A concise ROD manual

Elias Vlieg

Radboud University, Institute for Molecules and Materials, Heyendaalseweg 135,
6525 AJ Nijmegen, The Netherlands. Email: e.vlieg@science.ru.nl

Table of Contents

1 Basics

ROD is a program that can be used to do a refinement of a surface structure using surface X-ray diffraction data. It contains various options that were found to be useful in the past. Very likely, new options will be added if these are needed. ROD is thus a program that is frequently being modified. A general introduction to the technique of surface X-ray diffraction can be found in references [1-5]. A brief description of the program has been published [6]. Thanks to a project at the ESRF, ROD has been made available to a wide user community and on many platforms. More information can be found at the web site:

www.esrf.fr/computing/scientific/joint_projects/ANA-ROD/index.html

The program can be downloaded from that site as well. The use of ROD is completely free, but users are requested to cite reference [6] if they have used ROD for a structure analysis.

In some sense, all ROD does is to calculate structure factors F_{hkl}:

$$F_{hkl} = \sum_j f_j e^{-B_j Q^2/(16\pi^2)} e^{2\pi i(hx_j + ky_j + lz_j)} \ , \tag{1}$$

with f_j the atomic scattering factor of atom j, B the Debye-Waller parameter, (hkl) the diffraction indices and (xyz)$_j$ the position of atom j in fractional coordinates. For bulk crystallography, the summation would go over all atoms in the bulk unit cell. For surface X-ray diffraction we have to deal with two 'unit cells': (1) all atoms defined to be in the surface and (2) all atoms in the bulk, see fig. 1. The convention normally used in surface diffraction is that the lattice parameters $\mathbf{a}_1$ and $\mathbf{a}_2$ of the surface unit cell are lying in the surface plane and that $\mathbf{a}_3$ is pointing outwards. Then the diffraction index l is along the out-of-plane direction. The size of $\mathbf{a}_3$ would be arbitrary for the surface unit cell (there is no true periodicity along that direction), but is taken to be the same as that of the (well-defined) bulk cell.

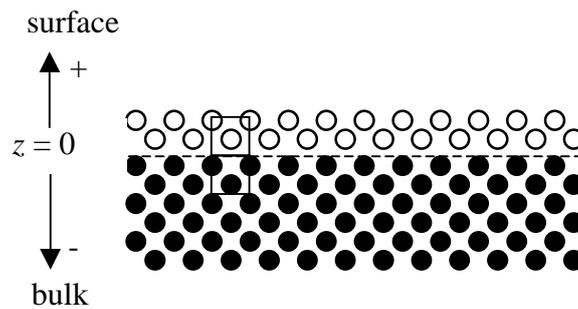Figure 1. Schematic of surface layer on top of a bulk crystal that extends to minus infinity. Unit cells for both sides are indicated.

The total structure factor is given by the interference sum of both contributions:

$$F_{sum} = F_{surf} + F_{bulk}, \tag{2}$$

with

$$F_{surf} = \sum_j^{\substack{surface \\ model}} f_j \theta_j e^{-B_j Q^2/(16\pi^2)} e^{2\pi i(hx_j + ky_j + lz_j)} \ , \tag{3}$$

3

$$F_{bulk} = \sum_{j=-\infty}^{0} F_u e^{2\pi i l j} e^{j\alpha} \tag{4}$$

and

$$F_u = \sum_{j}^{\substack{bulk \\ unit\,cell}} f_j e^{-B_j Q^2/(16\pi^2)} e^{2\pi i(hx_j+ky_j+lz_j)} \,. \tag{5}$$

In the definition of F_{surf} we included the occupancy parameter θ, because in the surface not all positions need to be fully occupied. F_{bulk} describes the bulk unit cell structure factors F_u summed from the top layer to -∞. Because of the attenuation factor α, only a finite amount of unit cells contributes to F_{bulk}. The summation (4) leads to:

$$F_{bulk} = F_u \frac{1}{1 - e^{-2\pi i l} e^{-\alpha}} \,. \tag{6}$$

F_{bulk} is the structure factor of a so-called crystal truncation rod (CTR). At integer values for l it has a very high intensity, but, due to the termination of the crystal at a sharp interface, even for non-integer l values there is a finite intensity.

It is important to define the bulk and surface models such that the surface starts exactly above the bulk unit cell. The surface unit cell can be chosen to extend arbitrarily deep into the 'bulk'. For example, in figure 1 the line dividing surface and bulk could be lowered by half a bulk lattice spacing. This increases the amount of layers in the surface model from two to three. In that case one has to choose the two layers immediately below the surface cell to form the bulk unit cell. When the atoms in this extra 'surface' layer are kept at their bulk positions, the calculated diffracted intensity will remain unchanged. (The phase will change, but the intensity is proportional to the square of the structure factor.) The atoms in the surface model can thus extend of many unit cells in the z-direction.

The computation of structure factor uses the coordinates of atoms in fractional coordinates, and therefore the lattice vectors of bulk and surface unit cells have to be the same. In addition, the coordinates should be given with respect to a common origin.

For a reconstructed surface, so-called fractional-order reflections will occur: expressed in the bulk lattice vectors such reflections have non-integer h and/or k indices. At such positions the bulk contribution is zero and the total structure factor equals F_{surf}. ROD has no problem calculating structure factors for fractional indices, but in general it is better to keep the in-plane diffraction indices integer by defining a larger unit cell. E.g. for a (2x1) reconstruction, (n/2,m) reflections would occur in terms of the bulk unit cell with lattice parameters $\mathbf{a}_1$ and $\mathbf{a}_2$. Choosing as lattice parameters $2\mathbf{a}_1$ and $\mathbf{a}_2$ leads to (2n+1,m) reflections being exclusively coming from the surface, while (2n,m) reflections are the interference sum of surface and bulk contributions. Only by choosing the larger lattice parameters, one uses a genuine *unit cell*. In the larger unit cell, the bulk unit cell will have twice the number of atoms (or a different factor for a different reconstruction). It is important to give all the atoms in the bulk unit cell the proper in plane

coordinates, because only then will the bulk contribution cancel for 'fractional-order' reflections.

2 More complicated situations

The simple situation described in the preceding section may not always represent reality. Things that may occur are:

1. the surface layer covers the bulk only partly
2. more than one type of surface layer is present (rarely occurs)
3. several symmetry-related surface unit cells are present
4. the crystal (bulk + surface) is rough.

All these situations can be dealt with, but a more complicated expression is necessary for F_{sum}. Figure 2 schematically shows how different parts of the crystal may be covered by different surface layers.
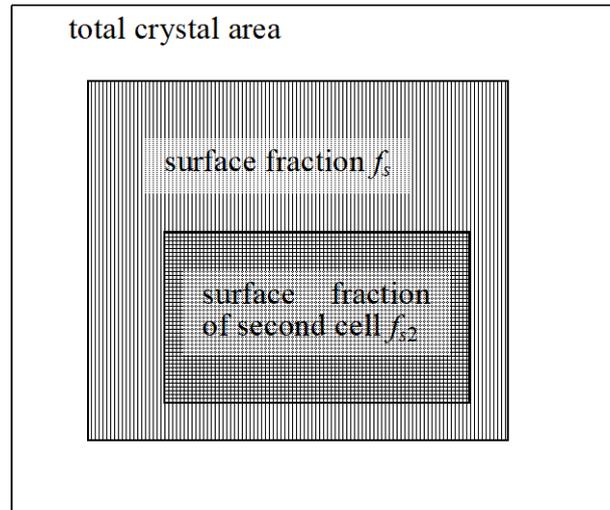
Figure 2. A schematic top view of a crystal that is partially covered by two different surface unit cells.

