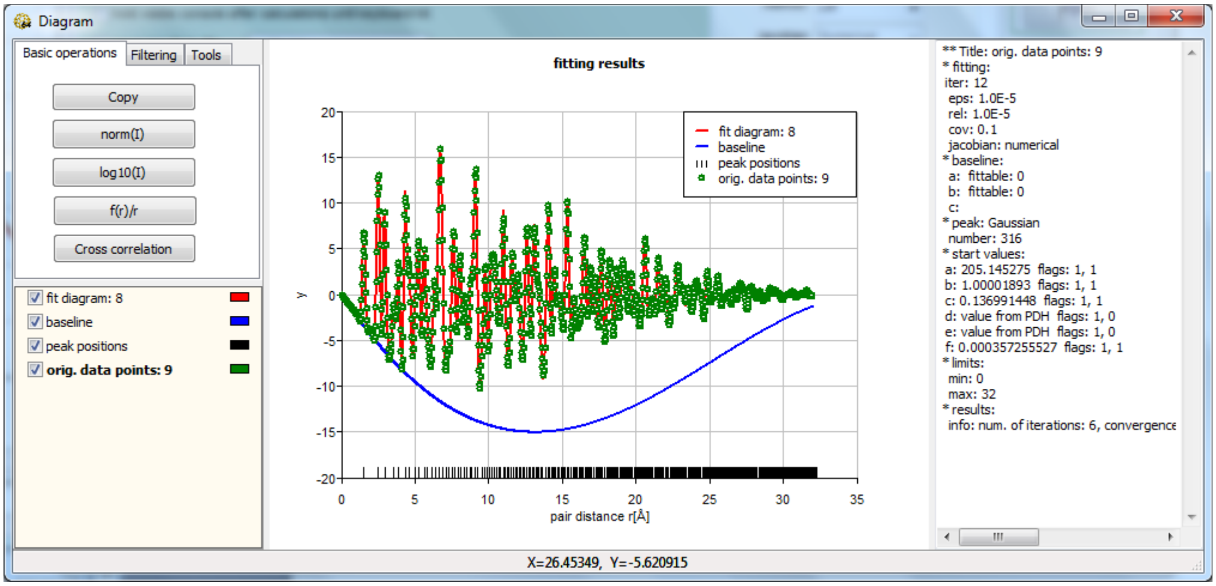
Default actions after calculations

☑ show diagram after fitting
☑ add original data to diagram
☐ plot error curve ○ subplot ● separate window
☑ add baseline data to diagram
☐ add peaks position to diagram
☐ short beep after fitting
☐ show full information about results
☐ update starting parameters after fitting
δ(r) correction 0
points per unit 101

Fig.5-19. The view of "Additional settings" page

6. Data presentation – graphical mode

For the user convenience the NanoPDF64 is equipped with its own system of data presentation in graphical mode (Fig.6-1). In general graphs are displayed in separate windows but it is possible to merge arbitrary number of diagrams in one place. There are multiple options available to customize the look of diagrams. Furthermore each graph window (GW) is equipped with tools for data post processing and extended information about results. The data can be saved in many different formats: ASCII or/and graphical format or/and copied to clipboard. Details are given below.



```
** Title: orig. data points: 9
* fitting:
 iter: 12
  eps: 1.0E-5
  rel: 1.0E-5
  cov: 0.1
  jacobian: numerical
* baseline:
  a:  fittable: 0
  b:  fittable: 0
  c:
* peak: Gaussian
  number: 316
* start values:
 a: 205.145275  flags: 1, 1
 b: 1.00001893  flags: 1, 1
 c: 0.136991448  flags: 1, 1
 d: value from PDH  flags: 1, 0
 e: value from PDH  flags: 1, 0
 f: 0.000357255527  flags: 1, 1
* limits:
  min: 0
  max: 32
* results:
  info: num. of iterations: 6, convergence
```

Fig.6-1. An example of data presentation in graphical mode of NanoPDF64

6.1. Operations hidden in the "Popup Menu"

The "Popup menu" is available by the right button mouse click (see Fig.6-2). The subitems allow to:

