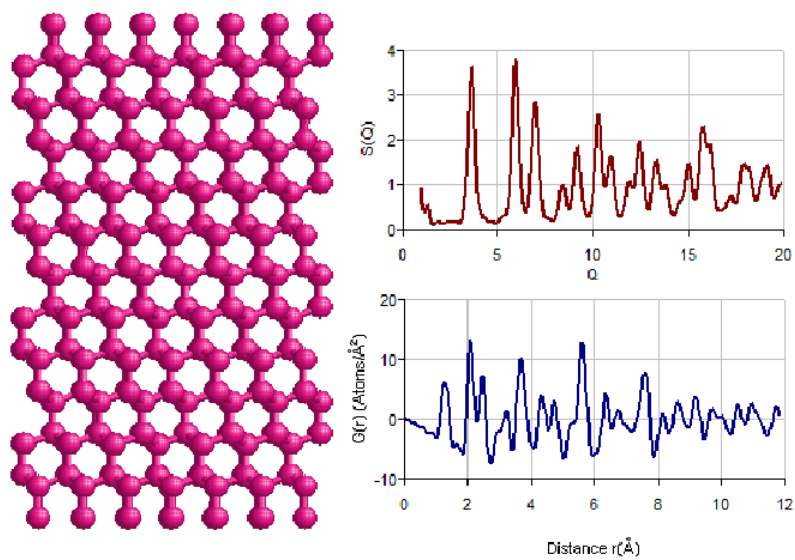


# ***NanoPDF***

program manual

version 1.0

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# Content

Introduction	6
1.1 Technical details	6
1.2 Configuration	7
1.3 General description of modeling	10
1.4 General description of calculations	11
Modeling	12
2.1 Building structure with a perfect lattice	12
2.1.1 Box 1 – atoms selection	12
2.1.2 Box 2 - structure (Bravais lattice)	13
2.1.3 Box 2 - lattice parameter	13
2.1.4 hcp structures	13
2.1.5 Building ABC sequence	15
2.1.6 Setting structural parameters of hcp model: Equivalent Cubic lattice parameter, EClp, (c/a) ratio and u	15
2.1.7 Box 3 – Grain shape (spherical or cylinder)	16
2.1.8 Box 3 – Dimension (radius)	16
2.1.9 Thermal vibrations	16
2.1.10 Building initial model – visualization and summary	18
2.2 Building structure with density modulation	19
2.2.1 Introducing density modulation	19
2.2.2 Parameters defining density waves	20
2.3 Projection of density modulation waves - derivation of $\delta(r)$ plot	22
2.4 Elaboration of experimental data - determination of apparent lattice parameter, $alp(r)$	25
Calculations	26
3.1 Introduction	26
3.2 PDH/ $\delta(r)$	27
3.3 Diffraction pattern	28
3.4 G(r)/PDF calculations	29
Mathematical background	31
4.1 Some elements of the theory of diffraction and PDF	31
3.2 Thermal vibration model	33
4.3 Metropolis algorithm	35
Data presentation	38
5.1 Introduction	38
5.2 Description of operations hidden under the left mouse button	40
5.3 Description of properties of mouse context menu	41

5.3.1 Full screen on/off.....	41
5.3.2 Save image.....	41
5.3.3 Save image to clipboard.....	41
5.3.4 Send image to mspaint.....	42
5.3.5 Title.....	42
5.3.6 Legend, Grid.....	42
5.3.7 Line(s) properties.....	42
5.3.8 Set axis X/Y parameters.....	43
5.3.9 Reset axis.....	43
5.3.10 Memo.....	43
5.3.11 Panel.....	43
5.3.12 Set default window size.....	45
5.3.13 Save size as default.....	45
5.3.14 Print BW, Print RGB.....	45
5.3.15 Save data to file.....	46
5.3.16 Save/Get data to/from clipboard.....	46
Technical details .....	47
6.1 File formats.....	47
6.1.1 Native formats - *.ndl, *.his, *.dij, *.diff, *.grp, *.sec.....	47
6.1.2 Program settings - Nanopdf.ini.....	47
6.1.3 Sfact.sft file.....	47
6.1.4 rms.scr file.....	48
6.2 Acknowledgment.....	48
6.2.1 List of auxiliary third-party programs.....	48
6.2.2 Others.....	48
6.3 Contact.....	48
Bibliography.....	49

## Abstract

NanoPDF 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:

1. modeling of spherical or cylindrical grains with diameter up to about ten nanometers
2. modeling of grains with implemented density waves,  $\rho(x)$ , with spherical or radial symmetry
3. calculation of pair distribution histograms (PDH)
4. calculation of x-ray diffraction patterns,  $I(Q)$  and  $S(Q)$
5. calculation of  $G(r)$  (PDF) from powder diffraction data for models with a perfect crystal lattice and for models with density modulation waves
6. 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 NanoPDF includes modeling and calculations only for cubic and hcp-type structures:

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

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

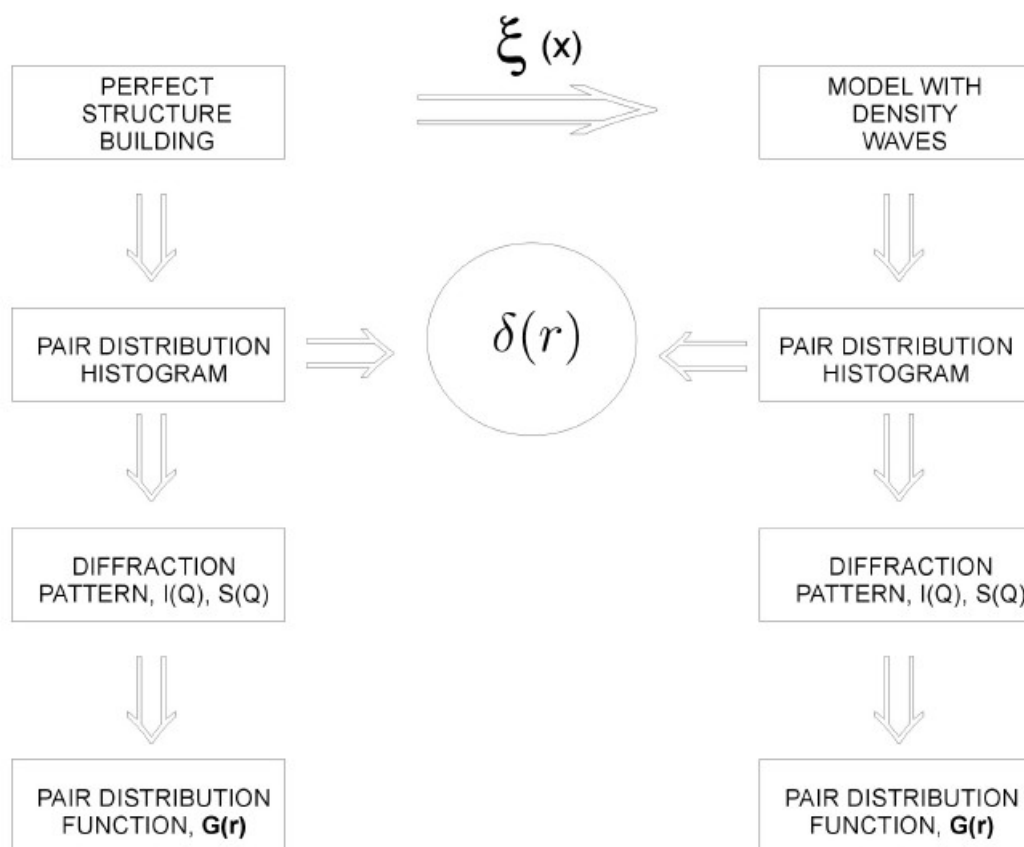


Figure 0-1 Flowchart of the NanoPDF.exe program

# Introduction

## **1.1 Technical details**

The NanoPDF.exe program is a 32 bit Windows application written with C++ Builder 6.0. It is a standalone application and does not depend on any additional programs or libraries. It should happily run under any currently popular flavor of MS Windows, both 32 and 64 bit (XP, Vista and 7 tested). Linux users may run NanoPDF using Wine environment (Fedora 17 and Ubuntu 12.04 tested). Any data calculated by NanoPDF may be conveniently visualized using built-in plotting routines. Atomistic models of nanocrystals created by NanoPDF may also be displayed. For that NanoPDF will call a dedicated external application such as RasTop or RasMol. Both are freely downloadable from the Internet, but must be installed separately.

The program does not make any modification to the Windows registry. It uses its own ini file.

NanoPDF.exe does not require installation. The executable only needs to be copied to an arbitrary folder along with 'scfact.scf' file. In order to use RasMol or RasTop, a template script 'rms.scr' should be added too. NanoPDF.ini is created during the first run of the program. It is used to store the parameters utilized inside NanoPDF 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. All the configuration files are plain ASCII files and may be but should not be edited by hand. For more information see chapter 5.

Standard PC class computer with 2.53 GHz processor and 4.0 GB of RAM memory allows to do the calculations for nanograins consisting of about 35 thousands atoms in less than 150 s. During operation memory usage for the above example was about 16 MB. The current version (ver. 1.0) of the NanoPDF.exe program does not perform any parallel computing so using processors with many cores and threads will not speed things up.

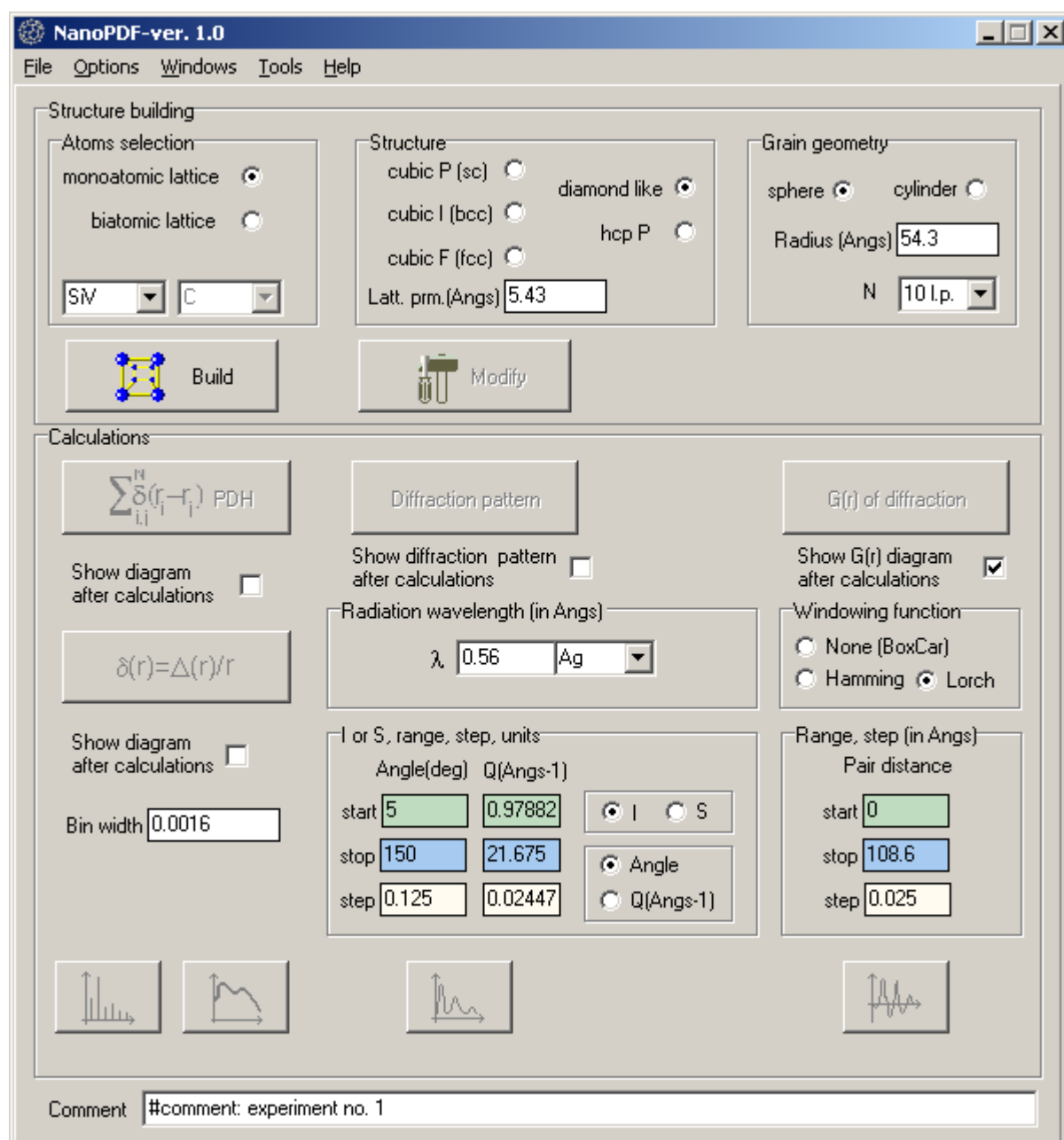


Figure 1.0-2 The main view of the NanoPDF.exe program

## 1.2 Configuration

All custom parameters are set via the **"Options"** menu. The first sub menu, **"Element properties"**, contains a list of elements and their scattering coefficients used for calculations of atomic scattering amplitudes, lattice parameter of the most common polymorph, atomic mass and Debye's temperature (see fig. 1-0-2). One can edit the current table and change the existing or add new values. To save changes one needs to use **"File"** menu or press the "F2" key. The new values are available after restart of the NanoPDF.exe program. All coefficients are stored in "scfact.scf" file.

Scattering factor values versus  $\sin(\theta)/\lambda$  are shown on a diagram after click on the "scat. fact. graph" button (see fig.1-0-3). It's possible to change temperature and the range of  $\sin(\theta)/\lambda$  before plotting.

coefficients for analytical approximation of scattering factors and chosen properties of elements													
Element	a1	b1	a2	b2	a3	b3	a4	b4	c	I.p.	I. type	mass	Td (K)
Si	4.43	1.64	3.20345	3.43757	1.19453	0.2149	0.41653	6.65365	0.746297	5.431	dm	28.0855	645
SiV	5.66269	2.6652	3.07164	38.6634	2.62446	0.916946	1.3932	93.5458	1.24707	5.43	dm	28.0855	645
C	2.31	20.8439	1.02	10.2075	1.5886	0.5687	0.865	51.6512	0.2156	3.5667	dm	12.0107	1860
Se	17.0006	2.4098	5.8196	0.2726	3.9731	15.2372	4.3543	43.8163	2.8409	4.36		78.96	251
Cd	19.2214	0.5946	17.6444	6.9089	4.4610	24.7008	1.6029	87.4825	5.0694	2.98	hcp	112.411	209
Au	16.8819	0.4611	18.5913	8.6216	25.5582	1.4826	5.86	36.3956	12.0658	4.0788	fcc	196.9666	170
Ni	12.8376	3.8785	7.292	0.2565	4.4438	12.1763	2.38	66.3421	1.0341	3.54	fcc	58.693	450

Figure 1.0-3 The view of list of coefficients for analytical approximation of scattering factors

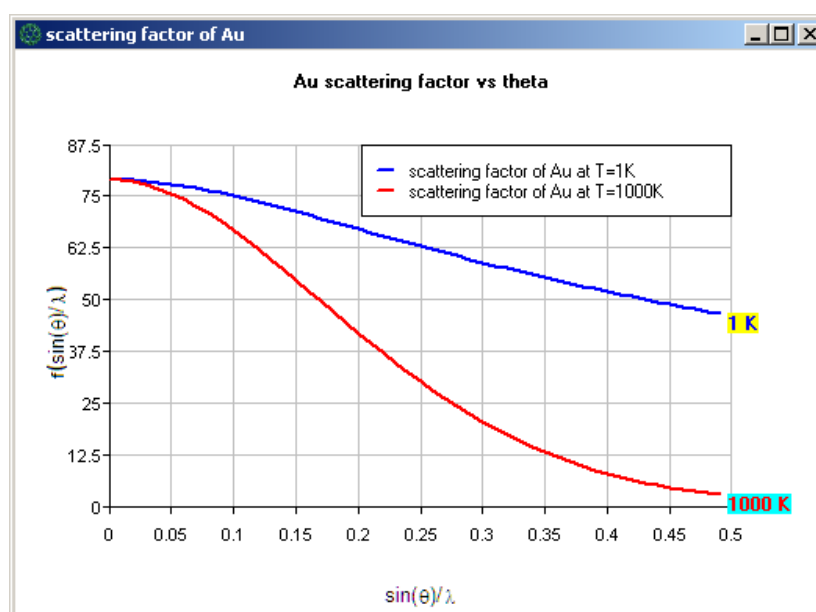


Figure 1.0-4 The view of the "Scattering factor" chart of Au

If one plan to use an external program for 3D visualization like the Rastop.exe, two paths should be set. Path to the Rastop.exe folder via the "Path to Rastop" menu and path to the folder where temporary files will be saved via the "Path to temp. dir" menu. If the "Remove temp. files" sub menu is checked temporary files will be deleted after one closes the application.