Define the following parameters:

S scale factor,
R roughness factor,
f_s fraction of crystal that is covered by surface layer,
f_{s2} fraction of f_s that is covered by second type of surface layer (normally 0),
N_d total number of symmetry-related domains,
α_j occupancy of domain j.

When calculating F_{sum}, the following structure factors play a role:

$F_{b,j} = F_{b,j,re} + iF_{b,j,im}$ structure factor of j-th domain of the bulk

$F_{s,j} = F_{s,j,re} + iF_{s,j,im}$ structure factor of j-th domain of first surface unit cell

$F_{s2,j} = F_{s2,j,re} + iF_{s2,j,im}$ structure factor of j-th domain of second surface unit cell.

The important structure factors are now:

$$F_{bulk} = SR\left[\sum_j \alpha_j F_{b,j}^2\right]^{1/2},$$ (7)

$$F_{surf} = SR\left[f_s(1-f_{s2})\sum_j \alpha_j F_{s,j}^2 + f_s f_{s2}\sum_j \alpha_j F_{s2,j}^2\right]^{1/2},$$ (8)

$$F_{sum} = SR\left[(1-f_s)\sum_j \alpha_j F_{b,j}^2 + f_s(1-f_{s2})\sum_j \alpha_j (F_{s,j}+F_{b,j})^2 + f_s f_{s2}\sum_j \alpha_j (F_{s2,j}+F_{b,j})^2\right]^{1/2}.$$ (9)

Rod always computes all three structure factors simultaneously. In these expressions, it is assumed that the symmetry-related domains are completely independent and large enough that their contributions add incoherently [7]. Depending on the distribution of the domains, it may also be true that the various contributions need to be added coherently. In that case first the summation is performed and after that the result is squared:

$$F_{sum,coh} = SR\left\{(1-f_s)\left[\sum_j \alpha_j F_{b,j}\right]^2 + f_s(1-f_{s2})\left[\sum_j \alpha_j (F_{s,j}+F_{b,j})\right]^2 + f_s f_{s2}\left[\sum_j \alpha_j (F_{s2,j}+F_{b,j})\right]^2\right\}^{1/2}$$

(10)

ROD allows choosing either of these situations, but incoherent addition corresponds to the most common situation.

2.1 Surface roughness

2.1.1 Approximate β-model

Various methods are available to include the effect of roughness. In general, surface roughness always leads to a decrease in scattered intensity. A very simple roughness model is the so-called β-model, in which surface level n has an occupancy β^n, see figure 3.
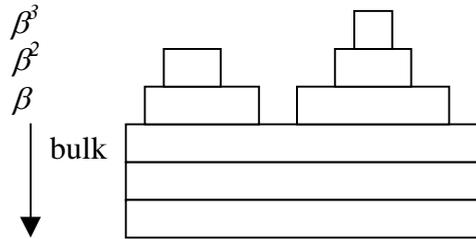

Figure 3. Surface roughness according to the so-called β model.

For the simple cubic case illustrated in figure 3 and assuming that each layer consists of a complete unit cell, it is straightforward to derive the roughness factor R by which the structure factor is reduced. For non-cubic crystals, or when also within a unit cell the occupancy varies

from layer to layer, the calculation becomes more complicated. A formula that nevertheless is valid in many cases is:

$$R = \frac{(1-\beta)}{\left[(1-\beta)^2 + 4\beta \sin^2 \frac{\pi(l - l_{Bragg})}{N_{layers}}\right]^{1/2}},$$ (11)

where l_{Bragg} is the l-value of a Bragg peak on the rod and N_{layers} is the number of layers in the unit cell. Equation (11) works fine if N_{layers} denotes the number of *equidistant* layers within the unit cell. This situation is described within ROD as 'approximated beta'. Different roughness distributions, or an exact calculation within the β-model, consume more computer time. It is therefore convenient to use equation (11) until proven otherwise.

2.1.2 Exact beta model

This model is intended as a test for the approximate beta model and works only for the bulk unit cell. The model is useful in order to illustrate the effect of the choice of N_{layers} on the structure factor, in particular when the layers are not equidistant or otherwise non-equivalent. It assumes that the last atom in the bulk unit cell has the lowest z-value (i.e., is the lowest atom). In the program, the contribution of the rough surface layers is stored in F_{surf}, thus surface unit cells cannot be used simultaneously.

2.1.3 Numerical models

All the other available models calculate the occupancies numerically, and are thus somewhat slower. They use a column approximation, i.e., they assume that all layers have an identical termination. When these models are used, there is no need for the l_{Bragg} parameter. The atoms in the bulk unit cell need to be properly ordered with decreasing z-values (topmost atom first), because the program determines the layer spacing vector $\mathbf{R}_{layer}$ from this and from the value of N_{layer}. The phase shift going from one layer to the next is assumed to be: $\psi_{hkl} = \mathbf{R}_{layer} \cdot \mathbf{H}$. The total structure factor is then the sum over identical column structure factors F_{column} shifted by the appropriate phase factor and weighted by the occupancy θ_n:

$$F_{tot} = F_{column} \sum_n \theta_n e^{in\psi_{hkl}} .$$ (12)

The reduction factor due to the roughness is now:

$$R = \left| \sum_n \theta_n e^{in\psi_{hkl}} \right|^{1/2} .$$ (13)

Using this approach, we make errors in the absolute phase factors (but these are hardly used). The following roughness models are available:

1. beta model: same as before, different type of calculation
2. Poisson model: BETA represents the total coverage (≥ 0) in level distribution according to Poisson (random) statistics.
3. Gaussian: BETA is decay length (> 0) of Gaussian: e^{-n^2/β^2} .

4. Linear: BETA is number of layers over which occupancy goes to zero (> 0).

5. Cosine: BETA is number of layers over which occupancy goes to zero over half the cycle of a cosine function.

6. Two-level: BETA is island coverage in simple two-level model ($0 \leq$ BETA < 1).

2.1.4 Fractional-order data

The models for surface roughness presented above are intended for integer-order data (CTR's) and show a (strong) l-dependence. When there are no lateral correlations across steps, this l-dependence should be absent, as typically expected for fractional-order reflections. Each terrace will then contribute to the total intensity, not to the total amplitude (incoherent addition). There is still an effect of the roughness, but without l-dependence. If the coverage of level n is θ_n, then the total intensity for a fractional-order peak is:

$$I_{fract}^{rough} = \sum_{n=0}^{\infty} (\theta_n - \theta_{n+1})^2 . \tag{14}$$

For the beta model, with $\theta_n = \beta^n$, this leads to:

$$I_{fract}^{rough} = \frac{1-\beta}{1+\beta} \Rightarrow R = \sqrt{\frac{1-\beta}{1+\beta}} . \tag{15}$$

Fractional-order reflections for which the roughness needs to be calculated in this incoherent way, should be labeled with a non-integer value of *dataflag* parameter (e.g. 0.5).