- Show memo – opens the "Memo" window on the right side of GW; the window consists the extended information about displayed results
- Show panel – opens the "Panel" on the left size of GW; more details about it are in section 6.3.
- Show parent window – in some cases when big number of GW covers a parent window the subitem allows to call its parent and bring it to front
- Show legend – enable/disable legend; the subdiagrams titles can be set by the "Diagram properties" subitem
- Show grid – enable/disable grid
- Graph title – the user can change the current graph title

- Diagram properties – the user can change: title, type (7 options: line, circle, …), style (avalaible if size is equal 1), size of type, color of each diagram displayed in GW; the keyboard shortcuts are available as well, see section …
- Publication – diagram prepared in the black – white look
- Axis X, Axis Y parameters – the user can set the new range, distance between ticks, title
- Axis Reset – recall the automatic values of axes ranges
- Print – very simple print of a given graph
- Set default window size – sets the default size for current GW; the subitem recalls values saved by “Save default window size”
- Save default window size – any time when the user changes the size of GW the new values of height and width can be saved; the next GW will be opened with the saved values of size or if the “Set default window size” subitem be selected
- Picture to clipboard – save the current view of GW to the system clipboard
- Data to/from clipboard – data in the text mode are sent/received from clipboard
- Save data to ASCII file – data are saved in two formats: the “2 columns (X and Y)” mode if the “dat” extension is selected or in the “multiple columns” mode if the “mdat” extension is selected; the number of columns is equal: 2 times number of diagrams
- Save image – the image is saved in ‘BMP’ format (always) or if script converter is given (see the “Settings window” of previous chapter) other formats are possible

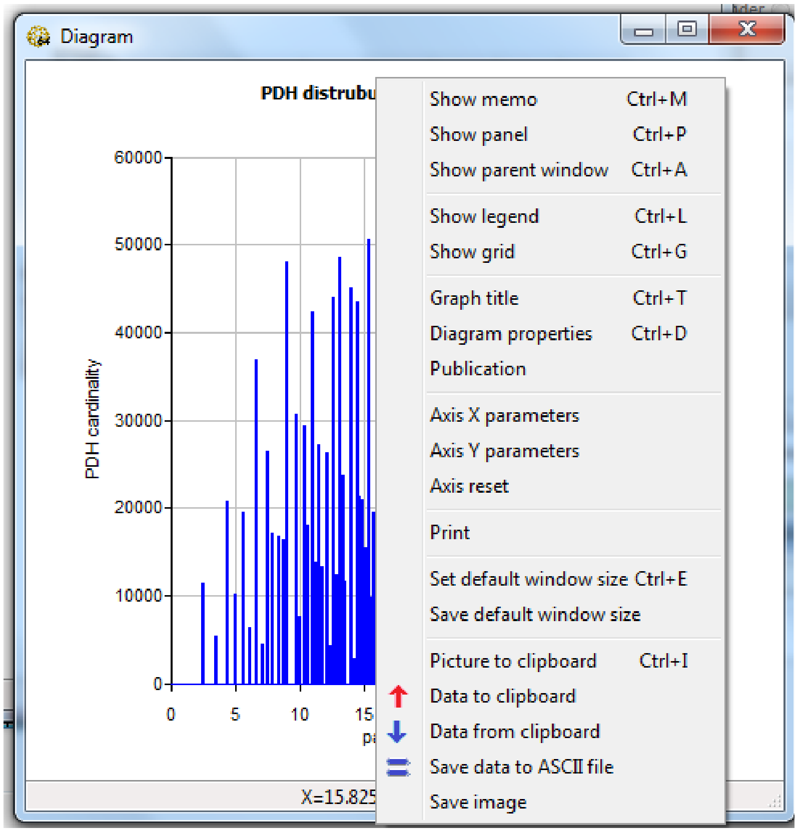


Fig.6-2. The expanded "Popup Menu" of GW window

6.2. Operations with the left mouse button

Two operations are available:

- Zoom in – if the "Ctrl" button is pressed the one can select the region to zoom (y – values are ignored); the zoomed region is displayed in a new GW window
- Merge diagrams – if the "Shift" button is pressed the "Drag & Drop" mechanism is activated; the user can copy whole content of GW to another GW window indicated by the mouse (see Fig. 6-3)

To remove a diagram from GW see the description of the checklist placed on the section 6.3.