The **"Set thread priority"** sub menu allows to change priority class for all threads devoted to calculations. After click on it a dialog window is displayed (see fig.1-0-4). The selection is limited to the three cases:

1. Normal (default)
2. High
3. Real-time

For each class a short description is given on the right side of the dialog window. The "High" and "Real time" priorities can improve the speed of calculations especially when the system is overloaded by processes running in the background.

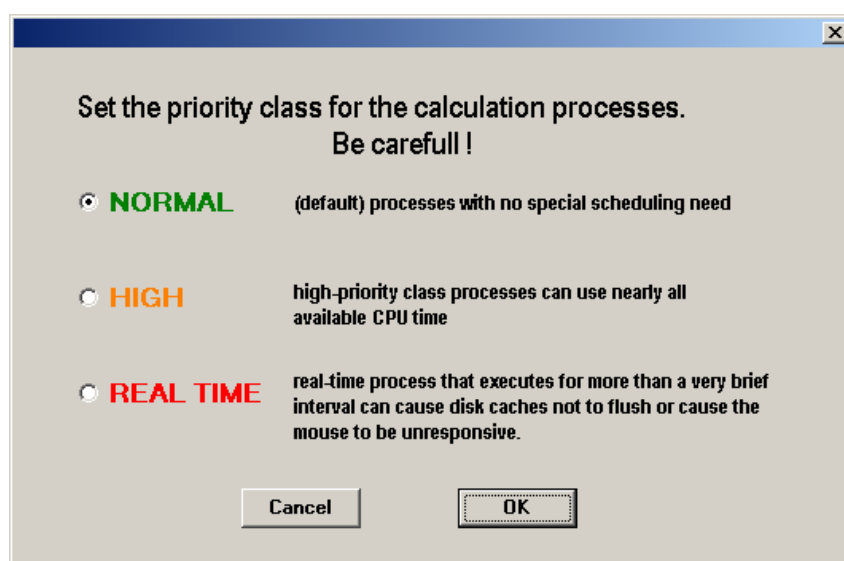


Figure 1-0-5 The view of the dialog window devoted to modification of **processes priorities**

Current information about program status is available in the "Diary window" (see fig.1-0-5). It can be turn on from the "Windows" menu. It shows:

1. all current structure parameters
2. type of calculations
3. time of start/stop calculations
4. status of calculations
5. atoms positions

More information is hidden under the mouse context menu.

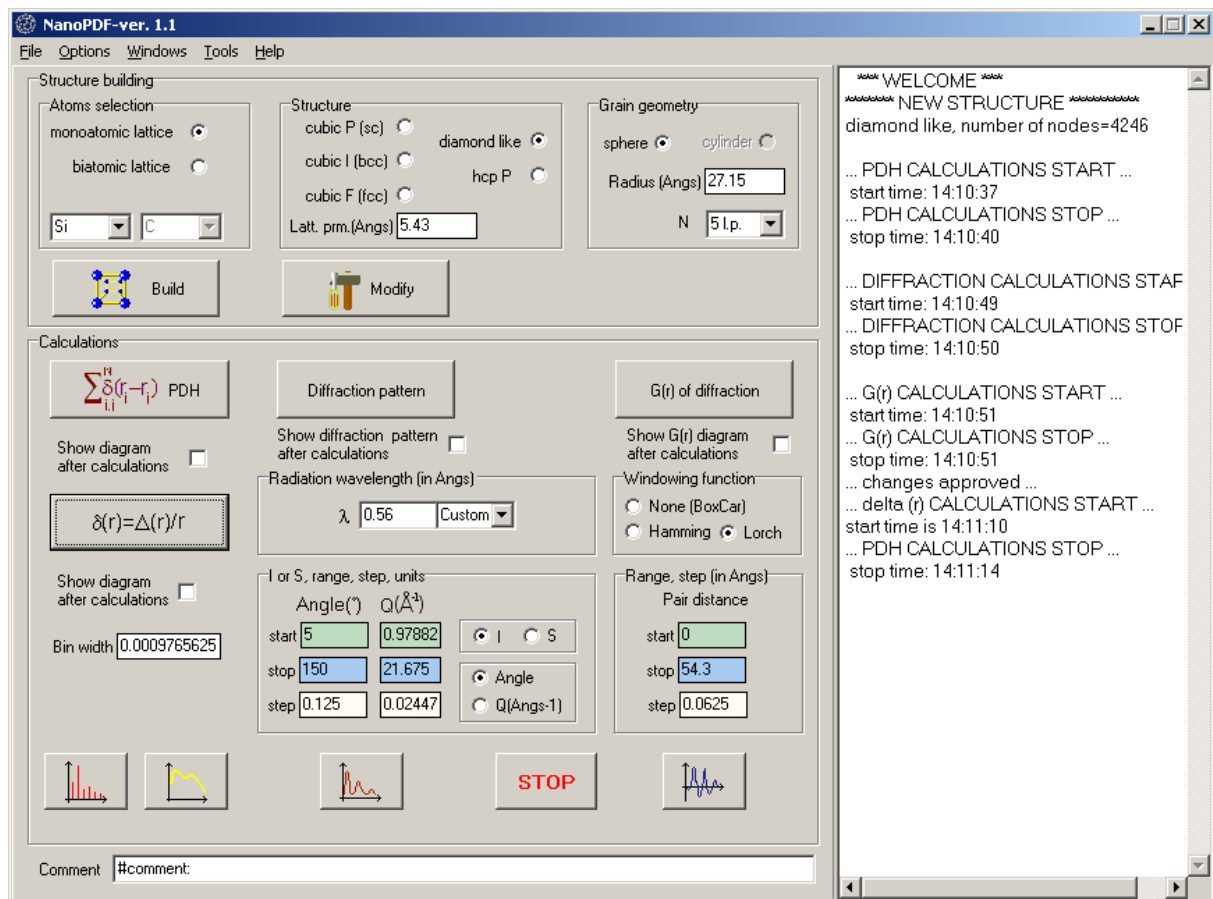


Figure 1-0-6 The main view of the **NanoPDF** program with the "**Diary window**" turn on

### 1.3 General description of modeling

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

1. Monoatomic lattices: primitive cubic, bcc, fcc , diamond-like and hcp with an arbitrarily chosen ABC layer stackings
2. Bi-atomic lattices: cubic zinc-blende-like and hcp structures with an arbitrarily chosen ABC layer stacking.

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

1. chemical composition (here: one or two kinds of atoms)
2. lattice type (Bravais lattice)
3. lattice parameter (here: only one parameter)
4. grain shape (spherical or cylinder)
5. dimension

All geometry dimensions are given in angstroms. The structure which has been built can be saved in an expanded xyz format with ndl extension, which stores all information needed to create crystal structure (more in Section 5).

The NanoPDF.exe program can read structure from a file. The preferred format is ndl. Program which uses this format doesn't need any additional work to recreate structure. After finished work the program saves the model parameters in "ini" file: chemical composition, radius, shape, lattice type, paths.

## 1.4 General description of calculations

For each model that one builds the NanoPDF calculate:

1. Pair Distribution Histogram: PDH
2. Powder diffraction pattern,  $I(Q)$  or  $I(2\Theta)$  and structure function  $S(Q)$
3. Fourier transform of diffraction pattern:  $G(r)$  - called reduced pair distribution function

$I(Q)$  and  $S(Q)$  are calculated using standard procedures [9]. Calculation of  $G(r)$  is described in Section 3.

Diffraction pattern is given in two forms. The first one is the intensity of the scattered beam given by a dot product of a scattered wave function by its complex conjugate:

$$I(Q) = \Psi(Q) \cdot \Psi^*(Q) \quad (1.1)$$

where  $Q$  is a scattering vector,  $Q = 4\pi \sin\Theta / \lambda$ .

The second form is normalized intensity known as a structure function:

$$S(Q) = \frac{I(Q)}{\sum_i f_i^2} \quad (1.2)$$

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

-

# Modeling

## 2.1 Building structure with a perfect lattice

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

Structure building

Atoms selection

monoatomic lattice ☒

biatomic lattice ☐

Si C

Structure

cubic P (sc) ☐ diamond like ☒

cubic I (bcc) ☐ hcp P ☐

cubic F (fcc) ☐

Latt. prm.(Angs) 5.43

Grain geometry

sphere ☒ cylinder ☐

Radius (Angs) 54.3

N 10 l.p.

Build Modify

Figure 2-1-0-7 The view of the "Structure building" group box

Box 1: "Atoms selection":

1. chemical composition (here: one or two kinds of atoms)

Box 2: "Structure":

1. lattice type (Bravais lattice)
2. lattice parameter (here: only one parameter)

Box 3: "Grain geometry":

1. grain shape (spherical or cylinder)
2. dimension (radius)

### 2.1.1 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 "scft.scf" File. The whole list is available after mouse click or by typing the name of element.

After selection of monoatomic structure of given element, Bravais type and lattice parameter of its most common polymorph appear in Box.2.

### 2.1.2 Box 2 - structure (Bravais lattice)

Currently there are 5 structure types implemented in NanoPDF program which one chooses with use of five radio buttons. First three radio buttons correspond to monoatomic cubic structures with three different Bravais lattices: primitive, fcc and bcc. Fourth button defines alternately diamond-like or zinc-blende-like lattice for mono- and bi-atomic structures, correspondingly. The fifth button defines a group of hexagonal close packed structures, hcp – see Section 2.2.

### 2.1.3 Box 2 - lattice parameter

The lattice parameter which is required to enter in Box 2 is that of a cubic unit cell,  $a_{\text{cubic}}$ . This parameter defines fully cubic structures of first four structure types. The initial values of lattice parameters required for description of hcp structures with trigonal symmetry and appearing in Box 3,  $a_{\text{trigonal}}$  and  $c_{0,\text{trigonal}}$  are calculated as that:

$$a_{\text{trigonal}} = a_{\text{cubic}} \sqrt{2} \qquad c_{0,\text{trigonal}} = a_{\text{cubic}} \sqrt{3}$$

Here,  $a_{\text{cubic}}$  has a meaning of Equivalent Cubic lattice parameter, EClp, see Section 2.3.1. The as-calculated parameters  $a_{\text{trigonal}}$  and  $c_{0,\text{trigonal}}$  can be changed in next steps of building hcp type models, c.f. Sections 2.1.4 -2.1.6.

### 2.1.4 hcp structures

hcp option serves for building close packed structures layer-by-layer, both for mono- and bi-atomic structures. When hcp-type structure is chosen, after pressing the **"Build"** button the **"Create hcp structure"** window is displayed (see fig.2.2). In this case one has a possibility to create from ABC layers his own stacking across the whole grain. In this notation wurtzite (2H) is described by ABABAB... and zinc blende (3C) by ABCABC... sequence. One can create a mixture of 2H and 3C phases, e.g. ABABABABCABCABC or implement stacking faults in given parent structure, e.g. ABABCBABABA etc.

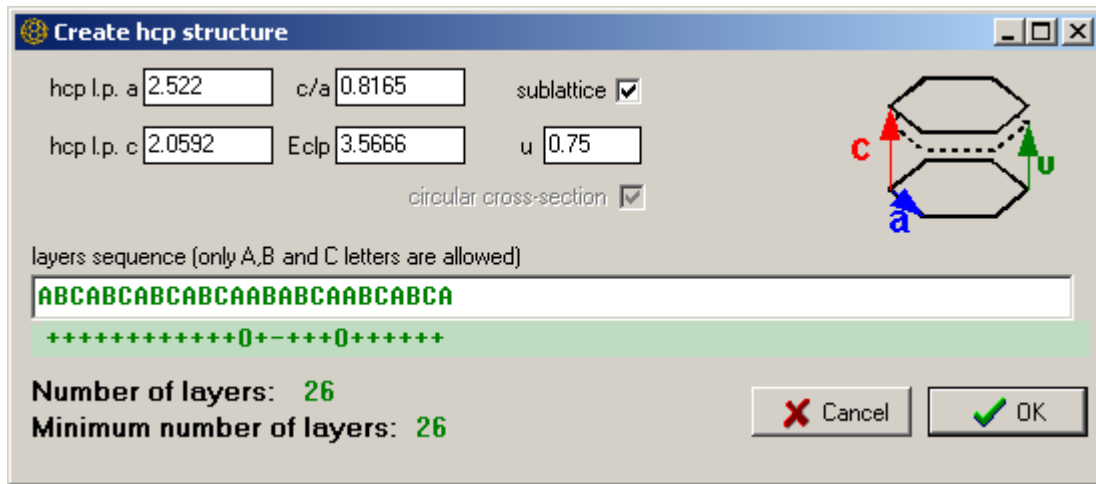


Figure 2-1-2 The view of the "Create hcp structure" window

The letters A,B,C denoting the layers should be placed in the "layers sequence" edit window. Below this window, on the green strip, the "ABC" code is converted to a sequence of signs "+", "-" (so named 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 11111..., 4H polytype is 22222, 6H - 3333, 3C  $\infty$  (infinity). 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. The number of layers in the built structure is displayed by the "Number of layers" label. One should notice that A, B and C layers forming hcp structures are in fact combined from two hexagonal layers one above another. In mono-atomic diamond-like hcp structures, like diamond or Si, both layers are formed from same atoms. In bi-atomic structures like ZnS or CdSe the neighboring layers are from different atoms, e.g. Zn and S or Cd and Se, respectively, Fig.2-1-3.