2.2 Symmetry-related domains

It may happen that on a surface many domains occur that are symmetry-related. E.g. a Si(100) surface that is (2x1) reconstructed will in general also have (1x2) domains (with normally the same occupancy). At 'fractional-order' positions, only one of the two domains contributes, but at CTR positions one has to add the contributions of both. Rather than adding a second unit cell to the computation, it is more convenient to add the structure factor for the original unit cell, but computed for the corresponding, symmetry-related diffraction indices. This is explained below.

Suppose the surface has N_d domains. The structure factor of domain 1 is evaluated using the normal fractional coordinates and the normal $\mathbf{H} = (hkl)$. The structure factor of domain n is given by (ignoring the atomic scattering factor and the Debye-Waller factor):

$$F_{n,\mathbf{H}} = \sum_j e^{2\pi i \mathbf{r}_{n,j} \cdot \mathbf{H}} , \tag{16}$$

Evaluation of this can be done in different reference frames. The real space position $\mathbf{r}_{n,j}$ is most easily expressed in terms of the lattice vectors of domain n, because in that case the fractional coordinates are (by definition) identical to those of domain 1, which are known. Thus it is convenient to use:

$$\mathbf{r}_{n,j} = x_j \, \mathbf{a}_{1,n} + \ y_j \, \mathbf{a}_{2,n} + z_j \, \mathbf{a}_{3,n} . \tag{17}$$

The reciprocal lattice vector $\mathbf{H}$ is most easily expressed in the reference frame of domain 1:

$$\mathbf{H} = h\mathbf{b}_{1,1} + k\mathbf{b}_{2,1} + l\mathbf{b}_{3,1} \ . \tag{18}$$

However, the dot product of these two terms is not simple, because there are many cross terms when multiplying the $\mathbf{a}_{i,n}$'s with the $\mathbf{b}_{j,1}$'s. Fortunately, it is easy to express $\mathbf{H}$ in terms of the reciprocal lattice vectors of domain n. If matrix $\mathbf{T}_n$ transforms the real space lattice vectors of domain 1 into those of domain n, then the same matrix transforms the diffraction indices:

$$\begin{pmatrix} \mathbf{a}_{1,n} \\ \mathbf{a}_{2,n} \\ \mathbf{a}_{3,n} \end{pmatrix} = \mathbf{T}_n \begin{pmatrix} \mathbf{a}_{1,1} \\ \mathbf{a}_{2,1} \\ \mathbf{a}_{3,1} \end{pmatrix} \Rightarrow \begin{pmatrix} h_n \\ k_n \\ l_n \end{pmatrix} = \mathbf{T}_n \begin{pmatrix} h \\ k \\ l \end{pmatrix} . \tag{19}$$

In the summation over all domains in equation (9) we can thus use one unit cell, but calculate the corresponding $\mathbf{H}_n$ for each domain.

2.3   Subscale factors

Ideally, measured structure factors are corrected in such a way that a single scale factor applies [6, 8]. In practice, however, this ideal is not always reached. It is particularly difficult to obtain reflectivity data on the same scale as non-specular rods. Also, an insufficient detector acceptance and a difference in line width between integer-order and fractional-order data can cause a difference in scale factor between these two types of data. For this reason it is possible to define subscale factors. These need to be set in the *dataflag* parameter, see the description of the data files.

2.4   Different energies

Data may have been acquired using different energies in order to make use of anomalous scattering. It is possible to use and fit data with different energies as a single data set, by using the *dataflag* parameter to tag the different cases. See description of the data files.

2.5   Molecule on surface

The surface structure factor F_{hkl} in principle allows any object on the surface to be taken into account. If a complete molecule is absorbed on a surface, however, it is more convenient to treat this as a single object rather than as separate atoms. ROD has therefore the option to define molecules with a fixed structure whose position, orientation and coverage can be defined with respect to the surface. These parameters can be used to fit data. It is possible to convert molecules to a normal surface model and thus to subsequently do a normal structure refinement.

The crystalline part of the interface may contain structural elements that are better treated as molecules than separate atoms, e.g. CO_3 groups in calcite. Such groups should then be removed from the fit file and be included as molecules. Note that this requires the coordinates of these atoms to be stored in Cartesian coordinates and in Angström units. A convenient way to do this conversion automatically, is to save the model as an .xyz file (using PLOT XYZ). Note that the atoms forming the molecule should form a unit in real space, thus without using

the translational symmetry of the lattice, because otherwise the rotation of the molecule leads to erroneous results.

2.6 Liquid layer

When studying solid-liquid interfaces, the liquid typically assumes bulk liquid properties away from the interface. This part of the liquid is invisible in all non-specular rods and typically only contributes to the specular rod for small *l*-values. In many cases therefore this bulk liquid can be ignored, but it is possible to add the contribution of a liquid layer.

2.7 Dynamical effects

At very glancing angles, refraction effects may occur, e.g. total reflection when the X-ray beam enters a medium with a higher electron density. Such effects can usually be neglected [5], but ROD allows these to be taking into account. This is set in ROD.SET.CALC>.

3 Working with ROD

3.1 General

ROD uses a simple command-line interpreter for interactive work (the subroutines for this are in the file MENU.C). There are several menu's available; when starting the program, one enters the main menu with prompt ROD>. Typing 'help' or '?' produces a list of the available commands with a brief description. At least the part of each command shown in capital letters needs to be typed in, in order for the command-line interpreter to accept it. One may type as many commands on a single line as one likes. Execution starts after typing <Return>. If a mistake is made somewhere, the remainder of the command line is deleted. The command-line interpreter will only prompt for input if this is not given (or incorrectly given) in the command line. For starting users it is therefore convenient to type only one command at a time. The subsequently displayed prompt will usually explain what the required next step is.

When leaving the program (typing QUIT), the most important parameters are saved in a macro file 'ROD_INIT.MAC'. Similarly the plot settings are saved in 'PLOTINIT.MAC'. When restarting ROD, these two macro files are read in and most settings are therefore restored. These macro files simply consist of text lines that form valid command sequences in ROD. One can also generate separate macro files that can be executed using the command MACRO.

There are a few commands reserved for the command line interpreter itself. DEBUG will print the commands of a running macro file to the screen, NODEBUG will turn this option off. Similarly, TOFILEON/TOFILEOFF will start/stop writing all the output to a file with name menulist.txt.

ROD runs under Windows and UNIX variations. Except for a special Windows version, all versions are distributed through the website at the ESRF.

The plotting routines used in the special Windows versions of ROD are from the commercial package GraphiC™. In order to make a plot, one only needs to use commands based on the command-line interpreter. In fact, only a plot file ('plot.tkf') is generated that can be visualized using the program playwnt.exe that is part of the GraphiC™ package. Appendix A lists the available symbols and line styles in GraphiC™.

3.2   Input files

In order to do a structure analysis, one needs to read in various types of files. These files can either be generated using a standard editor or saved within ROD using the LIST command. The default output of LIST is the computer screen, but by specifying a file name, the output is written in the proper format to a file.