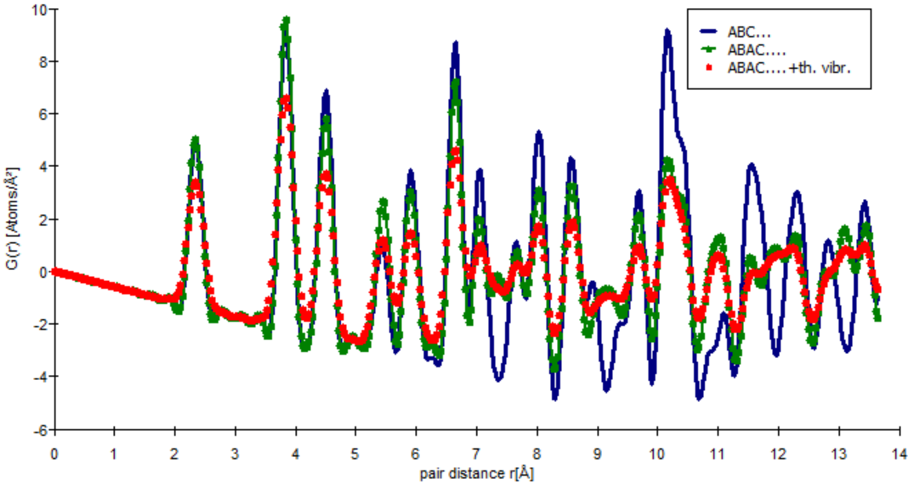


Fig.6-3. An example of diagrams merging

6.3. GW tools panel

In general the panel serves for post processing of diagrams data, consists of three pages: "Basic operations", "Filtering", "Distance" and the checkbox list.
The "Basic operations" page allows to select one of five operations:

1. copy – exact copy of GW
2. norm – data normalized to the maximum value; maximum values is set equal to 1
3. log10 – logarithm with base 10 of y – values; it is assumed the 0 value for values equal to 0
4. f(r)/r – values are divided by respective r
5. cross correlation – finds the cross correlation of data; it needs more than one diagram; after click the button user is asked to select the base for cross correlation operation; the default base is the last diagram (Fig.6-4)

Each operation creates a new GW where results are shown.

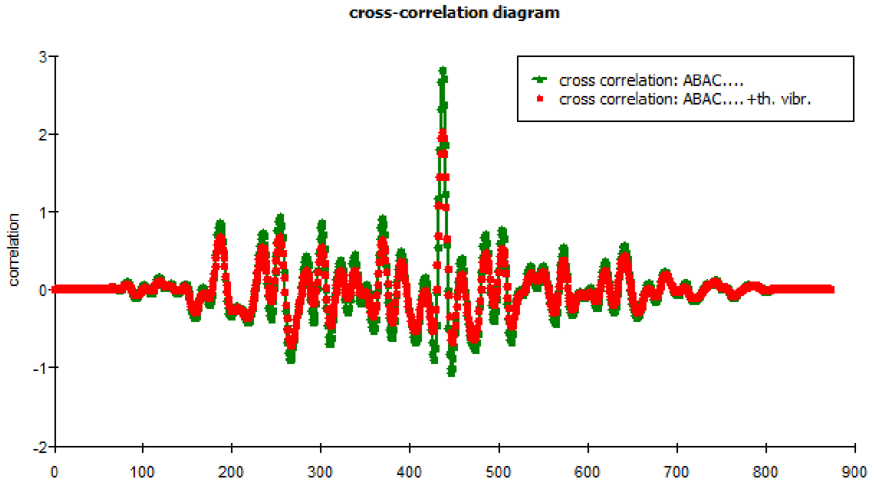


Fig.6-4. An example of data cross correlation

The “Filtering” page consists of two filtering operations:

1. Moving average
2. Savitzky – Golay 23

Both filters are designed to remove noise; they are low-pass filters. The “Moving average” (MA) filter is smoothing the data very effectively so, it may suppress some details; in that case the “Savitzky – Golay 23” filter is a better option.