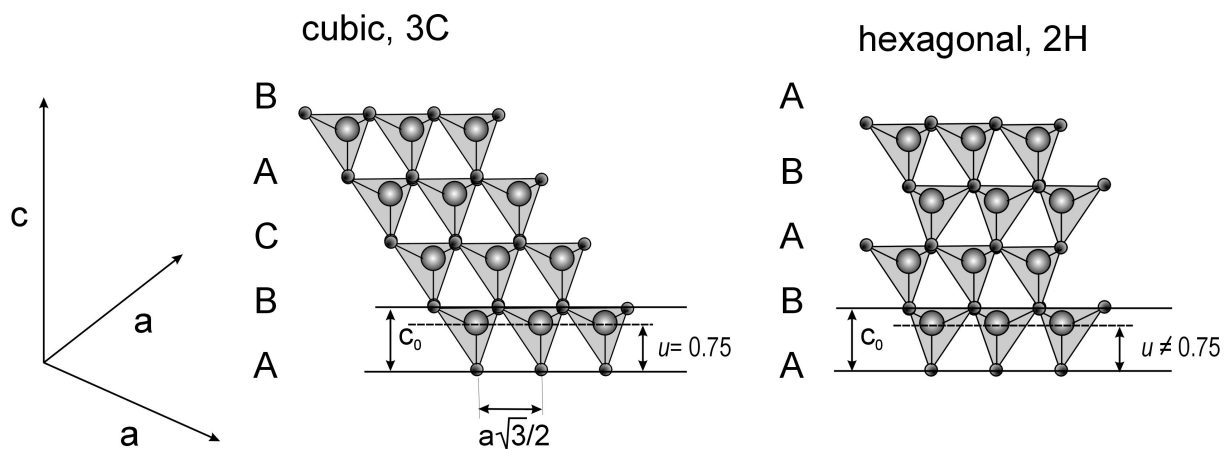


Figure 2-1-3 Layer stacking of 3C and 2H structures of bi-atomic hcp lattice

### 2.1.5 Building ABC sequence

For spherical grains the font in the editing 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 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:

1. black - sequence too short
2. green - proper/sufficient length of sequence
3. red - sequence too long

When cylindrical grain shape is chosen the font color is always black. Here, the number of layers defines the high/length 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.

### 2.1.6 Setting structural parameters of hcp model: Equivalent Cubic lattice parameter, $ECIp$ , $(c/a)$ ratio and $u$

For both spherical and cylindrical shaped grains the initial values of trigonal lattice parameters  $a_{\text{trigonal}}$  and  $c_{0,\text{trigonal}}$  are calculated from the "Lattice parameter" given in Box 2. For hcp structures this parameter has a meaning of Equivalent Cubic lattice parameter,  $ECIp$ , [8, 10]:

$$ECIp = \left[ 2\sqrt{3}a_{\text{trig}}^2 c_{\text{trig}} \right]^{1/3} \quad (2.1)$$

In the "Create hcp structure" Box there appear initial values of trigonal lattice parameters  $a_{\text{trigonal}}$  and  $c_{0,\text{trigonal}}$  calculated based on the assumption that relationship between interlayer  $c_{0,\text{trigonal}}$  and in-plane inter-atomic,  $a_{\text{trigonal}}$ , distances is that of cubic hcp-structure:  $(c_0/a)_{\text{trigonal}} = 0.8165$ . The parameters appearing in the "Create hcp structure" Box are:

$$a_{\text{trig}} = EClp / \sqrt{2}; \quad c_{0,\text{trigonal}} = EClp / \sqrt{3} \quad (2.2)$$

In general case, in hcp non-cubic structures, the  $(c_0/a)$  deviates from the value 0.8165. Therefore for given ABC sequence in the **"Create hcp structure"** Box one can freely modify/set  $(c_0/a)$  ratio. The  $a_{\text{trigonal}}$  is always calculated from  $EC_{lp}$  given in Box 2. For given  $(c_0/a)$  ratio  $c_{\text{trigonal}}$  is calculated as  $(c/a) a_{\text{trigonal}}$ .

**Note:** when for given set of  $a_{\text{trigonal}}$  and  $c_{\text{trigonal}}$  values for which  $c/a \neq 0.8165$  the layer stacking is modified, the  $a$  and  $c$  are set to default values.

For given ABC layer stacking and given  $(c_0/a)$  ratio additional free parameter is "u" which defines the distance between two sublattices forming hcp structure. For cubic structures with ABC sequence  $u = 3/4c_0$  but in real materials it can be either smaller or smaller than that, Figure 2-1-3. 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.

### 2.1.7 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.

### 2.1.8 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 in the "N" combo box. The radius will be updated also if one changes the value of lattice parameters:

$$R = lp \cdot N$$

where:  $R$  is the radius,  $lp$  is the lattice parameter and  $N$  is a value chosen or entered by user in the combo box.

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 interplanar spacing  $c_0$ , c.f. Section 2.1.5.

### 2.1.9 Thermal vibrations

Thermal vibrations can be added to any model (with a perfect lattice or with density modulation) after all structural and geometrical parameters are specified (in Boxes 1-3) and the building procedure is completed and confirmed by



**“Build”** button. A window allowing introduction of thermal vibrations opens after clicking on **“Modify”** box.

The first step is to click on the **“Add thermal vibrations”** check box (see fig. 2-1-4). Inside the **“Random displacement”** group box, a set of boxes for choosing parameters are activated:

1. the “Distribution” combo box
2. temperature T edit window
3. the “Amp.” edit windows
4. the “acp” edit window
5. the “decorr.level” edit window
6. the “number of bars” edit window

Two kinds of 3D distributions are possible: uniform and normal (Gaussian). In both cases the NanoPDF.exe program calculates deviation of positions of individual atoms from equilibrium positions in a perfect lattice). Angular dependence is disregarded.

Center of the sphere is the location of an atom in a perfect lattice. The normal distribution is generated based on the Metropolis algorithm (MA). The MA algorithm needs some additional parameters taken from the “acp” and “decorr. level” windows. In case of the uniform distribution the values in the “acp” and “decorr. level” are irrelevant. More details are given in section 3.2.

Values appeared (default) or typed by the user in the “Amp (Angs)” edit windows are amplitudes of thermal vibrations. The default values are calculated based on the Debye’s model which give the value of  $\bar{u}^2$  ( mean square displacement, see Section 3.2) and next the square root ( $=\sqrt{\bar{u}^2}$  ) is obtained. The square root value is taken as:

1. Amplitude in the case of uniform distribution
2. Standard deviation in the case of normal distribution

To accept thermal parameters of the created model one needs to confirm its choice of the parameters by clicking **“Modify”** button. Summary of parameters of the created model are displayed in the “Memo” window placed on the right side of the **“Modification”** window. To proceed to **“Calculations”** one needs to click on the **“Accept”** button.

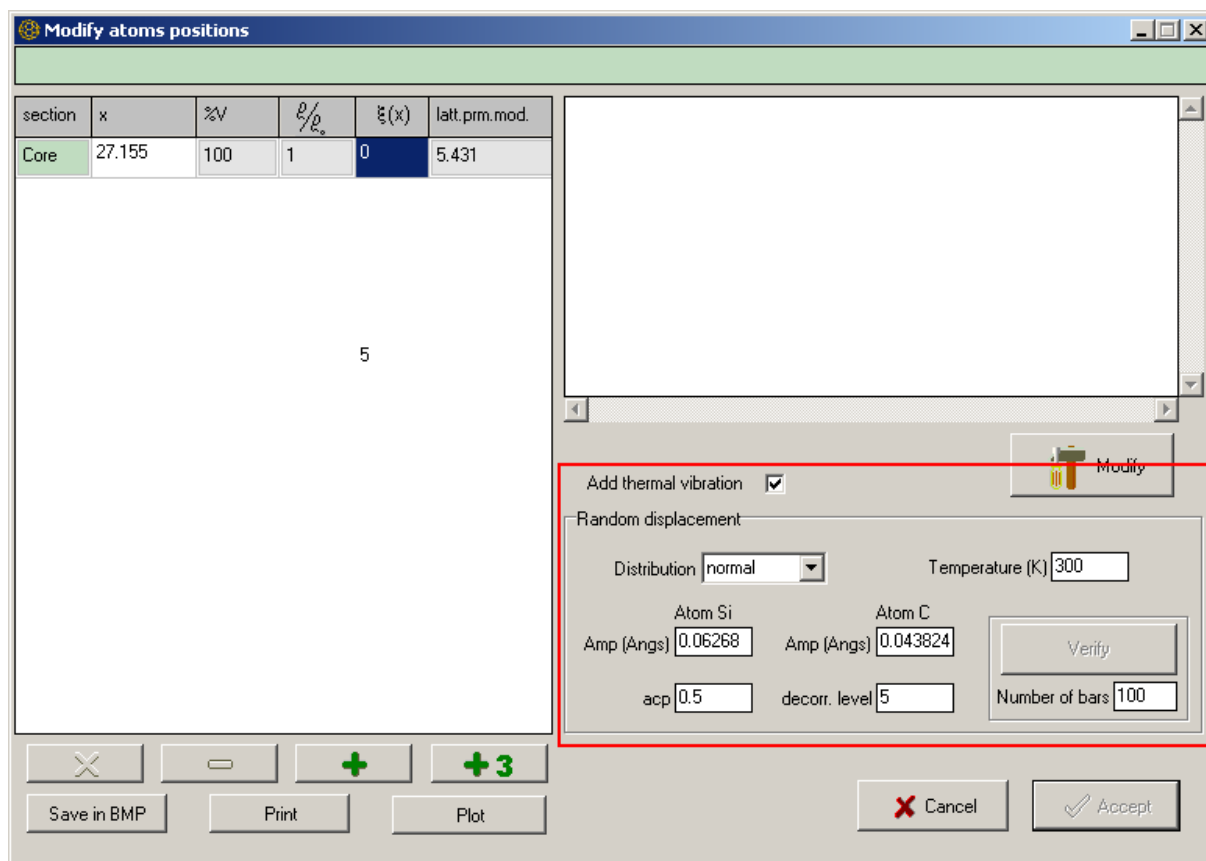


Figure 2-1-4 The view of the "Modify atoms positions" window with thermal vibration box inside the red box

### 2.1.10 Building initial model – visualization and summary

After setting all structural and geometrical parameters defining model of the nano-grains after click on "**Build**" button, NanoPDF program calculates atoms positions, saves them into the computer's memory and activates three buttons inside the "**Calculation**" group box. If the "Diary window" is enabled a short message "New Structure" will be displayed (see Section 1.2).

To view the created structure via external program in the "NanoPDF.exe" program there can be set paths to temporary directory and to the "Rastop.exe" program. Nanograin structure can be displayed using menu "Tools Rastop" or the keyboard shortcut "Ctrl+T".

To view the created structure via external program in the "NanoPDF.exe" program there can be set paths to temporary directory and to the "Rastop.exe" program. Nanograin structure can be displayed using menu "Tools Rastop" or the keyboard shortcut "Ctrl+T". An example of view of a model is shown in fig.2-1-5.

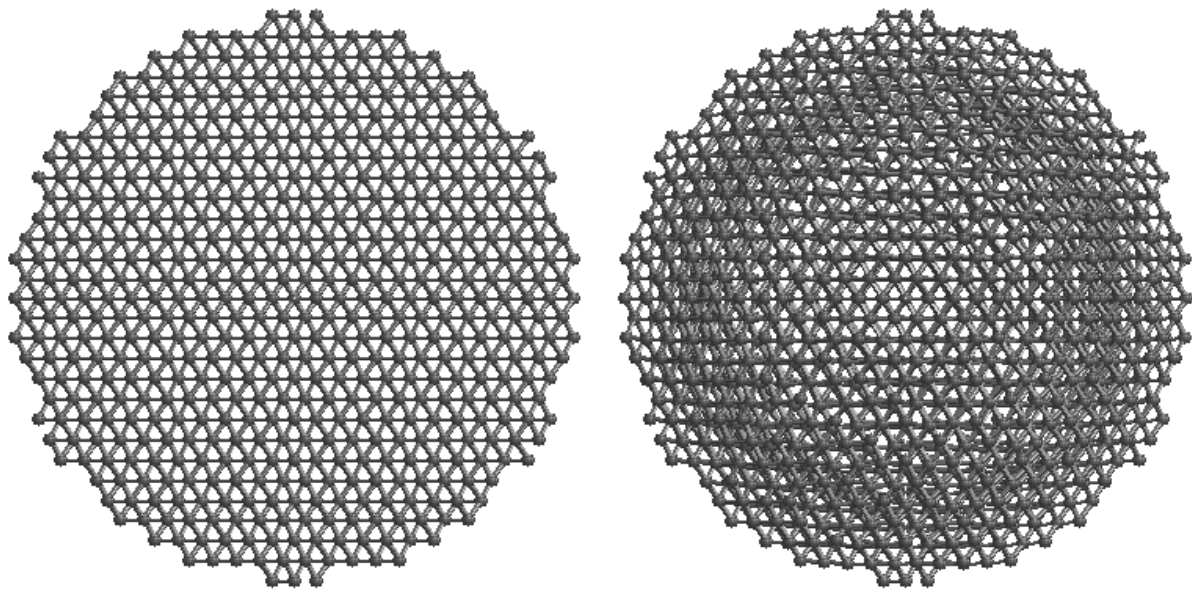


Figure 0-8-1-5 The perfect structure and structure with density modulation wave of diamond nanograin. The „Rastop”program was used for visualization

## **2.2 Building structure with density modulation**

### **2.2.1 Introducing density modulation**

We build models with a non-homogenous internal structure starting from an initial model with a perfect crystal lattice (see Section 2.1) and changing in it inter-atomic distances following a given procedure. In our tentative models with density modulation waves the space within the volume of spherical grain is subdivided by concentric spherical surfaces, see fig.2-2-1. The first spherical surface,  $r_0$ , defines/terminates the inner grain core. The spaces between two sequent concentric spherical surfaces form shells surrounding the grain core (between  $r_0$  and  $r_1$ ,  $r_1$  and  $r_2$ , etc.). The largest shell terminating the model we name is the surface shell while the shells between the core and surface we name density waves. The grain core and each shell has its own density determined by inter-atomic distances in the shell. (*Comment: 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.*) The density waves are described by  $\xi(x)$  diagrams which quantifies, in %, the deviation of inter-atomic distances  $r_i$  within every shell from corresponding distances in the parent perfect

structure,  $r_{i,0}$ ;  $x$  is the distance from the grain center, Figure 2-2-1. The atoms in the core, at the surface and the shells are shifted from their perfect lattice sites in radial direction according to the defined sign and magnitude of the shell (wave) density.

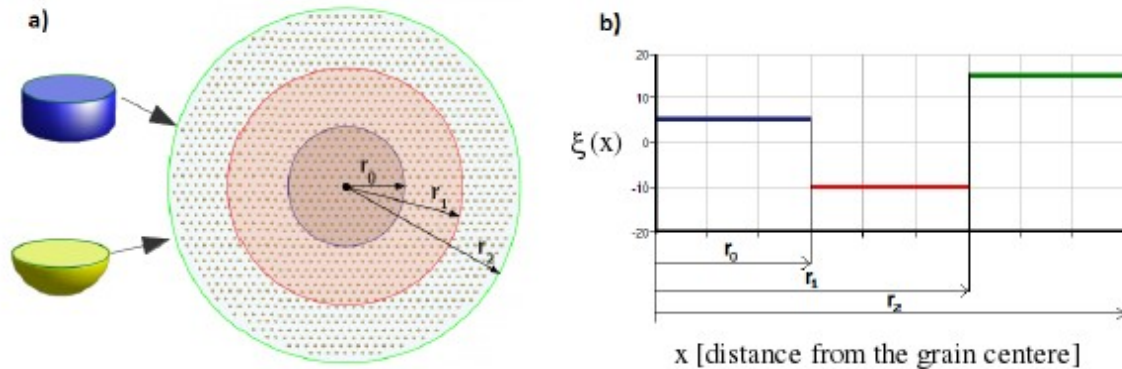


Figure 2-2-1 a) Cross section of sphere or cylinder in the plane containing the radius. Three shells have been highlighted: core, shell 1 and surface. b) Corresponding  $\xi(x)$  diagram: changes of interatomic distances in shells in relation to a perfect lattice

## 2.2.2 Parameters defining density waves

A window for creation of model with density waves (fig. 2-2-2) is activated by clicking on **"Modify"** button. On the left side of this window there appears a table which serves for setting parameters of models with the density waves. Each row defines one shell of nanograin. The first shell is named grain "core", the last is "surface". In between core and shell there are shells defining "density waves". 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 core and surface there appear shells denoted by numbers 1, 2 etc. The number of rows (thus shells) is unlimited.