3.2.1 Data files

Data files (default extension .dat) have the following format:

```
first line      comments
other lines:   h    k    l     f_data  sigma     [dataflag]
```

It is thus a list of diffraction indices (*hkl*) followed by the structure factor and the standard error on the structure factor. *dataflag* values are optional and, if provided, are used in the following way, where *dataflag* is a number written as *mnnii.x*.

x	:	if non-zero, this indicates a fractional rod (used in roughness calculation).
ii = l_{Bragg}	:	value of a Bragg peak on the rod (used in approximate β model)
$nn = subscale$	:	serial number of subscale parameter. 0 means no subscale.
$m = energy$	:	serial number of energy parameter. 0 means default energy.

When listing a data file on terminal, not the full value of *dataflag* is shown, but the values of the four relevant parameters.

Data files of this type and with properly estimated error bars can be generated from raw scan files by using e.g. the programs ANA and AVE. The data should normally consist of non-equivalent reflections. Converting measured integrated intensities to structure factors requires a whole range of correction factors, see refs. [8, 9].

The error bars near bulk Bragg peaks can be increased in order to give less weight to these parts of the data that have limited sensitivity to the interface structure. This is done in ROD.SET.CALC>.

3.2.2 Surface model files

Surface model files (default extension .sur) allow one to read in the coordinates of a surface model. Format:

first line: comments
second line: a_1 a_2 a_3 α_{23} α_{13} α_{12} (lattice parameters)
other lines: element x y z [N_{DW}] [N_{DW2}]

Each element is given its standard symbol, the (x,y,z) position should be given in fractional coordinates. N_{DW} and N_{DW2} are the *serial number* for the Debye-Waller parameter for that atom in the in-plane and out-of-plane direction, respectively (optional). There are five special 'elements', E1 through E5, in order to enable the use of special atomic scattering factors.

3.2.3 Bulk model files

Bulk model files (default extension .bul) allow one to read in the coordinates of the atoms in the bulk unit cell. The format is the same as for the surface model:

first line: comments
second line: a_1 a_2 a_3 α_{23} α_{13} α_{12} (lattice parameters)
other lines: element x y z [N_{DW}]

In order to calculate structure factors, at least one model (bulk or surface) has to be read in. If both are used, the lattice parameters have to be identical.

3.2.4 Fit model files

A surface model file contains fixed values for the coordinates of the atoms in the surface unit cell. When optimizing a surface structure, one needs to be able to change the positions of the atoms. Due to symmetry constraints, when one atom is moved, often also other atoms need to be displaced in a symmetric fashion. Bulk crystallography software often contains this symmetry information and only one atom from a symmetry-related set needs to be given by the user. This is not the case in ROD and all these relations have to be given by hand. This is done within ROD using displacement parameters. Figure 4 illustrates this for a simple model. Let δ be the common displacement parameter of the three atoms. Then the in-plane coordinates of these atoms are:

$(1/3+\delta, 1/3+\delta)$
$(-1/3-\delta, 0)$
$(0, -1/3-\delta)$.

The ingredients one needs to describe a position of an atom are therefore: starting position, displacement parameters and constants giving the direction and magnitude of the displacements. In order to be able to describe many situations, ROD has two sets of these parameters for each atom. In a structure refinement one may want to optimize in addition: in-plane and out-of-plane Debye-Waller parameters and the occupancy.

All these parameters together are put in a fit file (default extension .fit), which has the following structure:

first line: `comments`
second line: **a**$_1$ **a**$_2$ **a**$_3$ α_{23} α_{13} α_{12} (lattice parameters)
other lines:

`[N] el` x_{start} C_{x1} N_δ C_{x2} N_δ y_{start} C_{y1} N_δ C_{y2} N_δ z_{start} C_{z1} N_δ C_{z2} N_δ N_{DW1} N_{DW2} N_{occ}

where C are constants giving the magnitude of the displacement, N_δ are serial numbers of displacement parameters, N_{DW1} is the serial number of the in-plane Debye-Waller parameter, N_{DW2} is the serial number of the out-of-plane Debye-Waller parameter and N_{occ} is the serial number of the occupancy parameter.

[N] is an optional serial number of the atoms in the model, but the file should have N
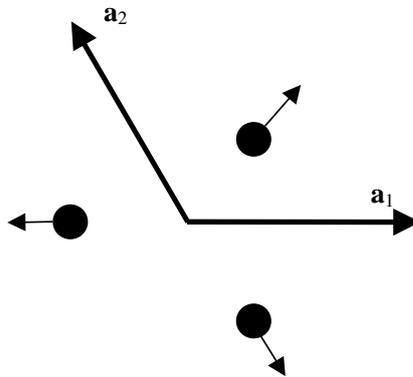
Figure 4. Top view of surface unit cell with lattice parameters **a**$_1$ and **a**$_2$ and with three atoms that are displaced in a symmetric fashion.

values for all atoms or for none. The actual value of N in the file is ignored, because ROD internally always uses serial number 1 for the first atom, etc. When listing the fit model, the N's are given corresponding to this internal numbering. N is provided for convenience when calculating distances between atoms, etc.

Symmetry-related atoms are given the same N_δ, N_{DW1}, N_{DW2} and/or N_{occ}. When $N_{DW2} = 0$, the program uses the value of N_{DW1} as an isotropic Debye-Waller parameter. When $N_{occ} = 0$, an occupancy of 1 is assumed. As an example, the x-value of atom i is computed as:

$$x_i = x_{start,i} + C_{x1,i} * V(N_{\delta 1,i}) + C_{x2,i} * V(N_{\delta 2,i}), \tag{20}$$

where $V(N_\delta)$ is the value of the displacement parameter with serial number N_δ.

In the *z*-direction, the combination of the two constants and displacement parameters can for example be used to model a thin film with a variable distance from the bulk and with variable layer spacing. An example of a fit file (with truncated decimals for clarity) of such a case is:

```
!three layer film with variable height and layer spacing
 3.8400 3.8400 9.4060  90.000  90.000 120.000
Ge 0.33333 0.0 0 0.0 0 0.66667 0.0 0 0.0 0 1.0000 1.0 1 2.0 2 0 0 0
Ge 0.66667 0.0 0 0.0 0 0.33333 0.0 0 0.0 0 0.6667 1.0 1 1.0 2 0 0 0
Ge 0.00000 0.0 0 0.0 0 0.00000 0.0 0 0.0 0 0.3333 1.0 1 0.0 2 0 0 0
```

The starting positions and the *z*-fitting parameters are highlighted. The displacement parameter with serial number 1 is de height of the entire film above the bulk. Displacement parameter 2 changes the layer spacing within the film, where the constants ranging from 0 to 2 make sure that all layers get the proper displacement.

When performing a structure refinement, ROD optimizes the values of all variable parameters listed above (the ones with a serial number) and uses in addition an overall scale factor, the roughness parameter β and the surface fraction f_s.

When using a .fit file, a .sur file is no longer needed, since the .fit file contains the same (and more) information. It is nevertheless often quicker to start with a .sur file, reading this into ROD and saving it as a .fit file using the list command (e.g., ROD>list fit test.fit). This will generate a template .fit file that can subsequently be edited.

In order to check whether a fit file has been correctly edited (with all the coupled displacements the file may become rather complicated), it is possible to make a very simple, in-plane projected plot of the surface unit cell. The parameters for this are set in ROD.SET.PLOT>, the actual plot is made in the ROD.PLOT> menu by using the commands MREFINED, MBOTH or MLARGE.