Both operations needs to be supplied with filter kernel; the size of filter kernel is controlled by the user according to the formula: kerSize=2*N+1; the values of the kernel are set by the NanoPDF64 (in the case of MA filter it is a series of ones). The bigger size of the kernel the more details are removed. An example is shown in Fig.6-5.

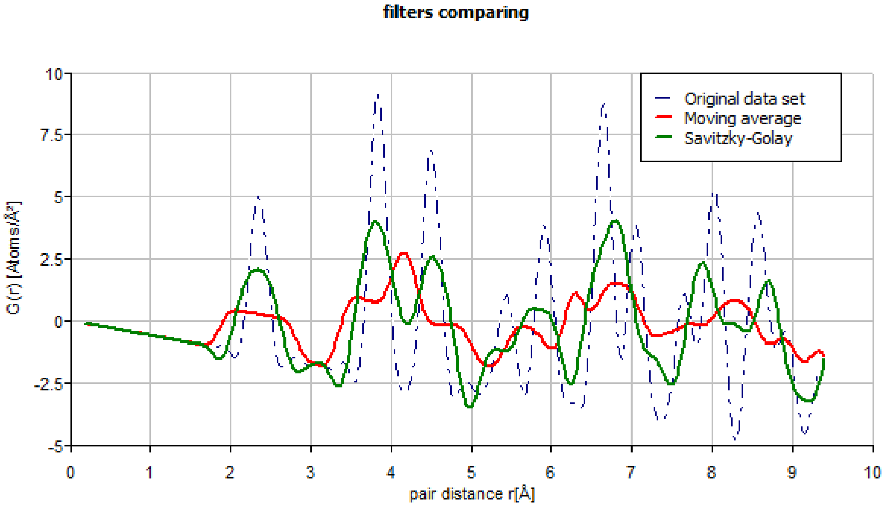


Fig.6-5. An example of different types of data filtering

The last page is the "Distance" page. It allows to read distances between pair of points placed by the user on the diagram (Fig.6-6). Some other information are shown as well: slope, Δx, Δy in the "Memo" window. To start the action the "Show distance" checkbox must be checked; next holding down the left mouse button the line connecting start point (green color) and the current point (red color) is drawn on the graph. Program doesn't hold values in memory.

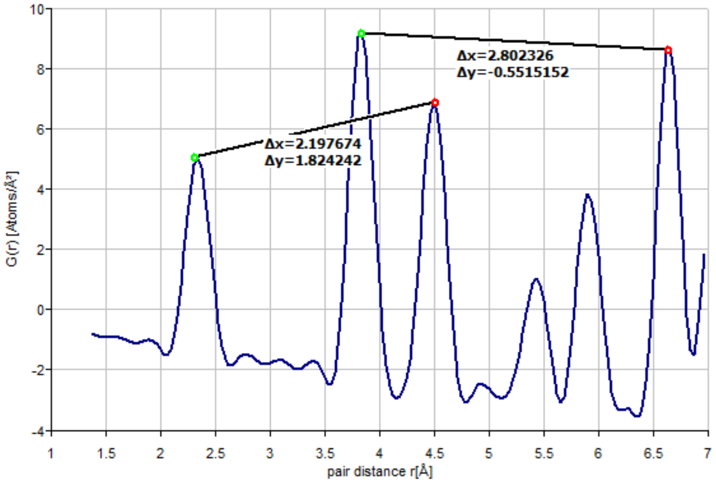


Fig.6-6. During presentation the diagram allows to measure distance between points selected by the user

The last component of GW tools panel is a checklist. The checklist consists of the checkboxes with the number equal to the number of diagrams coupled to the colored rectangles placed on the right margin. The title and color of rectangle of checkbox corresponds to the diagram properties. If checkbox is unchecked the corresponding diagram is not visible. The checkbox with bold font title indicates that the corresponding diagram can be removed. To remove the checkbox with corresponding diagram the user must call the Popup menu of the checklist (right button mouse click) and select the "Remove selected" subitem.

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