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

### Parameters defining density waves

Column	Symbol	Description
1	<b>name</b>	<b>name</b> of the shell: core, shell 1, shell 2,... surface
2	<b>x</b>	<b>distance from the grain center</b> = radius of the spherical surfaces defining the radius at which the density changes; the first value is the core radius, $r_0$ , which is, at the same time the inner radius of the spherical surface defining shell 1. (Note: in case of a model with only two shells, shell 1 is the surface). The radius is given in angstroms
3	<b>%V</b>	ratio, in %, of <b>volume of given shell</b> to the whole grain volume: $\%V = V_{\text{shell}} / V_{\text{grain}}$
4	<b><math>\rho/\rho_0</math></b>	<b>relative density</b> of given shell: $\rho_{\text{shell}} / \rho_{\text{perfect crystal}}$
5	<b><math>\xi(x)</math></b>	<b>the deviation, in %, of inter-atomic distances</b> within given shell from the corresponding distances in the parent perfect structure, $(r_i - r_{i,0})$ . The values of $\xi(x)$ are constant within given shell defined by $x = r_{i,\text{min}}$ and $x = r_{i,\text{max}}$ . The core extends from $x = 0$ up to $x = r_0$ , shell 1 from $x = r_1$ up to $x = r_2$ , etc., c.f. Figure 2-0-4.
6	<b>Latt.param.mod.</b>	lattice parameter corresponding to density of given shell.

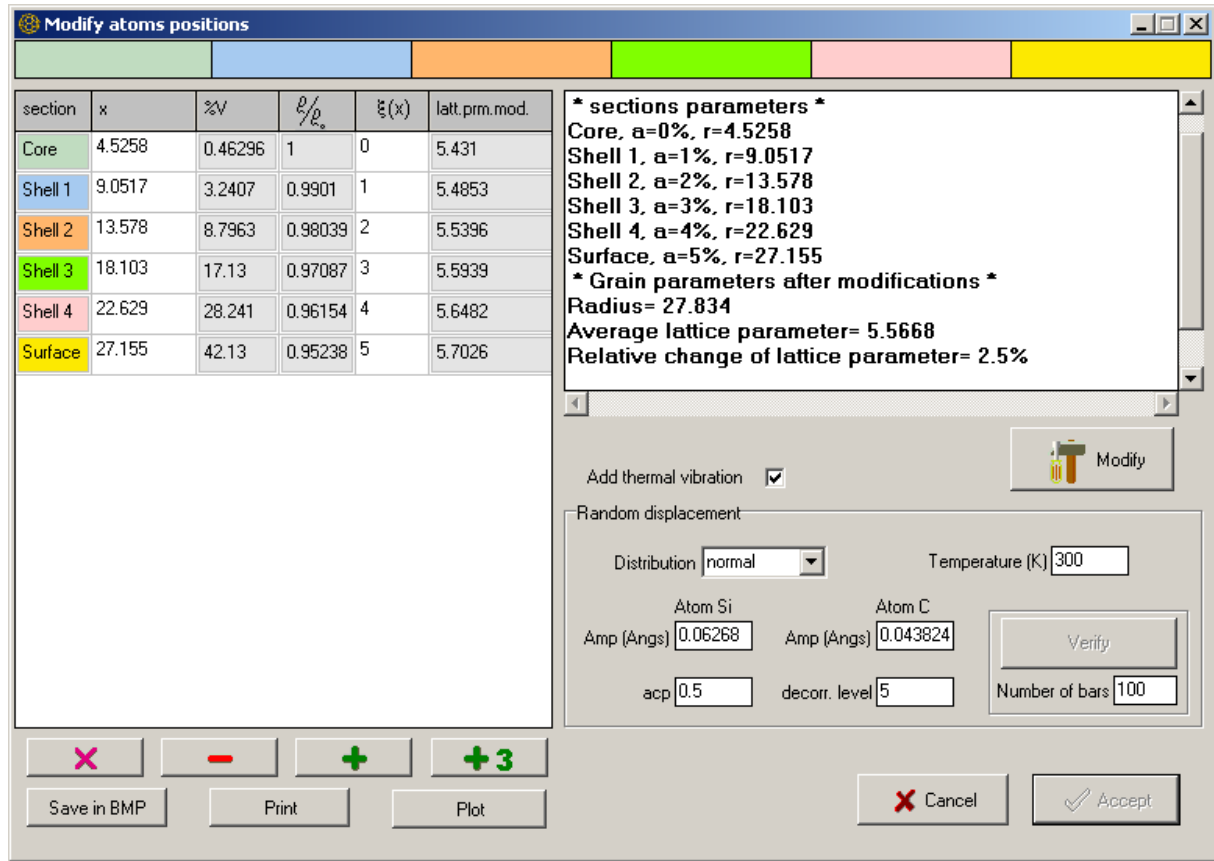


Figure 2-2-2 The view of the "Modify atoms positions" window

One can view graphical presentation of  $\xi(x)$  function as specified in the above table after clicking on "Plot" window, c.f. Figs....

### 2.3 Projection of density modulation waves - derivation of $\delta(r)$ plot

With introduction of density modulation, a number of additional inter-atomic distances appear about each inter-atomic distance  $r_{i,0}$ . As a consequence, average inter-atomic distances appearing in  $G(r)$  for a perfect lattice move to "new" average positions  $\langle r_i \rangle$ . The changes of  $\langle r_i \rangle$  distances caused by density modulation waves relative to those in the perfect lattice,  $r_{i,0}$ , can be presented in the form of  $\delta(r)$  plots, equation (1):

$$\delta(r) = \Delta r_i / r_{i,0}; \quad \Delta r_i = (\langle r_i \rangle - r_{i,0}), \quad (1)$$

where  $\Delta r_i = (\langle r_i \rangle - r_{i,0})$  is the deviation of a given (volume averaged) inter-atomic distance  $\langle r_i \rangle$  from the corresponding  $r_{i,0}$  distance in the perfect crystal lattice (in this text we use symbol  $r_i$  instead of  $\langle r_i \rangle$ ). 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  $2R$  ( $r_{i,0} \leq r_i \leq 2R$ ).

After implementation of density waves in a given model of a nanocrystal one gets  $\delta(x)$  plot by clicking  $\delta(r) = \Delta r/r$  button. Below two examples of  $\delta(r)$  plots corresponding to  $\xi(x)$  functions are given below.

The initial parameters of the nanograin are:

1. diamond lattice with a perfect lattice
2. lattice parameter  $a = 3.5667 \text{ \AA}$
3. spherical grain with  $25 \text{ \AA}$  radius ( $N = 7 \text{ l.p.}$ )

Parameters of  $\xi(x)$  function of Models I and II as defined in NanoPDF.exe program are given in Figs. 2-3-1 and 2-3-2 in a form of tables and  $\xi$ -diagrams.

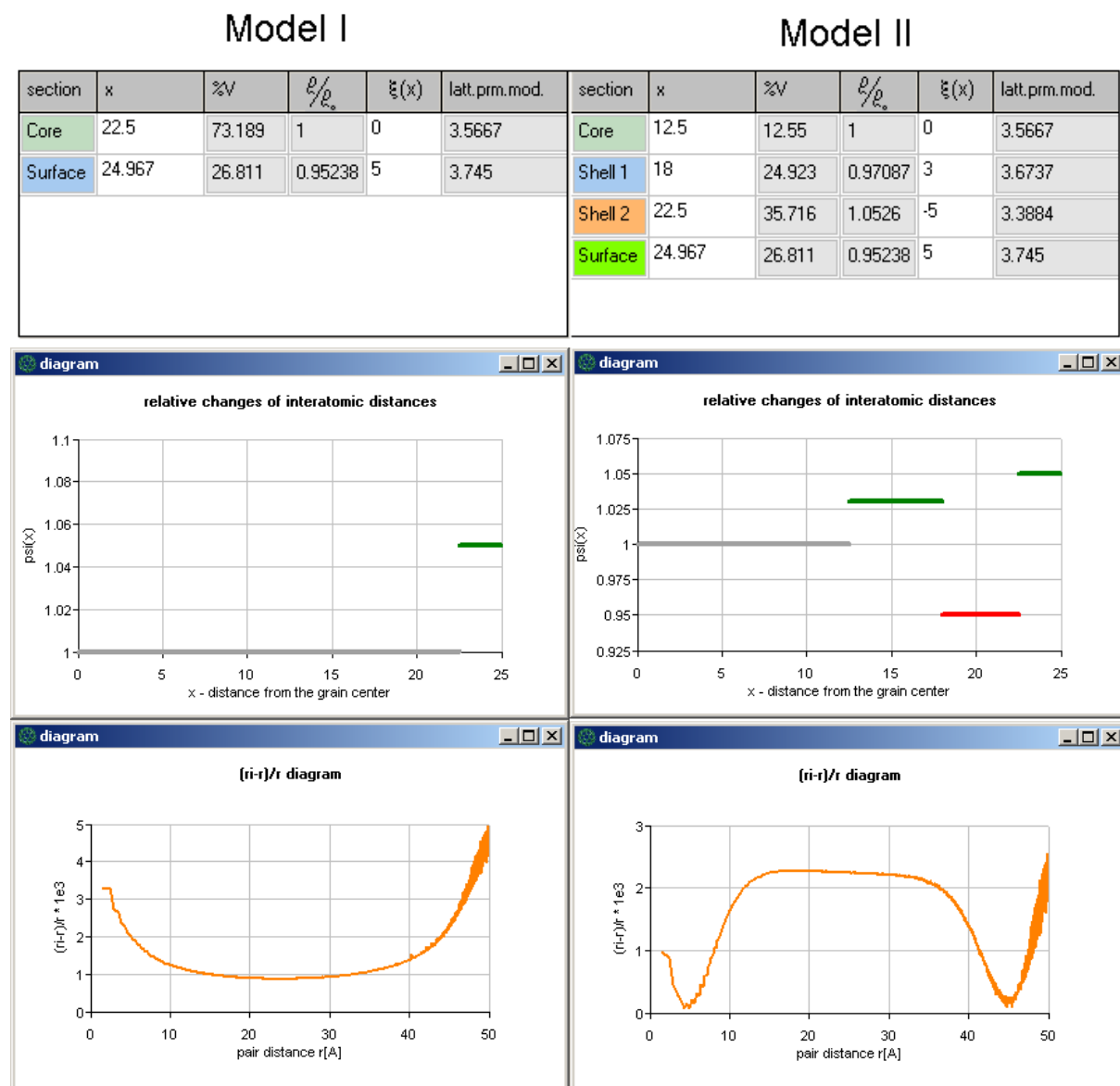
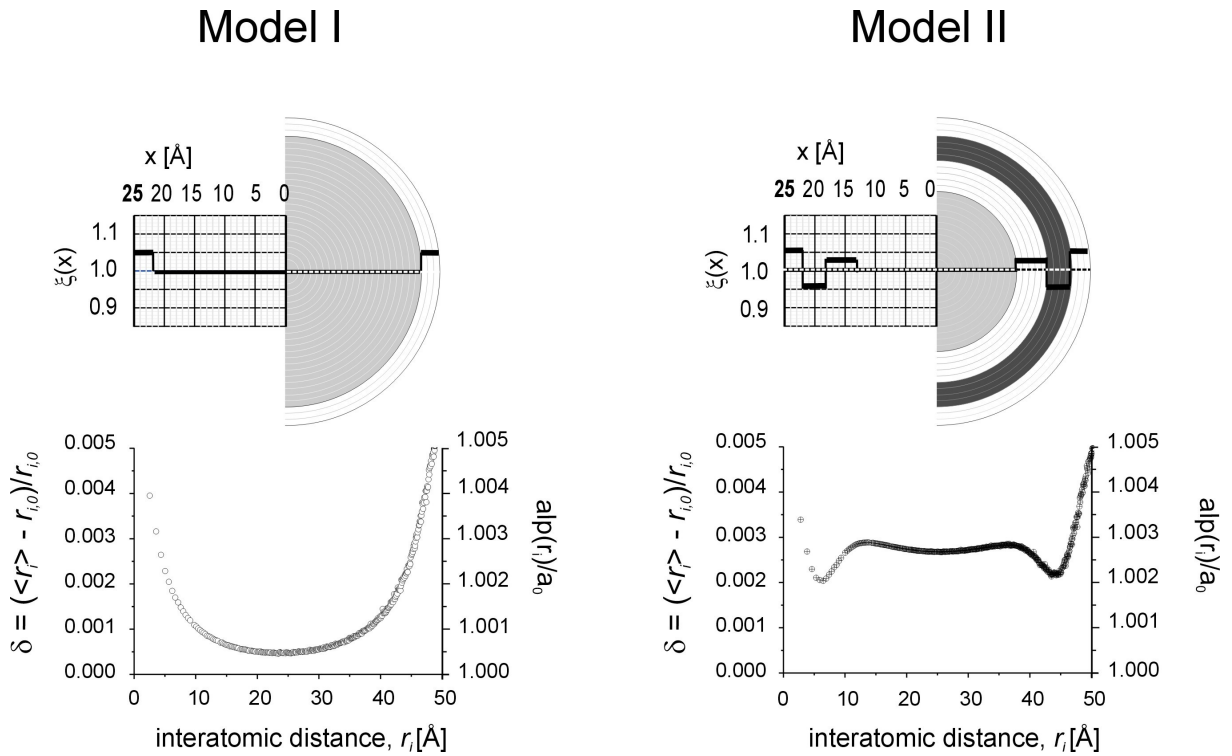


Fig. 2-3-1 Parameters of  $\xi(x)$  plot defining Model I and Model II, its graphical presentation and corresponding  $\delta(r)$  plots

The  $\delta(r)$  plots calculated for these two models together with the corresponding  $\xi(x)$  functions are given in Fig.2-0-8.

Fig. 2-2-5 shows very clearly that the shape of  $\delta(r)$  plots is closely correlated with  $\xi(x)$  function, i.e. it depends on relative changes in inter-atomic distances along the grain diameter. The sequence of “waves” appearing in  $\delta$ -diagrams, starting from the shortest distance, is determined by a sequence of density waves emerging from the grain surface towards the grain center and described by  $\xi(x)$  function: (i) The positions of “waves” appearing on  $\delta$ -plots are correlated with distribution of density waves along the grain diameter and, (ii) The amplitude of the  $\delta$ -waves is proportional to the magnitude of density variations about that of the reference parent structure.



**Figure 2-3-3.** Density modulation function,  $\xi(x)$ , and corresponding  $\delta(r)$  plots for Model I with only core and surface layer and Model II with 2 density waves between the grain core and the surface layer, calculated for 5 nm diamond grain [13].

There is a close correlation between  $\delta(r)$  plot, which can be determined directly for atomic models of nanocrystals, and *apparent lattice parameters*,  $alp(r)$  values which can be determined from experimental  $G(r)$  functions:

$$\delta(r) = \Delta r_i / r_{i,0} = [1 - alp(r_i) / a_0]. \quad (2)$$



## **2.4 Elaboration of experimental data - determination of apparent lattice parameter, $alp(r)$**

The values of lattice parameters “as refined” in routine 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), have no specific meaning. To examine experimental  $G(r)$  functions one can apply PDFgui program for calculation of the lattice parameters for different intervals of the inter-atomic  $r$  distances. The values of such lattice parameters as-calculated from PDFgui we call the apparent lattice parameters,  $alp(r)$  [8,10].