3.2.5 Surface molecule file

A molecule file (default extension .moc) contains a description of a molecule as a list of its atoms. Since the structure of a molecule is not defined with respect to a particular crystal lattice, the coordinates of the atoms in the molecule are given in Angstroms with respect to a Cartesian coordinate frame. For an actual structure factor calculation, the positions of the atoms in the molecule are converted to the usual fractional coordinates. To describe the location and orientation of the molecule, it is characterized by three position (x,y,z) in and three rotation (xrot, yrot, zrot) parameters, expressed in fractional coordinates and degrees, respectively. The molecule has starting values for these six parameters (given in the file that defines the molecule) and also six fitting parameters that are simply added to the starting values. All these parameters act with respect to the molecule centre that also needs to be defined (this is again in Angstroms),

see figure 5. The coverage is the final parameter that characterizes the molecule. Thus the seven available fitting parameters are:

MOLPAR 1,2,3:   molx, moly, molz

MOLPAR 4,5,6:   molxr, molyr, molzr
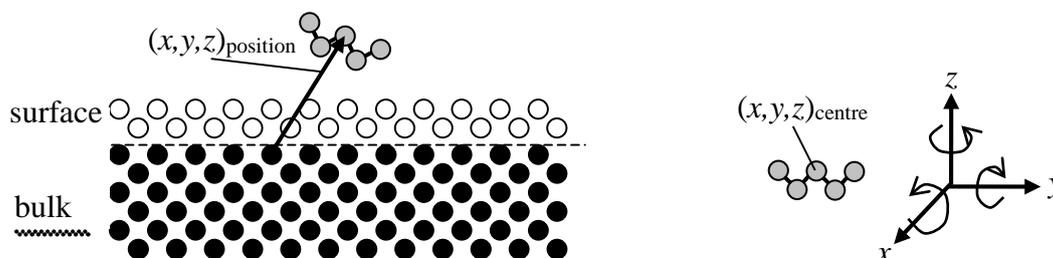
MOLPAR 7:   molocc

Figure 5. A molecule on a surface is characterized by position and rotation parameters as shown here. The positions of the atoms and the centre of the molecule are given in Angstroms in a Cartesian frame. The rotations about the three axes are in the same frame, but the position with respect to the surface model is in fractional coordinates..

For orthogonal lattices the rotations about x, y and z correspond to rotations about the **a**, **b** and **c** axes, respectively. In general, the x-rotation is about the **a** axis, the y-rotation is in the plane defined by **a** and **b** and the z-rotation is perpendicular to that plane. Since the molecule can be oriented in any direction, the Debye-Waller parameters are only allowed to be isotropic for the atoms of a molecule.

The structure of the file is:

```
1st line:     comments
2nd line:     xs ys zs xrs yrs zrs      (start values, frac.)
3d line:      x_centre      y_centre      z_centre      (centre, Å)
other lines:  element   x    y    z    [N_DW] (values in Å)
```

The serial number of the Debye-Waller parameter is optional.

When listing the parameters of the molecule model using ROD>LIST MMOLECULE, the parameters are listed in fractional coordinates and include the effect of position and rotation operations, if applied. This allows saving the molecules as a standard surface file that can subsequently be incorporated in a fit file if fitting beyond a fixed object is required.

3.2.6 Liquid layer files

Files describing the model used for a liquid layer (default extension .liq) have a content
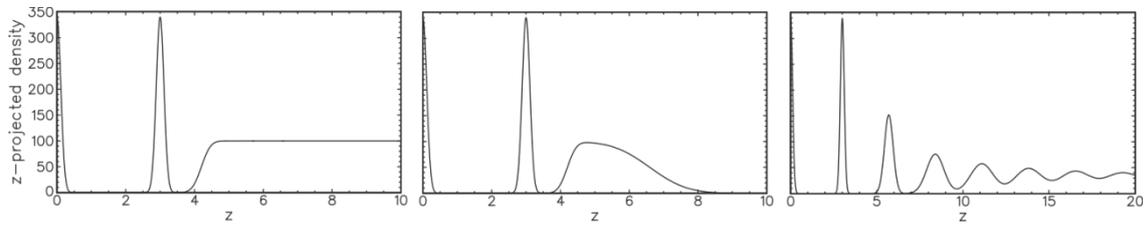

Figure 6. The profiles of three different liquid layer models: step, film and layered.

that depends on the liquid model used. At the moment four types are implemented, STEP, FILM, DFILM and LAYERED. The profiles they describe are shown in figure 6. The structure of the liquid model file is:

```
first line:     comments
2nd line:       model identifier [step, film, layered]
next lines:     list of parameters
```

The list of parameters depends on the model:

```
step:        density   zpos   width
film:        density1  zpos   width1
             density2  zthickness  width2
dfilm:       density1  zpos   width1
             density2  zthickness1  width2
             density3  zthickness2  width3
layered    el coverage  zpos  zspace  Bstart  Bdamping
```

In the layered model, the last two parameters are the temperature B parameters (in Å^2), where the value for layer n is given by:

$$B_n = B_{start} + nB_{damping}.$$

The density is expressed in electrons/bulk unit cell. The positions and widths are in fractional coordinates. For the layered model, the electron density per bulk unit cell is given by:

$$density = \frac{Z_{element} \times coverage}{zspace}.$$

3.2.7 Fit parameter files

Fit parameter files (default extension .par) contain values of all fit parameters. They have the format of a macro file, i.e., all parameters are specified as a series of valid ROD command lines with the format:

```
<parameter name> [serial number] <value> <lower limit> <upper limit> <fit yes/no>
```

16

When the lower and upper limits are both set to 0, no limits are applied during fitting (only possible for Levenberg-Marquardt fit).

When during a structure refinement a particularly nice fit is generated, the corresponding parameter values can be saved to a file by using the ROD>LIST PAR command. See Appendix B for an example.

3.2.8 File with parameter constraints

Constraint parameter files (default extension .con) describe mathematical relations between fitting parameters. For the moment this is implemented for occupancy parameters of atoms, the position, orientation and occupancy parameters for molecules, and liquid layer parameters. Format of the file:

first line: `comments`

other lines: `name1` N_{par} `= offset + multiplier (*,/) name2` N_{par}
                 `[+ multiplier (*,/) name3` N_{par}`]`

'name' is the parameter type ('occup', 'liquid', 'molx', 'moly', 'molz', 'molxr', 'molyr', 'molzr' or 'molocc') and N_{par} is the corresponding serial number; spaces are needed between the different items. The multiplier can either be multiplied (*) or divided (/) by the value of the input parameter(s). Optionally, a second input parameter (name3) can be added. The parameter name1 has to be a fixed parameter during fitting, as its value depends on the other parameter value(s).

Example for case when the sum of the occupancies of parameters 2 and 3 has to equal 1:

     `occup 2 = 1.0 + -1.0 * occup 1`

Example for case when the occupancies of molecules 1 and 2 have to be equal:

     `molocc 2 = 0.0 + 1.0 * molocc 1`

Example for case when the sum of the occupancies of parameters 1, 2 and 3 has to be equal to 1:

     `occup 3 = 1.0 + -1.0 * occup 1 + -1.0 * occup 2`

In this example, the parameter range of occup 1 and 2 needs to be properly constraint in order for occup 3 not to become negative.

When a fit result is displayed, a value of name1 can be shown that is not fulfilling exactly the defined mathematical relationship. This is an artefact of the way the algorithms are working: the calculation is correct and the true value of the parameters can be seen by listing their values (e.g. LIST PAR T).

3.2.9 Atomic scattering factors

For (almost) all elements, ROD uses default values for their atomic scattering factors. This uses the coefficients for an analytical approximation as listed in the "International Tables for X-ray Crystallography, Vol. IV", p. 99-101. The expression is:

$$f = \sum_{i=1}^{4} a_i \exp\left[-b_i \left(\frac{\sin\theta}{\lambda}\right)^2\right] + c \,. \qquad (21)$$

When these scattering factors are not correct, e.g. when the element is in a charged state or the atomic position contains a random mixture of different elements, the coefficients can be changed in the ROD.SET.FATOMIC> menu. The values can be saved to a file with extension .fat using the ROD>LIST FATOMIC command. This generates a macro file that can be read in using ROD>READ FATOMIC.

In addition to the option of changing the coefficients of a particular element, five fake elements, E1 through E5, are available that have no default coefficients and that should be given user-defined coefficients.

For each element the dispersion correction (anomalous scattering) factors f_1 and f_2 can also be set. Each energy used gets a serial number; if only one energy is used (very often the case) only serial number 0 is active. The total atomic scattering factor is thus:

$$f(Q,\lambda) = f_0(Q) + f_1(\lambda) + f_2(\lambda) \,.$$

The dispersion corrections are saved in the .fat file as well. A good source of the dispersion corrections is henke.lbl.gov or skuld.bmsc.washington.edu/scatter/AS_periodic.html.

3.3 Pre-set parameter values

In many calculations of rod, parameter values are used that can be pre-set in the ROD.SET> menu. Many are self-explanatory, but here we give a brief explanation of some of them.

3.3.1 Calculation parameters

These are the parameters that can be set in ROD.SET.CALC>. When calculating a rod profile, the range of l-values used is specified by: l_{start}, l_{end} and N_{points}.

For special cases it is possible to use two different surface models. These are read in from one file (*.sur or *.fit). The second half of these files should contain the second model. The parameter N_{surf2} tells how many atoms there are in the second model.

In order to avoid zero structure factors, start with a scale factor set at 1.

The roughness parameter β (discussed in section 2.1) is also set in this menu. In the sub-menu ROD.SET.CALC.ROUGH> a particular roughness model can be selected.

The data near bulk Bragg peaks contains little information about the interface structure, but can have a significant effect on the χ^2 of the fit. It is therefore a good idea to reduce the weight near Bragg peaks and this is done using the command BWEIGTH that uses the l-interval and the fractional error as parameters. At the Bragg peak the full fractional error is added, and this decreases to zero over the specified interval.

The specular, or (00), rod is the only sensitive to structural features without in-plane ordering. In a data set, the amount of specular data is usually limited compared to the non-

specular rods, and thus it may be convenient to increase or decrease the relative importance of the specular data. The command SWEIGHT allows changing the weight of the specular data with respect to the other rods.

A flag can be set to include correction for dynamical effects. This should normally be switched off, since the dynamical effects are usually negligible and the calculation takes some extra time. The calculation needs to know if the critical angle is positive (from low to high-density medium) or negative.

3.3.2 Fourier maps

A number of Fourier maps can be generated by ROD: Patterson map, electron density map and electron density difference map. In order to generate such a map, in principle all reflections, including symmetry-equivalent ones, are needed. By setting the appropriate plane group in ROD (ROD.SET.SYMMETRY>) these equivalent reflections will be automatically generated. The parameters needed for calculating the Fourier maps can be set in ROD.SET.PLOT>.

3.3.3 Symmetry-related domains

In ROD.SET.DOMAIN> the parameters needed to describe symmetry-related domains can be set. The domain matrices are the transformation matrices $\mathbf{T}_n$ described above. $\mathbf{T}_1$ is the identity matrix. For a properly chosen unit cell, the indices (hk) are integer. Application of a transformation matrix may lead to fractional coordinates. This means that the reflections are non-overlapping and that the contribution of the corresponding domain to that reflection is zero. The "fractional coordinates" flag should therefore be set to 'no' in those circumstances. For properly integrated scans, the summation over the various contributions is *incoherent* [7]. Typically, all domains will be equally occupied. When the calculated structure factors are found

number of domains
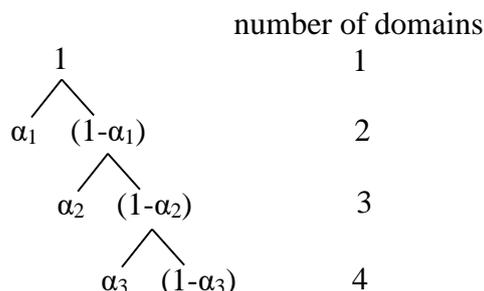
Figure 7. The occupancy of n domains can be described by n-1 fractional occupancy parameters such that the total occupancy equals 1. Each subsequent domain is a fraction of the remaining fraction of the previous domains.

to be always equal to zero, the origin is sometimes that the domain occupancy is accidentally set to zero.

The domain size in most systems will be much smaller than the beam footprint and thus assuming that all domains are equally occupied is typically a good assumption. If this is not the case, the values can be set in this menu, but in addition a flag can be set such that the domain

occupancy can be fitted are part of the structure refinement. In order to assure that the sum over the N domain occupancies equals 1, N-1 occupancy fractions (between 0 and 1) are used during fitting that are translated back to the actual occupancies. Figure 7 gives the relation between the actual occupancies and the fractions for a system with 4 domains.

3.4   Structure refinement

3.4.1   X-ray data

One normally refines a structure on the basis of a measured X-ray diffraction data set by using a χ^2 minimisation. The standard minimisation procedure is the Levenberg-Marquardt method. When the theory varies very strongly as a function of the fitted parameters or when it is difficult to find the global minimum, the method of simulated annealing is available. This is more robust, but slower than Levenberg-Marquardt. The method of adaptive simulated annealing (ASA) is implemented in ROD [10], which is far more efficient than standard simulated annealing. It has successfully been used for quite complicated systems [11]. The main improvement in ASA with respect to normal simulated annealing is that each parameter has its own annealing temperature that is adapted during the optimisation procedure according to its sensitivity. The two minimisation methods can be selected in ROD.FIT> using RUN or ASA for Levenberg-Marquardt or adaptive simulated annealing, respectively.

Several control parameters that determine how a fit is done, can be set in ROD.FIT.CONTROL>. In most cases the default parameters are sufficient. For the Levenberg-Marquardt method there are two ways in which errors are estimated for the fitting parameters. By default the covariance matrix is used [12]. This does take into account the correlation between parameters and derives an error corresponding to an increase in the *non-normalised χ^2* of 1. If the *normalised χ^2* value is larger than 1 (often the case!), the errors should (at least) be multiplied by the square root of the normalised χ^2 (the same is true when this value is smaller than 1). A second method to estimate the errors is to find the true increase in χ^2 by doing full fits with all parameters free except the one for which the error is estimated (this is set by typing the command CHISQR in ROD.FIT.CONTROL>). This is repeated for all free parameters in a fit, and is thus much slower than the method using the covariance matrix. The desired increment in χ^2 needs to be specified after the fit.