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 dots [13,14].

# Calculations

## 3.1 Introduction

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/ $\delta(r)$ , diffraction pattern, PDF/G(r) (see fig.3-0-1). Computation progress is shown by yellow strip at the bottom of the "Calculations" group box. The yellow – blue circle above the strip is visible when computations are in progress.

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 "Diary" window.

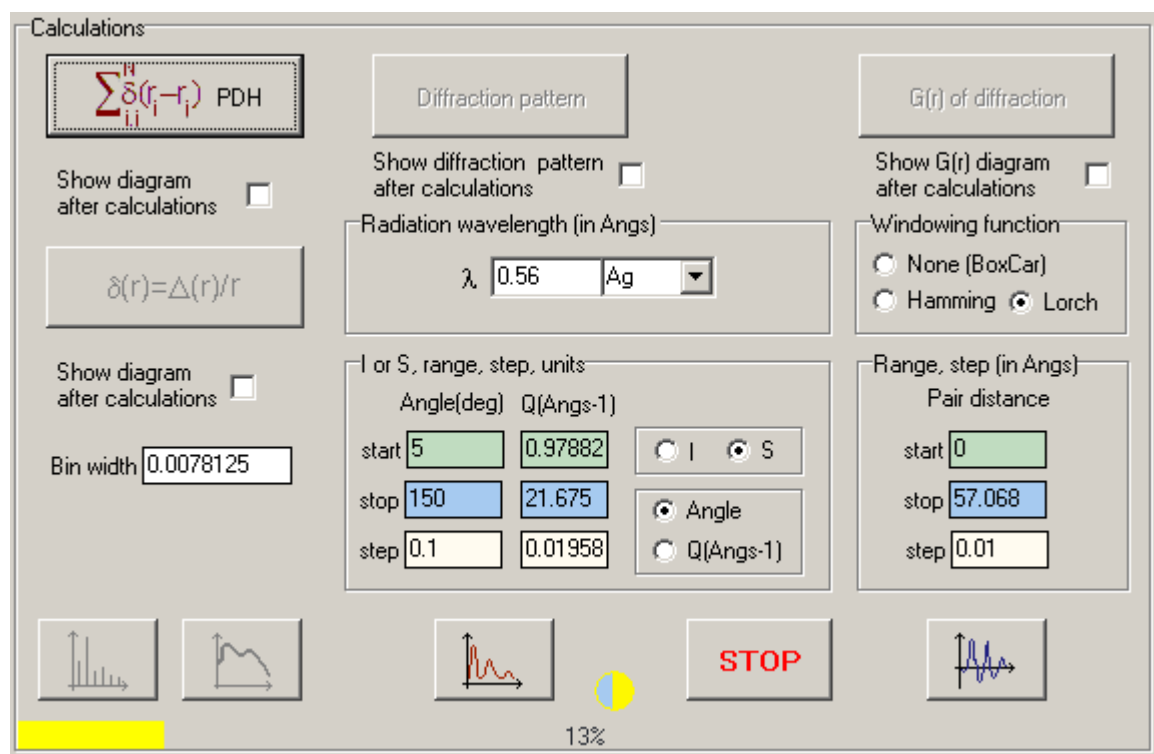


Figure 3-0-9 The "Calculations" group box of main view of the NanoPDF program

### 3.2 PDH/ $\delta(r)$

The result of PDH/ $\delta(r)$  calculations may depend only on one parameter: **Bin width**. The "Bin width" value approximates the Kronecker delta function. Typical value should be about  $0.01 \div 0.001 \text{ \AA}$ . Values above 0.01 give very rough approximation and it can be a reason of big errors in the intensity or PDF calculations (e.g. negative values on diffraction patterns). Values below 0.001 consume computer memory and they have a negative effect on speed of calculation but can enhance quality of numerical results.

The value of bin width (bw) in some conditions has a great influence on results. In the case shown in fig.3-0-2. the effect of quite small change of bw equal to  $\Delta bw = 1/1000 - 1/1024 = 2.534375e-5$ , is very well visible. Much better result for bw=1/1024 is the result of admission to the computation a value which is a negative power of 2. Such solution helps to disregard some effects of the "round-off" errors between binary and decimal systems. So, our general advise is to use the bw values which are the negative powers of 2. To enter the bw value equal to: 1/128, 1/1024 or 1/16384 one can use the context mouse menu of the "Bin width" edit window.

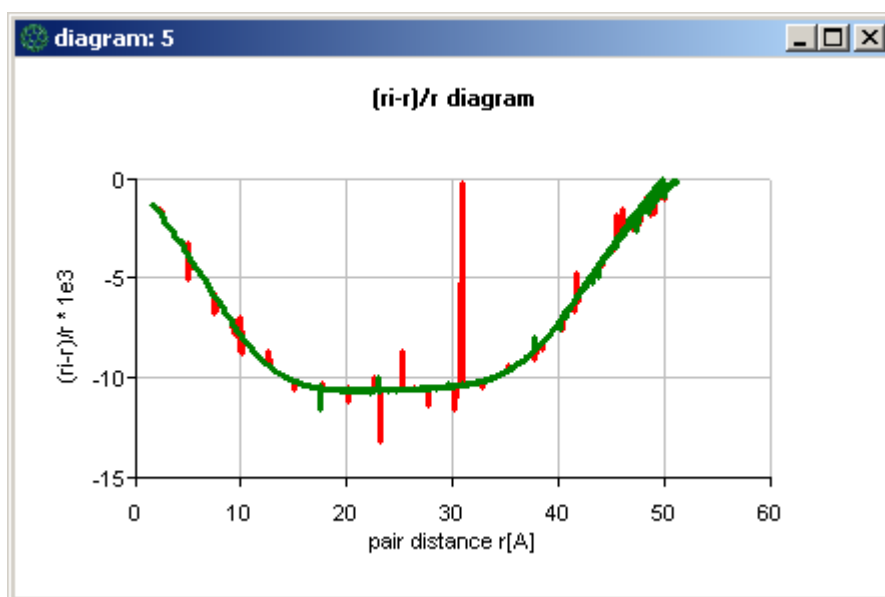



Figure 3-0-10 The delta(r) diagram calculated for two values of bin width: red line: bw= 1/1000, green line: bw= 1/1024

The PDH calculations are activated after click on the "PDH" button, the  $\delta(r)$  after click on the " $\delta(r) = \Delta(r)/r$ " button. Results are stored in memory and can be presented after calculation either if the "Show diagram after calculations" checkbox is checked or after click on the button with diagram icon: 

Number of PDH diagrams depends on the lattice type. For monoatomic lattices only one diagram is shown. In the case of biatomic lattices three diagrams will be shown (see fig. 3-0-3).

The results can be stored to hard disk. The “PDH/ $\delta(r)$ ” data are saved in respectively: “\*.his” or “\*.dij” files. To save data to disk one can use the sub menu: “Save PDH” or “Save delta(r)/r”. Both sub menus have keyboard shortcut, respectively: F3 or F7.

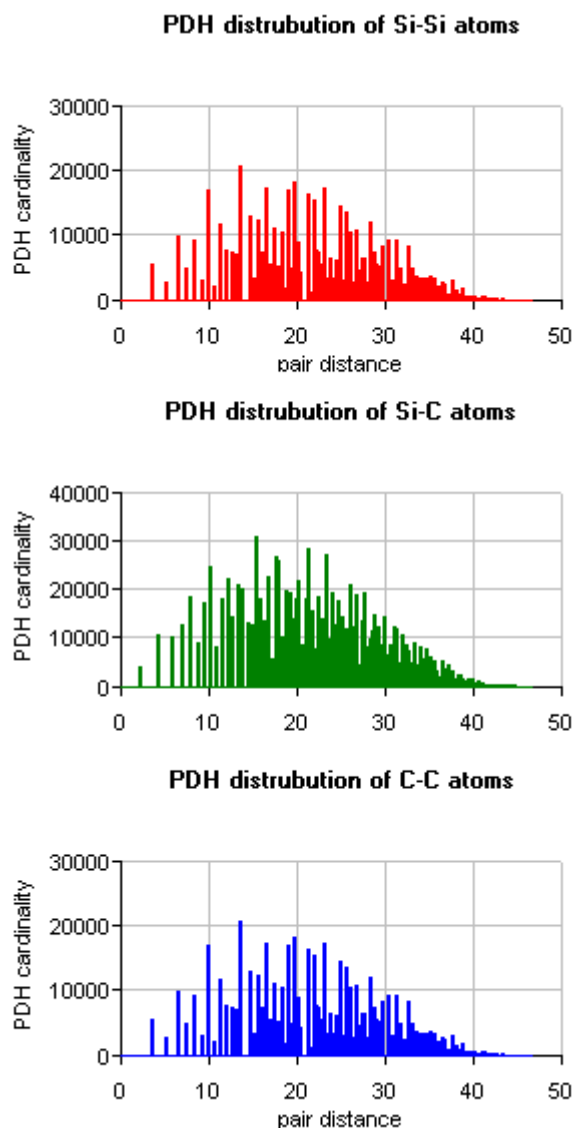


Figure 3-0-11 The PDH histograms for SiC structure

### 3.3 Diffraction pattern


A Diffraction pattern is computed only after PDH is calculated. The required parameters are specified in two group boxes: "**Radiation wavelength**" and the "**I or S, range, step, units** " group box. The "**Radiation wavelength** " group box allows to choose the source/wavelength of X-Ray beam. It's possible to

choose one of standard sources (e.g. Cu, Mo, Ag) from the list of the "XRay anode" combo box or, type .

The "**S or I, units, ...**" group allows to set  $2\Theta$  range (start, stop), step and units (angle or Q, degree or  $\text{\AA}^{-1}$ ) and choose between Intensity (I) and Structure function (S). The range and step should be set before calculations, other parameters can be changed after the diffraction pattern calculations.

Note that  $Q_{\max}$  is defined through wavelength and  $2\Theta$  range.

The diffraction pattern calculations are activated after press on the "**Diffraction pattern**" button.

The results can be stored in "\*.diff" files (keyboard shortcut F4) or can be displayed after push the  button (see fig.3-0-4). Diagram of intensity is plotted against angle ( $2\Theta$ ) or wavevector Q. Structure function chart is limited only to plotting  $S(Q)$ .

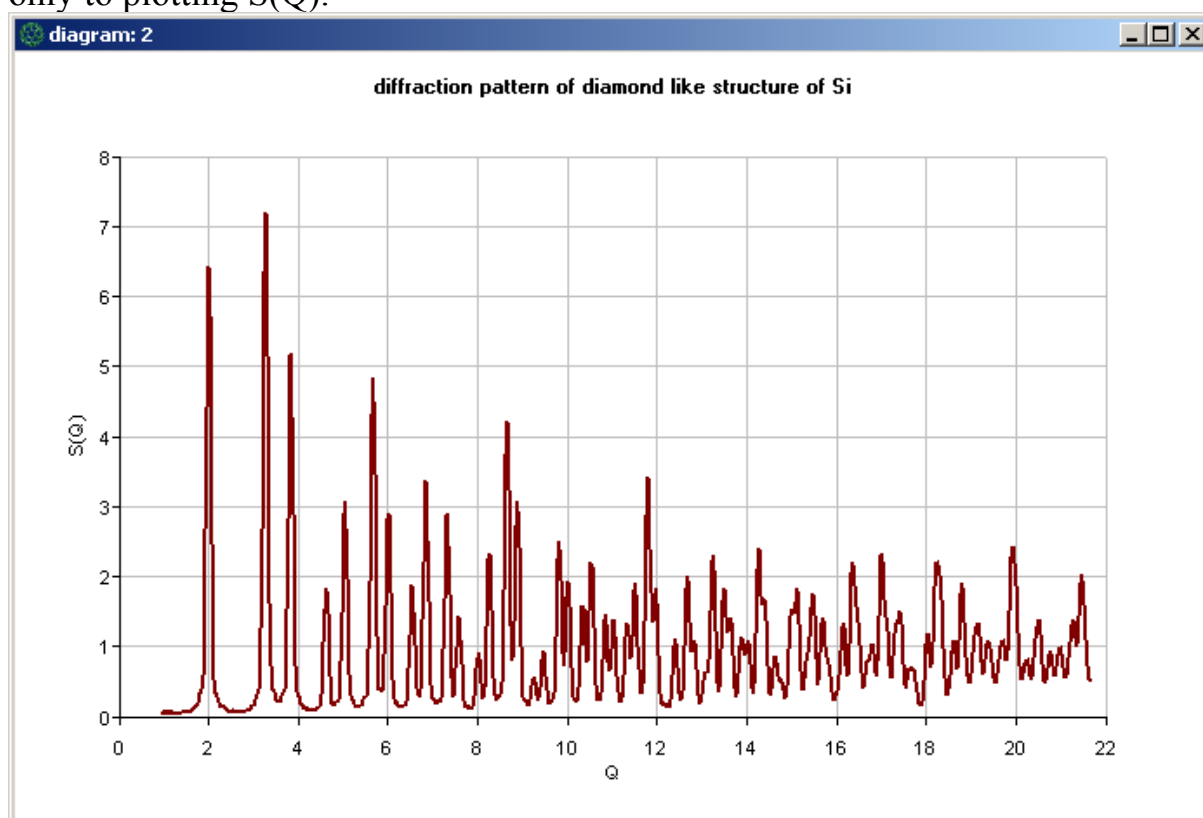



Figure 3-0-12 The  $S(Q)$  chart of diamond like structure of Si atoms

### 3.4 $G(r)$ /PDF calculations

The last block is devoted to PDF calculations. User can change windowing function, and range, step of the calculated  $G(r)$  function. All values should be set before calculation. The default value of interatomic distance, r-range, the largest ID in the model.

The description of windowing function is given in section 3.1. Generally the "Box Car" window allows to obtain the highest resolution but with high level of ripples amplitude. The "Hamming" window gives partially suppressed ripples and the "Lorch" window gives very high level of ripples suppression with the high value of the FWHM (low resolution). Default the "Lorch" window is set., The PDF/G(r) calculations are activated after press on the "**G(r) of diffraction**" button.

The results can be stored in "\*.grp" files (keyboard shortcut F5) or can be displayed after push the  button (see fig. 3-0-5).