When using ASA, all fitting parameters need to be given a lower and upper limit. An advantage of ASA is that a wide range of fitting parameter values can be explored. Setting the parameters in the middle of their range (command ACENTER) is often sufficient to find the optimum fit for the model being tested. The default settings of the ASA parameters (in ROD.FIT.CONTROL>) should be fine for most problems, but are somewhat optimised for speed. Therefore also ASA may find a local rather than the global minimum. It is thus advisable to perform a number of ASA runs. Close to a minimum, ASA is less efficient than Levenberg-Marquardt, so one would typically do a normal fit after ASA. This will also estimate the error

bars (which ASA doesn't do). The results of several fits can be saved automatically by opening a log file (command OPEN).

The cost temperature (which is basically the allowed variation in the non-normalised χ^2 value) during an ASA run is given by:

$$T(k) = T_0 \exp\left(-ck^{1/n}\right), \tag{22}$$

with k the number of accepted parameter states, n the number of fitting parameters and c a constant that equals:

$$c = -\log(S_{ratio}) * \exp\left[\frac{-\log(S_{anneal})}{n}\right] * S_{cost}, \tag{23}$$

with

S_{ratio} = ratio of final to initial temperature (command RATIO)

S_{anneal} = desired number of iterations (command ANNEAL)

S_{cost} = parameter to cool down more slowly (command COST)

The value for c is shown as the c_cost parameter. For the various parameter temperatures, the same relations hold, except that the S_{cost} parameter is missing (listed as c_par). Since only the value for c is used, varying S_{ratio} or S_{anneal} is equivalent. For a very slow anneal, c should be small, thus one should use high values for S_{ratio} and S_{anneal} and a low value for S_{cost}.

After a specified number of accepted states, ASA will redefine the parameter temperatures based upon their sensitivity. The command REANNEAL sets this interval. An ASA minimisation will finish if in 20 consecutive accepted states, the change in χ^2 is less than 0.05, or if the maximum number of iterations is reached (command LIMIT). In addition, a time limit can be defined, to prevent spending too much time on a very slowly converging optimization run.

The results of a fit can be viewed in several ways. After an optimisation cycle, the program will display the values of the fit parameters and the corresponding χ^2-value. Using the command ROD>LIST COMPARE a list of experimental and calculated structure factors is given, together with their χ^2 differences. One can plot the calculated rod profiles together with the data as a function of the diffraction index l using ROD.PLOT>ALLBOTH (there are also other ways). An in-plane data set can be plotted by using ROD.PLOT>FBOTH: this will draw the calculated (left-side) and experimental (right-side) structure factors as half-circles in the reciprocal plane.

Since most of the time several ASA runs are needed to arrive at the optimum fit, a command FITPLUS is available that will execute a given number of ASA plus RUN cycles, always using as starting values for the fit parameters the values centred on the allowed parameter range. All unique fits are written to parameter files that can later be used for analysis. This is still somewhat experimental, but is meant to save time of the operator during data

analysis. By opening a log file (in ROD.FIT.CONTROL>), the actions of FITPLUS can be seen in detail.

3.4.2 Lattice energy

For complicated surface models and/or small X-ray data sets, a structural refinement based on the X-ray data may not yield satisfactory results. It may happen, for example, that some bond lengths between atoms become smaller than expected chemically/physically. In ROD.ENERGY> it is possible to calculate and optimise the lattice energy of a structure model and thus to try to prevent unrealistic models. At the moment, two potentials are implemented: the Keating potential and the Lennard-Jones potential.

In 1966 Keating introduced a model for the elastic energy of a solid in order to describe the bulk elastic properties of covalent crystals. For models containing several kinds of atoms, the Keating elastic energy is [13]

$$E = \alpha \sum_{\substack{all \\ bonds}} \left[r_{ij}^2 - (b_i + b_j)^2 \right]^2 + \beta \sum_{\substack{all\, bond \\ angles}} \left[\mathbf{r}_{ij} \cdot \mathbf{r}_{ik} - \cos(\alpha_{equ})(b_i + b_j)(b_i + b_k) \right]^2 , \quad (24)$$

where r_{ij} is the distance between atoms i and j, b_i is the (covalent) radius, α and β are the parameters describing the energy cost of bond-length and bond-angle deformation, respectively, and α_{equ} is the equilibrium bond angle. The Keating model is often used for tetrahedrally-bonded crystals for which $\cos(109.47°)=-1/3$.

The Lennard-Jones potential between two equal atoms at separation r is given by:

$$V_{LJ} = \varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - 2 \left(\frac{\sigma}{r} \right)^6 \right]. \quad (25)$$

(Note: different forms exist, this is a convenient one). This potential has a value of $-\varepsilon$ for $r = \sigma$. For our purpose, it is more convenient to have a value 0 at the equilibrium bond distance. For a structure with different atoms, we then obtain the following energy of the entire surface unit cell:

$$E'_{LJ} = \sum_{\substack{all \\ bonds}} \alpha \left\{ 1 + \left[\left(\frac{(b_i + b_j)}{r_{ij}} \right)^{12} - 2 \left(\frac{(b_i + b_j)}{r_{ij}} \right)^6 \right] \right\}, \quad (26)$$

where we have replaced the conventional ε in the potential by α in order to use the same parameter name as in the Keating energy.
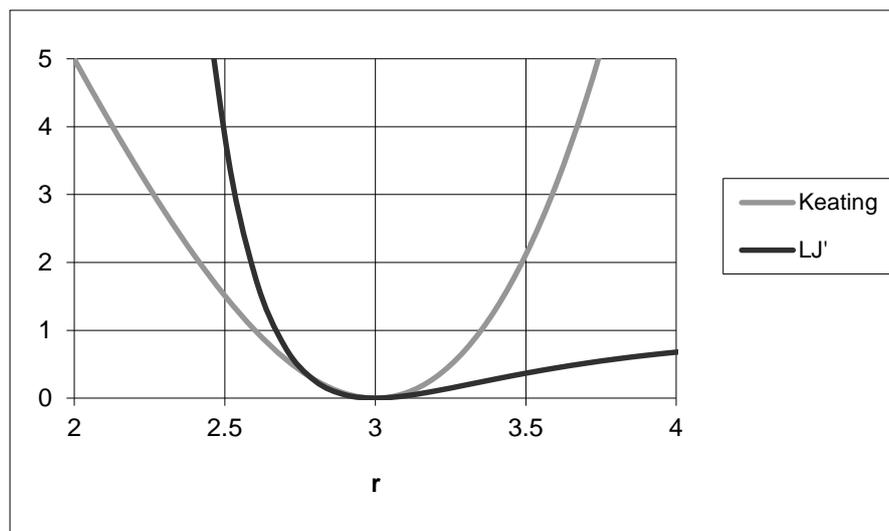

Fig. 8. The difference in the Keating and (modified) Lennard-Jones potential for an equilibrium bond distance of 3 Å and $\alpha = 0.2$ for Keating and $\varepsilon (= \alpha) = 1$ for Lennard-Jones.

Fig. 8 shows the difference between the two potentials. If the lattice energy is used to prevent too short bond distances, the Lennard-Jones is most appropriate, because it only has a mild energy penalty for too long bonds. Even though the real potential in a system may be neither of the Keating or the Lennard-Jones type, the two can nevertheless be used as a penalty function during a fit.