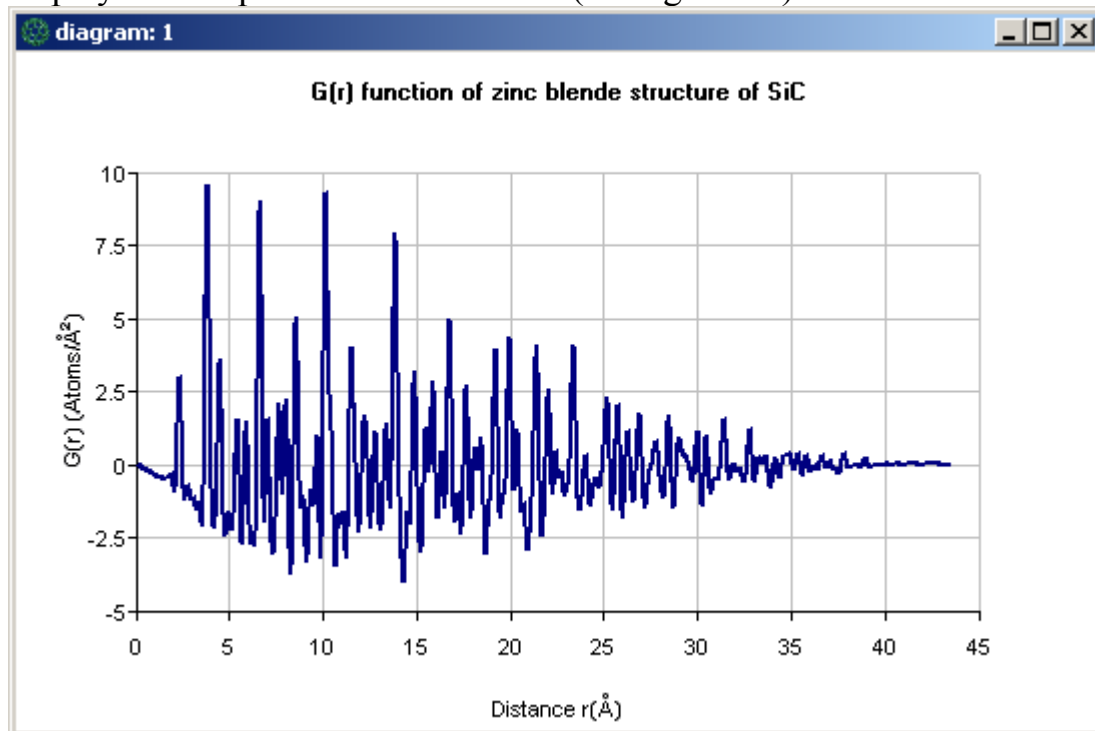


Figure 3-0-13 The  $G(r)$  function of SiC structure

## Mathematical background

### 4.1 Some elements of the theory of diffraction and PDF

Numerical simulations of the NanoPDF.exe program are based on well known the Debye scattering equation (DSE) for powder diffraction (e.g. [4]):

$$I(Q) = \sum_{i \neq j}^N f_i(Q) f_j(Q) \frac{\sin(Qr_{ij})}{Qr_{ij}} = \sum_i^N I_i(Q) + 2 \sum_{i=1}^{N-1} f_i(Q) f_j(Q) \frac{\sin(Qr_{ij})}{Qr_{ij}} \quad (4.1)$$

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 code but for large set of atoms (above a few hundreds) becomes useless. It is inefficient because it requires multiple counting of  $\sin(Qr_{ij})$  (or shorter the  $\text{sinc}(x)$  function) with the same argument. To avoid this problem the sinc functions must be computed only once for each value. This approach requires advance preparation of the pair distance histogram  $h(r)$  (PDH) of the  $r_{ij}$  distances. Formally for monoatomic lattices, the equation 3.1 can be written:

$$I(Q) = f^2(Q) \left[ N + 2 \sum_{i=1}^{N_b} h(r_i) \frac{\sin(Qr_i)}{Qr_i} \right] \quad (4.2)$$

where  $N_b$  is the number of histogram bins. Results of calculations for ideal Si crystall are shown in fig. 3.1.

The  $h(r_i)$  is obtained by summation of pairs:

$$h(r) = \sum_i^N \delta(r - r_{ij}) \quad (4.3)$$

where  $N$  is the number of atoms. From obvious reasons the  $\delta(r - r_{ij})$  function must be approximated by a finite width  $\Delta w$  bin:

$$\delta(r - r_{ij}) \approx \begin{cases} 1 & |r - r_{ij}| < \Delta w \\ 0 & \text{elsewhere} \end{cases} \quad (4.4)$$

In the case of biatomic lattices with atoms type A and B, three PDH distributions are needed because in pairs are connected atoms of type: AA, AB and BB. The 4.1 equation takes the form:

$$I(Q) = 2[fA(Q)^2 \sum_{i=1}^{Nb} hA(ri) \frac{\sin(Qri)}{Qri} + fB(Q)^2 \sum_{i=1}^{Nb} hB(ri) \frac{\sin(Qri)}{Qri} + fA(Q)fB(Q) \sum_{i=1}^{Nb} hAB(ri) \frac{\sin(Qri)}{Qri}] + N[fA(Q)^2 + fB(Q)^2] \quad (4.5)$$

where  $f_A(Q)$ ,  $f_B(Q)$  are scattering factors for A and B atoms,  $h_A$ ,  $h_{AB}$ ,  $h_B$  are pair distributions for A-A, A-B and B-B atoms connections.

According to formula 1.2 given in chapter 1 and equations 4.2, 4.5 the structure function of monoatomic lattice is (e.g.[12]):

$$S(Q) = \left[ 1 + \frac{2}{N} \sum_{i=1}^{Nb} h(r_i) \frac{\sin(Qr_i)}{Qr_i} \right] \quad (4.6)$$

and for biatomic lattice:

$$S(Q) = [fA(Q)^2 \sum_{i=1}^{Nb} hA(ri) \frac{\sin(Qri)}{Qri} + fB(Q)^2 \sum_{i=1}^{Nb} hB(ri) \frac{\sin(Qri)}{Qri} + fA(Q)fB(Q) \sum_{i=1}^{Nb} hAB(ri) \frac{\sin(Qri)}{Qri}] \frac{2}{N[fA(Q)^2 + fB(Q)^2]} + 1 \quad (4.7)$$

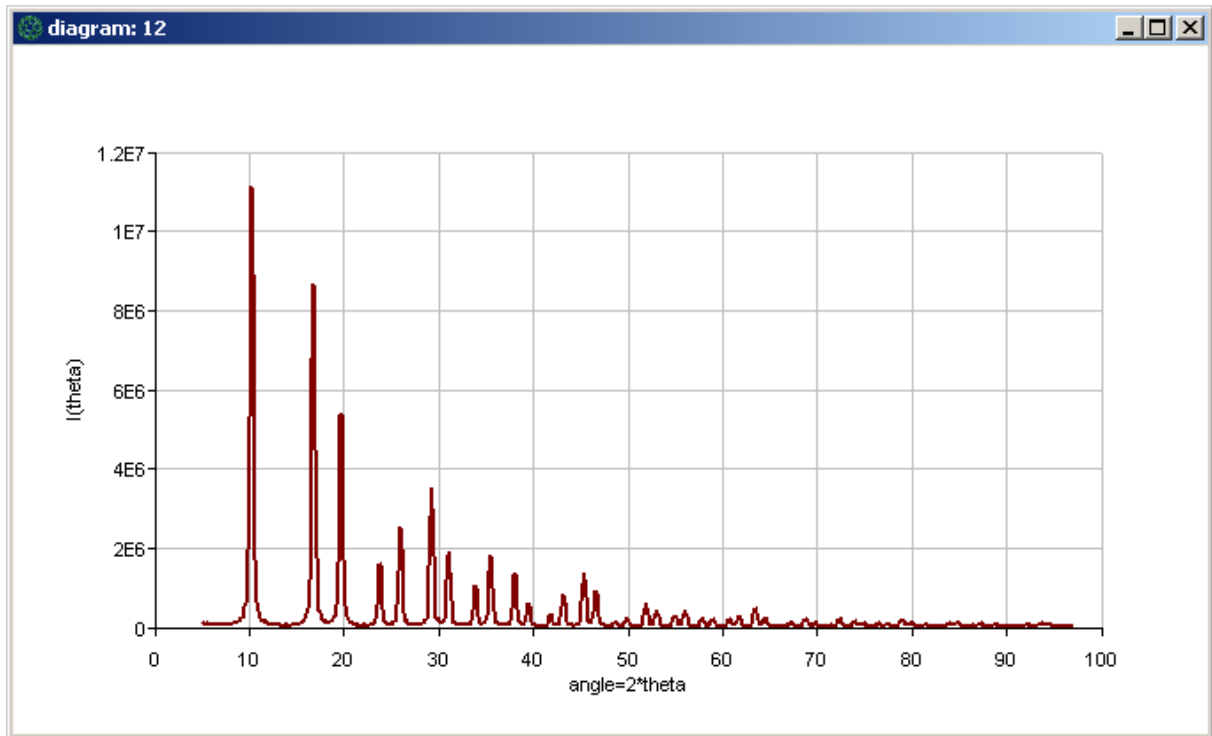


Figure 4.1 The diffraction pattern of diamond like structure of ideal Si nanograin (T=0 K)

Based on the equation 4.6 or 4.7 the reduced pair density function  $G(r)$  is evaluated. The  $G(r)$  function is calculated from the following equation:



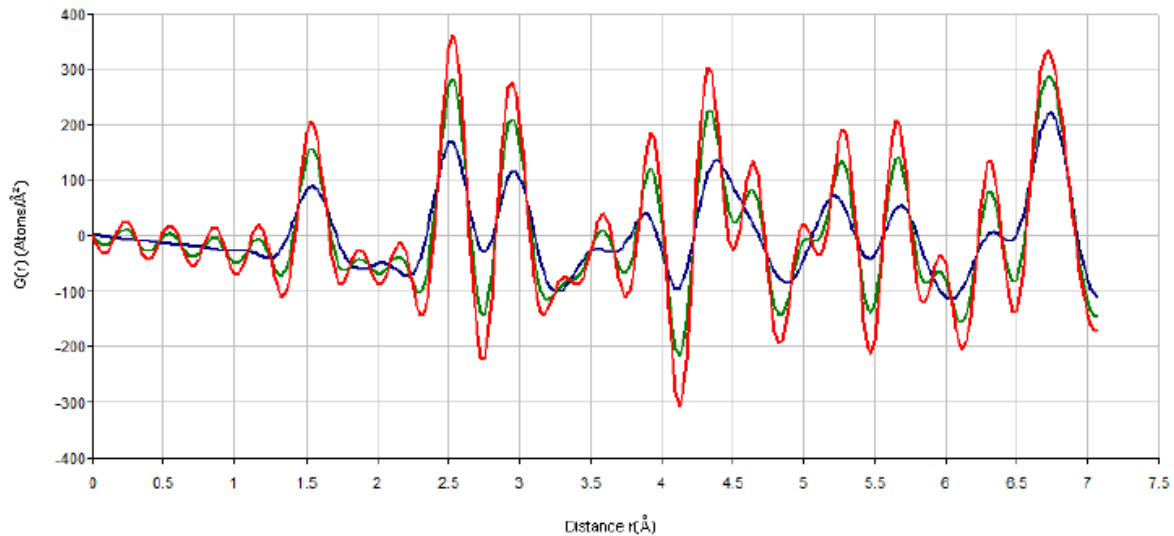
$$G(r) = \frac{2}{\pi} \int_0^{\infty} Q(S(Q) - 1) \sin(Qr) W(Q) dQ \quad (4.8)$$

The additional factor  $W(Q)$  is called a windowing (damping) function. The windowing function helps to remove ripples of the Fourier Transform of the finite length sample. In the simplest case  $W(Q) = 1$  and it's called the "Box Car" function. It gives high level of ripples which suppress the low intensity peaks or gives false peaks. The advantage is the best resolution of  $G(r)$  function. Other functions are defined as follows:

$$\text{Hamming} : W(x) = 0.54 + 0.46 \cos\left(\frac{x\pi}{2L}\right) \quad (4.9)$$

$$\text{Lorch} : W(x) = \text{sinc}\left(\frac{x\pi}{L}\right)$$

The Hamming function is very popular in applications in digital signal processing domain. The Lorch function [5] is known from neutron spallation studies. The comparison of these function is placed in fig.4.0.1. The default function in the NanoPDF.exe program is the Lorch function.



**Figure 4-0-14 Comparison of the  $G(r)$  function calculated for three windowing functions: red Box Car, green - Hamming, blue - Lorch**

### 3.2 Thermal vibration model

The kinematic theory of diffraction includes the impact of the deployment of different type atoms in the unit cell by the structure factor (SF):

$$F(hkl) = \sum_j f_{oj} \exp[2\pi i(hx + ky + lz)] \quad (4.11)$$

where  $f_{0j}$  is atomic scattering factor.

Structure factor reaches its maximum value when the crystal lattice is perfect. In fact, atoms are in motion and oscillate around the equilibrium position, with the result that the coherence of scattered waves is disturbed. It manifests itself in an increase of level of background and a decrease of the intensity of diffraction peaks. A typical way of dealing with this type of behavior is an introduction to SF (3.11) an atomic scattering factor dependent on displacement  $f = f_0 \exp(-M)$  where:

$$M = 8\pi^2 \bar{u}^2 \left( \frac{\sin(\theta)}{\lambda} \right)^2 = B \left( \frac{\sin(\theta)}{\lambda} \right)^2 \quad (4.12)$$

The  $\bar{u}^2$  factor is the mean square displacement of the atoms from their equilibrium positions. This quantity is directly dependent on temperature.

The B quantity is not easily derived theoretically and for numerical calculations must be replaced by approximation. The most known model is based on the Debye expression ([1, 3]):

$$B = \frac{6h^2}{m_a k_B \Theta} \left[ \frac{1}{4} + \frac{T}{\Theta} \varphi \left( \frac{\Theta}{T} \right) \right] \quad (4.13)$$

where  $\Theta$  is the Debye temperature,  $m_a$  is atomic mass,  $k_B$  is the Boltzmann constant, and  $\Theta$  are expressed in units of Kelvin,  $\varphi(\Theta/T)$  is given by:

$$\varphi \left( \frac{\Theta}{T} \right) = \varphi(x) = \frac{1}{x} \int_0^x \frac{\zeta}{e^\zeta - 1} d\zeta \quad (4.14)$$

**Note:** above equation is strictly applicable only to cubic crystals. For other structures it gives only the starting point for further research.

The NanoPDF.exe program calculates the value of the integral of the 4.14 equation by the following function (see [3]):

$$\phi\left(\frac{\Theta}{T}\right) = \begin{cases} \frac{T}{\Theta} + \frac{1}{36} \frac{\Theta}{T} - \frac{1}{3600} \left(\frac{\Theta}{T}\right)^3 & \frac{T}{\Theta} \geq 1 \\ \frac{1}{4} + \frac{\pi^2}{6} \left(\frac{T}{\Theta}\right)^2 - \sum_{j=1}^3 \left[ \frac{1}{j^2} \left( j \frac{T}{\Theta} + \frac{T^2}{\Theta^2} \right) \exp\left(-j \frac{\Theta}{T}\right) \right] & \frac{T}{\Theta} < 1 \end{cases} \quad (4.15)$$

Results of scattering function calculation of Au atoms for two temperatures are shown in fig.1.3.

### 4.3 Metropolis algorithm

One of algorithms derived from Monte Carlo simulations is the Metropolis algorithm. The algorithm has been developed over 50 years ago and its main use is calculation of multidimensional integrals. One of the features of Metropolis algorithm allows to generate any type of distribution. In this method, two main steps can be distinguished:

1. generation of a new configuration  $r_{n+1}$  based on the current one  $r_n$
2. acceptance or rejection of a new configuration values depend on the acceptance parameter  $p$

The first step can be formally written:

$$\overline{r}_{n+1} = \overline{r}_n + \Delta \overline{r} \quad (4.16)$$

where  $\Delta r$  is a vector taken from the uniform distribution.

Definition of the acceptance parameter is the following (see [7]):

$$p = \frac{W(r_{n+1})}{W(r_n)} \quad (4.17)$$

where  $W(r)$  is required distribution.

During the second step computer compares the acceptance parameter  $p$  with uniform distribution value  $w$  from  $[0, 1]$  range. If  $p > w$  the new configuration is accepted. Otherwise the previous configuration is taken.

Disadvantage of the Metropolis algorithm is high correlation between subsequent atom distances  $r_n$  from its equilibrium position. To decorrelate, a number of values determined by the "Decorr. parameter" is omitted before a

new atom position is taken. Formally the quality of decorrelation process can be evaluated by an autocorrelation parameter (see [7]):

$$C(l) = \frac{\langle r_{n+l} r_n \rangle - \langle r_n \rangle^2}{\langle r_n^2 \rangle - \langle r_n \rangle^2} \quad (4.18)$$

$$\langle r_{n+l} r_n \rangle = \frac{1}{M} \sum_{n=1}^M r_{n+l} r_n \quad \langle r_n^2 \rangle = \frac{1}{M} \sum_{n=1}^M r_n^2 \quad \langle r_n \rangle = \frac{1}{M} \sum_{n=1}^M r_n$$

where M is the number of configurations.

The  $C(l)$  values are in  $[0, 1]$  range. If  $C(l) = 0$  atom positions are totally decorrelated. The highest autocorrelation level is obtained for  $C(l) \approx 1$ .

The autocorrelation tests for the quasi-gaussian distribution (with std = 0.05) generated by the Metropolis algorithm are shown in fig.4-0-2 and fig.4-0-3.

In the first case the number of configurations M was tested for three values:  $M = 1000$ ,  $M = 2000$ ,  $M = 4000$  with the same value of the acceptance parameter  $p = 0.2$ . Two important features are visible: 1. the  $C(l)$  value quickly reaches the zero about  $l = 6$  and its independent of the M value 2. for higher values of M the amplitude of oscillations of  $C(l)$  are much lower. Another calculations were devoted to generation of distributions for a few values of the acceptance parameter. For tests the  $M = 2000$  was assumed. The lowest level of correlation was obtained for  $p = 0.5$  after one step. This value is often assumed as default in integration calculation. Above  $l = 8$  behavior of all three cases is quite similar. Summarizing, the results suggest values of the acceptance parameter about 0.5 and the decorrelation value above 5. Based on above interpretation the following default parameters have been set for the NanoPDF.exe program: the acceptance parameter  $p = 0.5$  the deccorelation value  $l=6$  User can change and adapt them to studied structures.

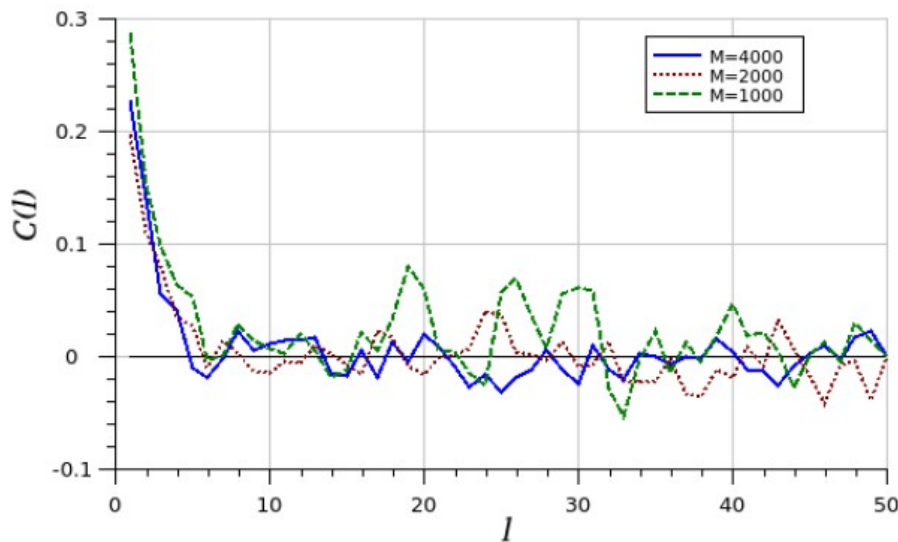


Figure 4-0-15 Autocorrelation test for the quasi-gaussian distribution (std=0.05) and three values of M and  $p = 0.2$  (see text)

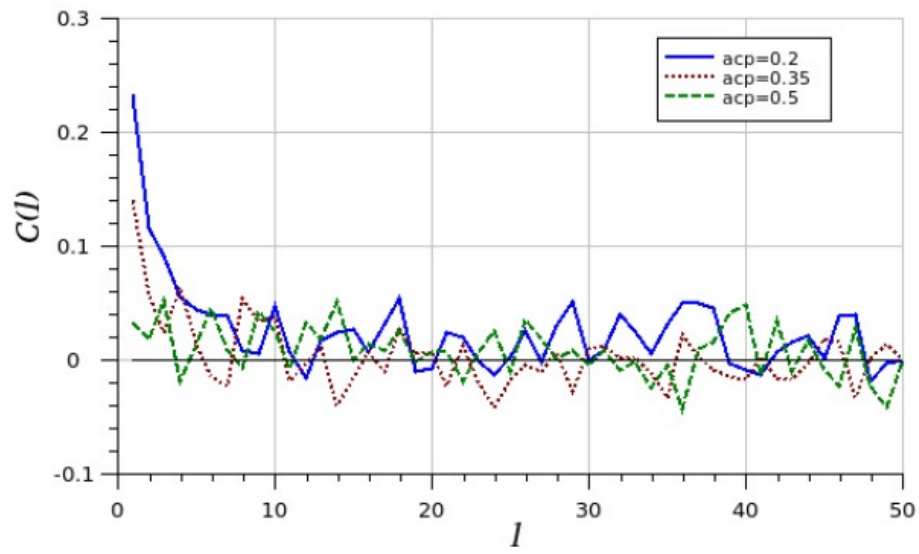


Figure 4-0-16 Autocorrelation test for the quasi-gaussian distribution (std=0.05) and three values of  $p$  and  $M = 2000$  (see text)

# Data presentation

## 5.1 Introduction

The NanoPDF.exe program was equipped with its own system of data visualization based on charts. It allows to manipulate data placed on many different windows. Some elementary operations enhancing chart details or increasing the readability are possible too.

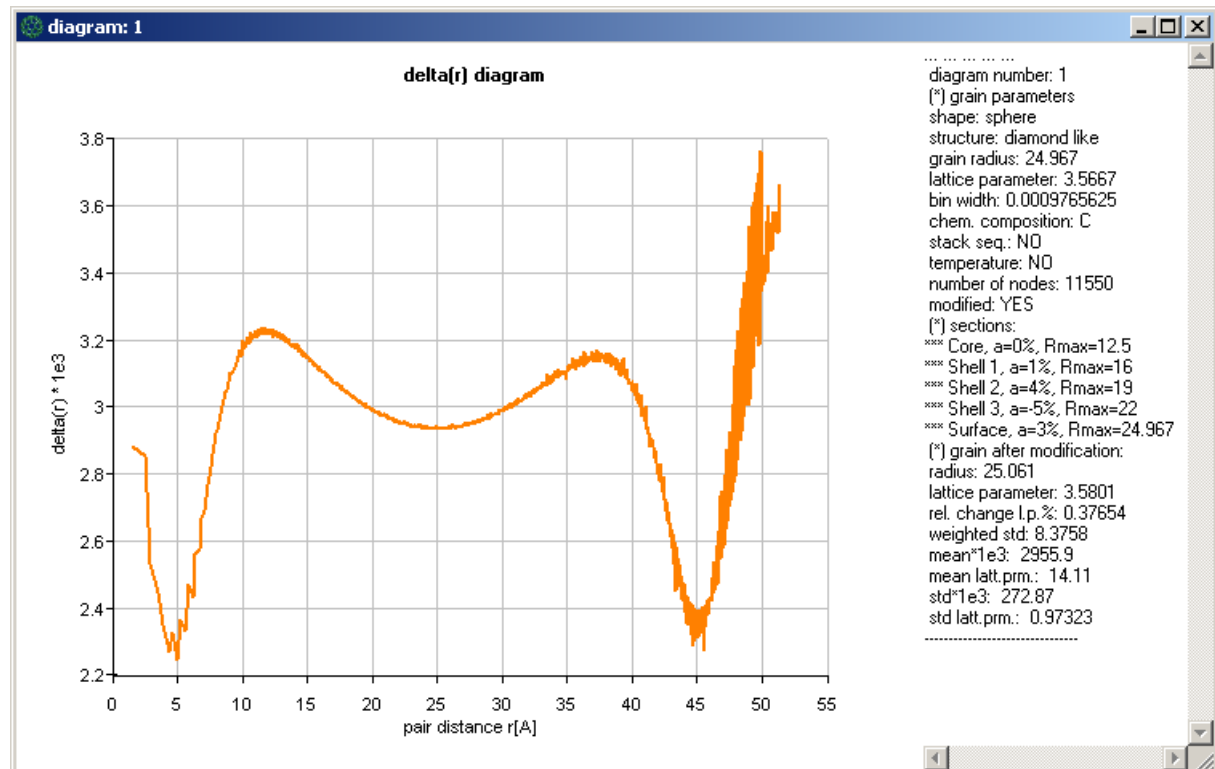


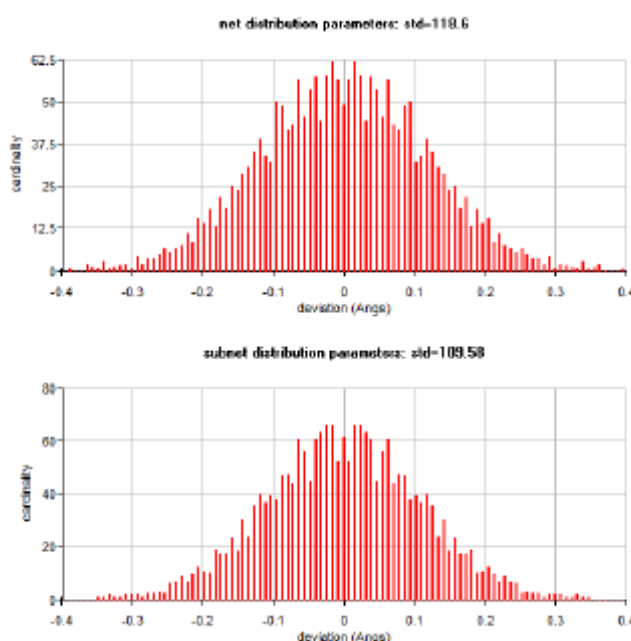
Figure 5-0-17 The view of the "Diagram window"

The properties of diagrams (see fig.5.1) and listed bellow:

1. automatic/manual axis scaling
2. zooming, visibility switching
3. adding/removing grid or legend
4. setting the title of axis and diagram
5. combine charts thanks to Drag&Drop mechanism
6. change the style, color, size of plotting
7. saving images to file in BMP/PNG format
8. saving raw data points to ASCII file
9. copying images to clipboard or to the mspaint.exe program

10. copying raw data to clipboard
11. printing in RGB or BW mode
12. do some numerical operations on data like: normalization to 1, peak reduction by square root or logarithm calculation
13. data denoising by using the moving average or Savitzky-Golay filters
14. derivation calculation
15. obtaining extended information about data

To start the action press the left or right mouse button but it is good to note that the most frequently performed operations have their own shortcut key. The detailed description of actions are given in sections 4.2 and 4.3. Some actions like: hints and sub plotting are available only for the special cases. In the first case, hints are added to scattering function diagrams where information about temperature is displayed (see e.g. 3.2). In the case of sub plotting, it's added if the thermal simulation of biatomic lattices is switched on. This option allow to visual verification of generated distribution (see fig.4.2).



**Figure 5-0-18 The view of the "verify distribution" window**

The NanoPDF.exe program allows to arrange the windows on the desktop. There are four possibilities all of them are accessed by the "Windows" menu or by a shortcut key:

1. Diagrams disperse 3x3 - shortcut key "F9"
2. Diagrams show all - shortcut key "F10"

3. Diagrams send back - shortcut key "F11"
4. Diagrams close all - shortcut key "F12"

In the first case the "Diagrams" windows are dispersed on desktop into array consists of three rows and three columns. If a window is a parent of a few windows (see section 4.2 and "inset" option) all of them are placed on the top of a parent window.

## ***5.2 Description of operations hidden under the left mouse button***

Four operations are possible with the left mouse button (LMB):

1. if only the LMB is pressed coordination points of pointer position are displayed and removed after release.
2. if the user presses the "Alt" key, coordination points of pointer will not be removed after release of the LMB
3. an inset of part of the "Diagram" window is displayed in a new window if the user presses the "Ctrl" key and then select a rectangular section with pressed LMB (see 4.3).
4. if the user presses the "Shift" key the Drag&Drop mechanism will be turned on. This option allows to move the current diagram(s) to the neighboring "Diagram" window(note: Drag&Drop works only within one instance of the NanoPDF.exe program)



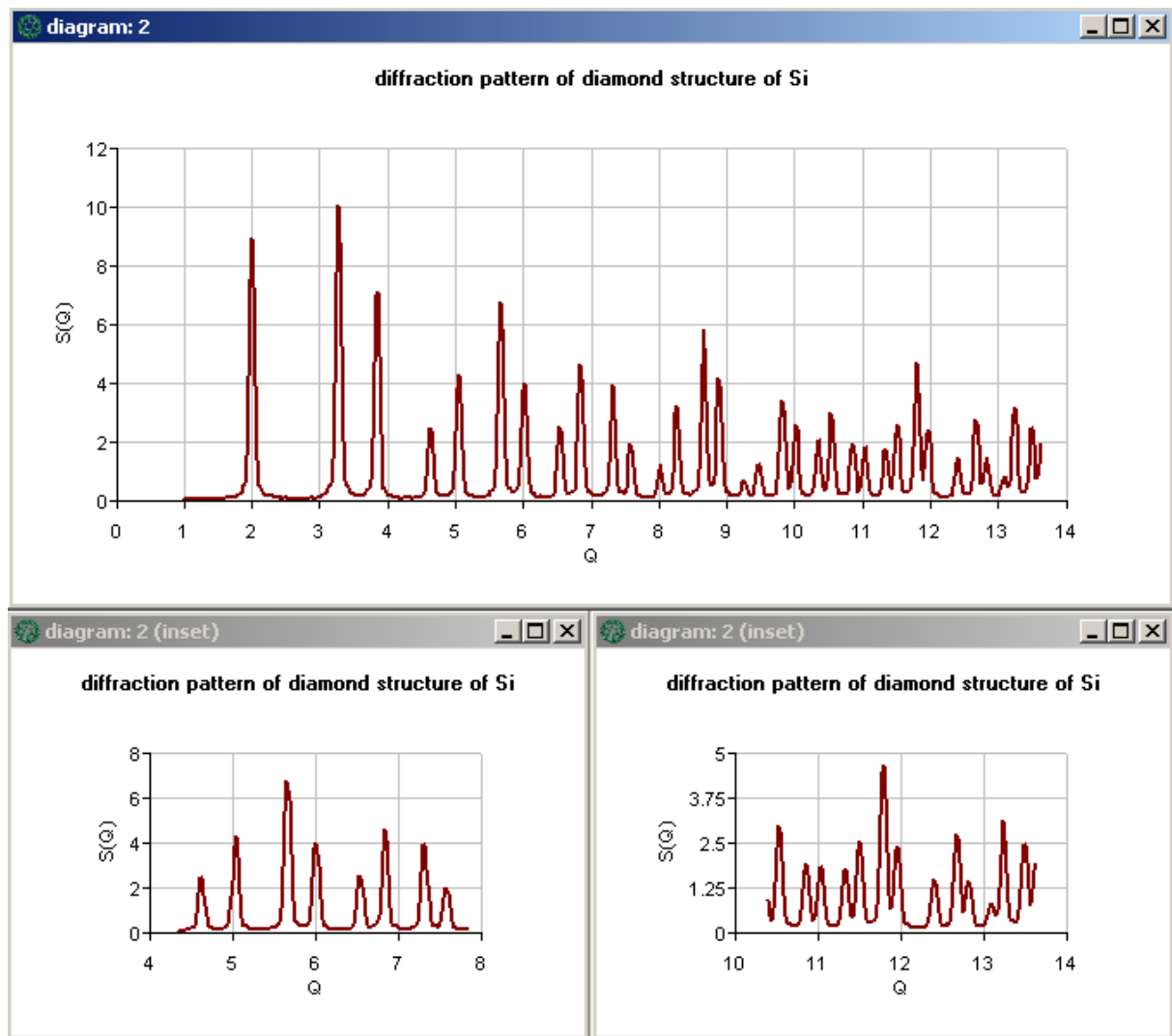


Figure 5-0-19 The view of diffraction diagram of Si with insets

### 5.3 Description of properties of mouse context menu

#### 5.3.1 Full screen on/off

Resizing the window between normal and full screen view. Shortcut key: "Ctrl+F".

#### 5.3.2 Save image

Save the current image into file preserving the size. Two formats are available: bmp and png. In the second case the "ncovert.exe" program must be installed and path to temporary folder is necessary.

#### 5.3.3 Save image to clipboard

Save the current image to clipboard.

### 5.3.4 Send image to mspaint

Program sends an image to the "Paint" program.

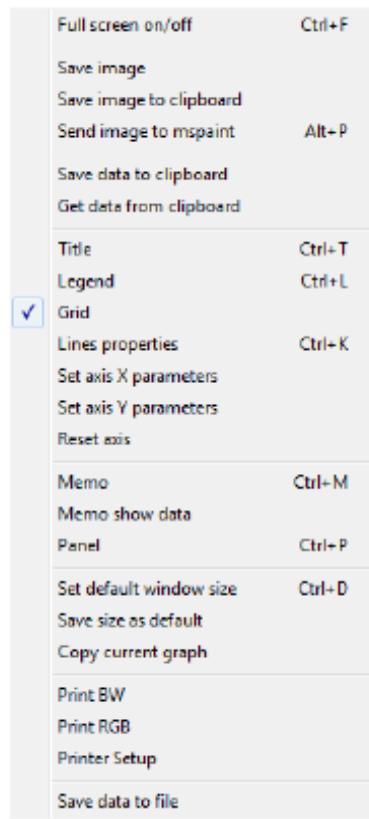


Figure 5-0-20 The context menu of the Diagram window

### 5.3.5 Title

The "Title" context menu allows to change the text of the diagram title. It is not possible

to change the properties as size, color, type of font. Shortcut key: "Ctrl+T"

### 5.3.6 Legend, Grid

Turn on/off the chart legend or grid. Shortcut key: legend - "Ctrl+L", grid - "Ctrl+G"

### 5.3.7 Line(s) properties

Change the drawing: color, style or size (see 4.5). To change a color click the colored rectangular and next from the "Color dialog" window select color. To change a style choose one of four style: line, dots, circle, comb in the "Style" combo box. To change a size choose one of three possibilities from the "Size" combo box. Note: a caption in the edit window is read only value.

Shortcut key: "Ctrl+K".

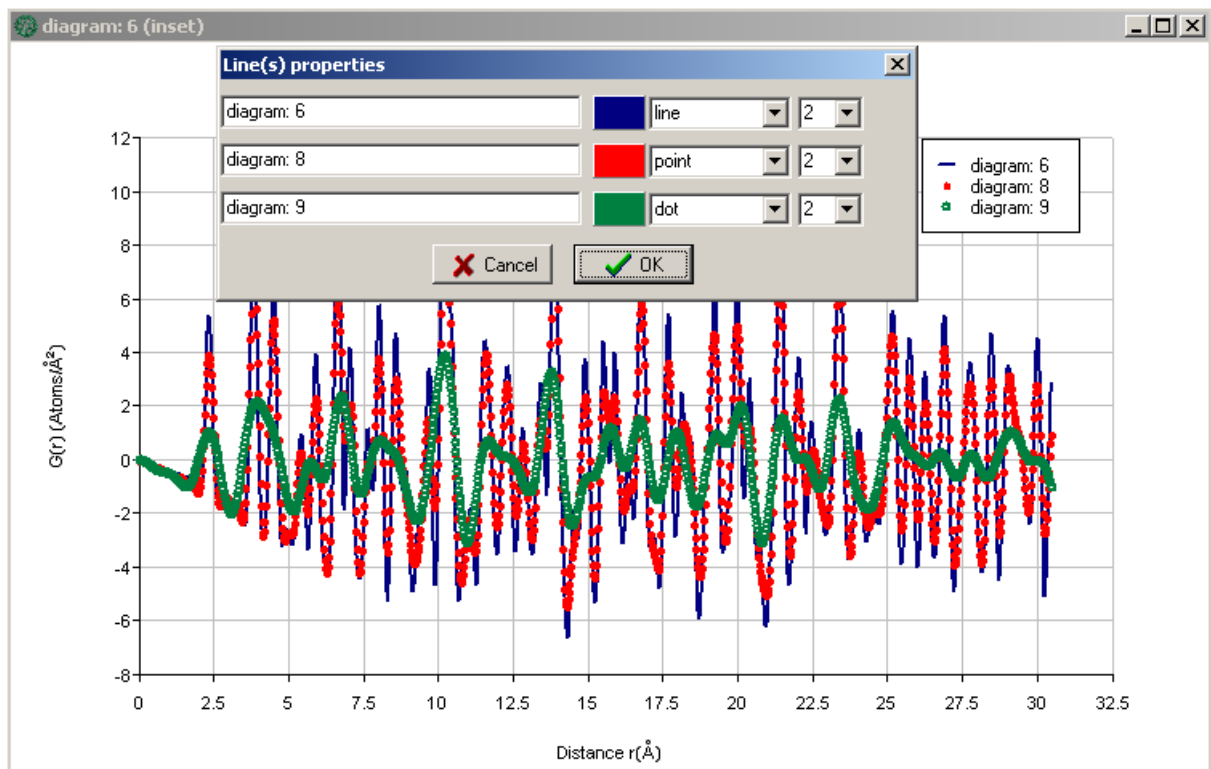


Figure 5-0-21 The view of "Lines properties" dialog window

### 5.3.8 Set axis X/Y parameters

User can turn off the automatic X/Y axis scaling and set custom ranges and tick distances, if the "OK" button is selected. In the "Title" edit window, title of an axis can be set. Shortcut key: x axis - "Alt+X" y axis - "Alt+Y"

### 5.3.9 Reset axis

Restore automatic X/Y axis scaling. Note: an axis title will not be changed.

### 5.3.10 Memo

User can turn on/off a "Memo" window placed on the right side the "Diagram" window (see 4.6). The "Memo" window displays all simulation parameters needed to create diagram(s). Shortcut key: "Ctrl+M".

### 5.3.11 Panel

User can turn on/off a "Panel" on the left side of the "Diagram" window.

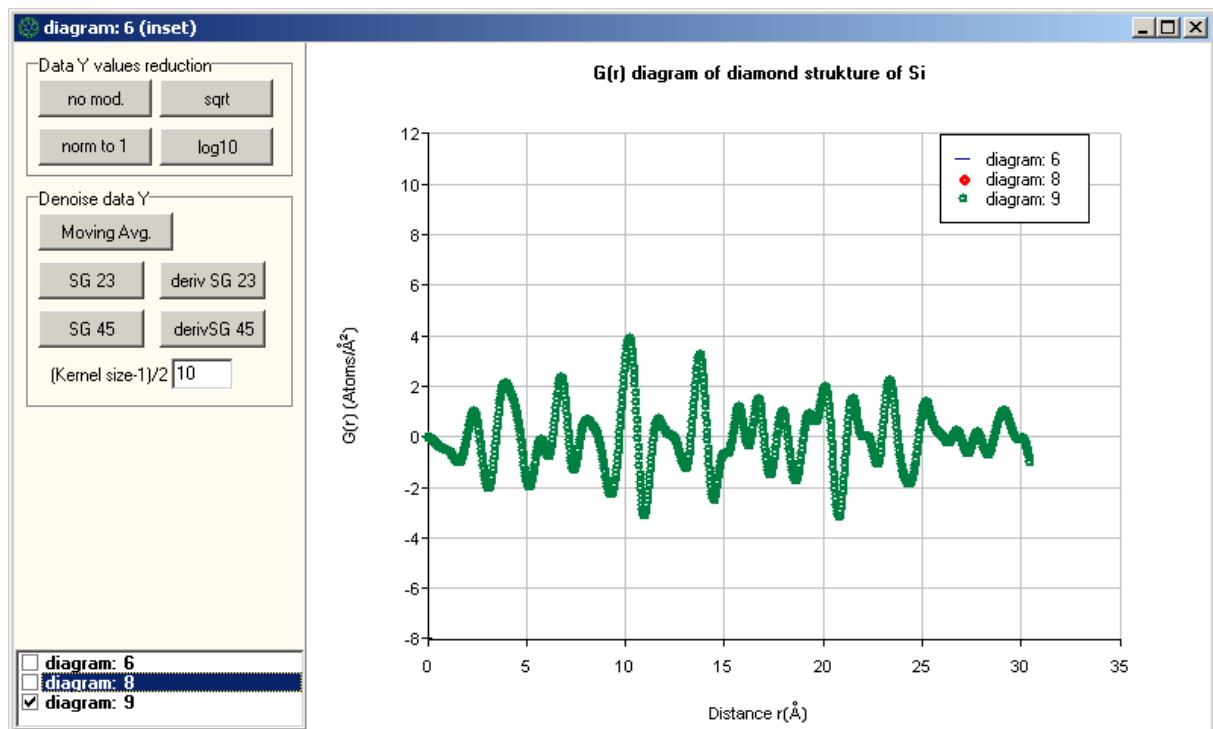


Figure 5-0-22 The view of the "Diagram" window with the "Panel" turned on

The "Panel" consists of a few methods to manipulation of data of diagrams placed in three groups:

1. reduction of "y values"
2. denoising data, computing first derivative
3. charts visibility switching

Except the last one group each operation causes opening a new "Diagram" window. The last one allows to turn on/off visibility of chosen diagram(s) by clicking on a caption in the "Drop List" window. Hidden diagrams are also omitted during actions placed in first or second group. The "y values" reductions consists of four methods:

1. "no mod." - no modification (data are simply copied to a new window)
2. "sqrt" - square root of "y values" is computing
3. "norm to 1" - normalization of the maximum "y value" to 1 with proportion saving of other values
4. "log10" - logarithm with base 10 of "y values" is computing

The "Denoise data Y" group box consists of five filters. Filters allow to smoothing data by the "noise" removing in the case of original set of values or

their first derivatives calculation. The size of kernel of each filter is adjustable by the "(Kernel size -1)/2" edit window. Increasing the size of kernel results in a higher level of smoothing.

$$y[n] = k[n] * x[n] = \frac{1}{M} \sum_{i=-M}^M k[i] \cdot x[n+1] \quad (4.1)$$

where  $k[n]$  are filter coefficients (kernel), in the case of MA all of them are equal to one,  $2 \cdot M + 1$  is a kernel size. This kind of filter can remove important details, so for "soft" filtering the Savitzky-Golay filters (SGF) are much better (see [2, 6]). The "SG23" or "SG45" filters smooth the original set of values. The "deriv SG23" and "deriv SG45" filters allow to first derivative calculation. The principle of operation of SGF filter is the same as the MA filter and is based on an appropriate set of coefficients in 4.1 equation. In the case of "SG45" or "deriv SG45" more high frequency components are present after their application. Shortcut key: "Ctrl+P".

#### **5.3.12 Set default window size**

User can resize the window to default size. This option is useful when diagrams are copied to other graphical programs and the preservation of size helps during image processing. To change default values of the width and height read subsection 4.3.13.

Shortcut key: "Ctrl+D".

#### **5.3.13 Save size as default**

The current size of the "Diagram" window is saved to ini file (keys: "gw", "gh"). For each call of 4.3.12 option or data presentation the window will be resized to default size.

#### **5.3.14 Print BW, Print RGB**

Simple printing of the current image. Printing customization is not possible. User can print the contents of the "Diagram" window in two formats:

1. BW - black and white colors only
2. RGB - full pallet of colors

Image is always placed on the top of paper and is stretching to take half of the page. If the "Memo" window is turned on the contents is printed on the bottom of paper but the number of topics is limited to five. If topics are longer than 20 lines, next lines will not be printed.

### **5.3.15 Save data to file**

User can save all data points to ASCII file independent on methods placed in the main menu.

The format description is given in the section...

### **5.3.16 Save/Get data to/from clipboard**

Program sends all data points to clipboard in ASCII format. It allows to read data by programs such as "Notepad".

## Technical details

### 6.1 File formats

#### 6.1.1 Native formats - \*.ndl, \*.his, \*.dij, \*.diff, \*.grp, \*.sec

All native formats consists of a standard header and simulation results. They are ASCII files, so it is easy to view their contents. Depending on the extension, files consist:

- \*.ndl - atom names with their coordinates (x,y,z)
- \*.his - pair distribution histogram values
- \*.diff - diffraction points (S or I)
- \*.grp - pair distribution function values
- \*.dij -  $\delta(r)=\Delta(r)/r$  values
- \*.sec - list of section parameters

The header contains standard information like:

- date: day/month/year, hours/minutes/seconds
- data size
- structure information: lattice parameter, grain radius, structure type, modification flag, atoms names
- comment

and some information dependent on extension.

Data values are separated with tabulation sign. Precision is limited to 6 digits after dot.

#### 6.1.2 Program settings - Nanopdf.ini

The Nanopdf.ini file is well known the INI format. INI files have basic structure composed of "sections" and "properties" (see e.g. [11]). The Nanopdf.ini file is created during first run and it shouldn't be opened beyond the main program.

#### 6.1.3 Scfact.sft file

The Scfact.sft file consists properties of elements like: names, scattering factors, lattice parameters of the most popular structures, type of the Bravais lattice, the Debye temperature and mass. Technically the 'sft' file is the 'ini' file. The "gen"

section consists of the "num" key where the number of elements is stored and "namX" keys where names of elements are stored. The name of an atom is also one of the section name. Contents modification via the NanoPDF.exe program is described in section 1.2. Note: This file must be placed in the same directory as the NanoPDF.exe program.

#### **6.1.4 rms.scr file**

The rms.scr file is a Rasmol/RasTop script file. The script can be generated by the RasTop.exe program (main menu: File ->Export ->Script,data) but remember to remove first 6 lines with: comments, "zap" and "load" commands. Note: This file must be placed in the same directory as the NanoPDF.exe program.

### **6.2 Acknowledgment**

#### **6.2.1 List of auxiliary third-party programs**

1. RasMol/RasTop.exe program - molecular visualization software,

website: [www.geneinfinity.org/rastop](http://www.geneinfinity.org/rastop)

2. ncovert.exe - graphic formats conversion program,

website: [www.xnview.com/en/nconvert.html](http://www.xnview.com/en/nconvert.html)

#### **6.2.2 Others**

word processor - LED,

website: <http://www.latexeditor.org/index.html>

### **6.3 Contact**

In case of any problems you can contact with me via email:

[kskrobas@mail.unipress.waw.pl](mailto:kskrobas@mail.unipress.waw.pl)



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