In ROD.ENERGY> a lattice-energy minimisation can be performed using either of these potentials. First the potential has to be chosen and values have to be given for the corresponding parameters: α, β, b_i and α_{equ} for Keating and $\alpha (= \varepsilon)$ and b_i for Lennard-Jones. Second, all atoms participating in the lattice-energy calculation need to be specified (not all have to be included). The program can then automatically find all bonds and angles in the surface unit cell that are smaller than 110% of the equilibrium values (command FINDBONDS). Bonds that should not be included (e.g. because the parameters for such bonds are not known) can subsequently be removed. Please note that the bond-searching algorithm ignores (for simplicity reasons) bonds of an atom to itself on an equivalent position (in a neighbouring unit cell). This means that the lattice energy may fail for small 1x1 unit cells. If only a limited number of bonds needs to be included, alternatively the command ADDBOND allows selecting a single bond to become part of the energy calculation.

In a lattice-energy minimisation a refinement is done using the same displacement parameters as are used in fitting X-ray data. In practice, when the X-ray data set is not large enough to fit all independent parameters, one may e.g. want to fit the large, top-most displacements using the X-ray data and estimate the smaller, deeper displacements from the lattice-energy model. When the Keating energy is used for non-covalent crystals, the bond-

angle term may be ignored by putting the parameter β to zero (or by setting α_{equ} to such a small value that no angles will be included in the calculation).

When separating the lattice-energy minimisation from the X-ray fit, one typically performs a number of iterations between an X-ray and a lattice-energy refinement. It is also possible to include the lattice-energy in the χ^2 minimisation of the X-ray data and thus to optimise these two terms simultaneously. This option is switched on by setting the 'chisqr' flag in ROD.ENERGY>. This will simply add the lattice energy (in eV's!) to the (non-normalised) χ^2 value. The relative weight between the energy term and the X-ray χ^2-term can be adjusted by changing the values of α and β. The addition of the lattice energy to the total χ^2 is done using a trick that may lead to errors if the minimisation fails (due to mathematical exceptions or an abort). In that case the data should be read in again.

3.5 Plotting results

Data and calculations can be plotted in several ways using the ROD.PLOT> menu. When performing a fit, one usually wants to plot the data and calculation of a single rod, while a data set consists typically of several rods. There are two ways to select a single rod: (1) one can read in a data file that contains only this rod (the programme AVE has an option to make such files from a large set). The command DATA will then plot this single rod. (2) One can use the command RDATA that will select the data with the most recently used hk values (typically in a calculation). Since data is also characterized by optional energy and subscale parameters, these need to be selected as well. These flags are set in the ROD.SET.CALC> menu. For simple data sets, these parameters assume their 0 default values. The command BOTH plots data and calculation using the same selection as RDATA.

The final model can be plotted in a very simple projected view within ROD (ROD.PLOT>MREFINED), but far better graphs are obtained using commercial software like Discovery Studio Visualizer (freely available from Accelrys) or Mercury (freely available from the CCDC in Cambridge). The command XYZ will generate a file with the correct .xyz format for these plotting packages.

It may be useful to show the disorder (thermal or static) as well, e.g. when entering the liquid at a solid-liquid interface. In X-ray diffraction this type of disorder is normally displaced as probability ellipsoids, but XYZ files don't contain this type of information. Therefore ROD can also generate so-called results files (extension .res) in the SHELX format. In principle such files contain all the crystallographic information of a structure, but ROD produces a fake cubic unit cell with lattice parameters of length 100 Å and writes all coordinates as fractional coordinates. The vibration parameters are listed in the order U11 U22 U33 U23 U13 U12 (in Å). Use the command RES to generate such a file. Mercury, for example, can make nice plots from .res files.

It may also be useful to plot the electron density as projected on the z-axis. This is particularly useful when analysing solid-liquid interfaces and the extent to which different

Fourier components probe this interface [14]. The command ROD.PLOT>ZDENSITY will generate this density (as electrons per unit cell), using the diffraction indices h and k as parameters and z in Å. In the ROD.LIST> menu, the results can be listed as well.

Individual bond lengths and angles can be calculated in ROD.CALC>, while a range of bond lengths can be listed in ROD.LIST>.

Acknowledgements

4 References

[1] R. Feidenhans'l, *Surface structure determination by X-ray diffraction,* Surface Science Reports, 10 (1989) 105-188.

[2] I.K. Robinson, *Surface crystallography*, in: G.S. Brown, D.E. Moncton (Eds.) *Handbook on synchrotron radiation*, North-Holland, Amsterdam, 1991, pp. 221-266.

[3] E. Vlieg, I.K. Robinson, *Two-dimensional crystallography*, in: P. Coppens (Ed.) *Synchrotron Radiation Crystallography*, Academic Press, London, 1992, pp. 255-299.

[4] I.K. Robinson, D.J. Tweet, *Surface X-ray diffraction,* Reports on Progress in Physics, 55 (1992) 599-651.

[5] E. Vlieg, *X-ray diffraction from surfaces and interfaces*, in: K. Wandelt (Ed.) Surface and Interface Science, Wiley, 2012, pp. 375-425.

[6] E. Vlieg, *ROD, a program for surface crystallography*, Journal of Applied Crystallography, 33 (2000) 401-405.

[7] E. Vlieg, J.F. van der Veen, S.J. Gurman, C. Norris, J.E. Macdonald, *X-ray diffraction from rough, relaxed and reconstructed surfaces*, Surface Science, 210 (1989) 301-321.

[8] E. Vlieg, *Integrated intensities using a six-circle surface X-ray diffractometer*, Journal of Applied Crystallography, 30 (1997) 532-543.

[9] E. Vlieg, *A (2+3)-type surface diffractometer: mergence of the z-axis and (2+2)-type geometries*, Journal of Applied Crystallography, 31 (1998) 198-203.

[10] L. Ingber, *Very fast simulated re-annealing,* J. Mathl. Comput. Modelling, 12 (1989) 967-973.

[11] E. Vlieg, S.M. Driver, P. Goedtkindt, P.J. Knight, W. Liu, J. Ludecke, K.A.R. Mitchell, V. Murashov, I.K. Robinson, S.A. de Vries, D.P. Woodruff, *Structure determination of Cu(410)-O using x-ray diffraction and DFT calculations*, Surface Science, 516 (2002) 16-32.

[12] W.H. Press, B.P. Flannery, S.A. Teukolsky, W.T. Vetterling, *Numerical Recipes in C*, Cambridge University Press, Cambridge, 1988.

[13] J.S. Pedersen, Surface Science, 210 (1989) 238.

[14] M.F. Reedijk, J. Arsic, F.F.A. Hollander, S.A. de Vries, E. Vlieg, *Liquid order a the interface of KDP crystals with water: evidence for icelike layers*, Physical review letters, 90 (2003) 066103.

Appendix A. GraphiC™ information

GraphiC is a no longer supported set of graphics routines, first developed for MSDOS, but also made available for OS/2(!), Windows and MAC. The ESRF version of the ROD does *not* use Graphic but PGPLOT. The current Windows version of ROD generates a plot file that can be read by the programme PLAY, provided as part of the GraphiC package.

Below the available line styles and symbols are shown.
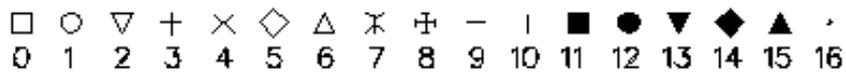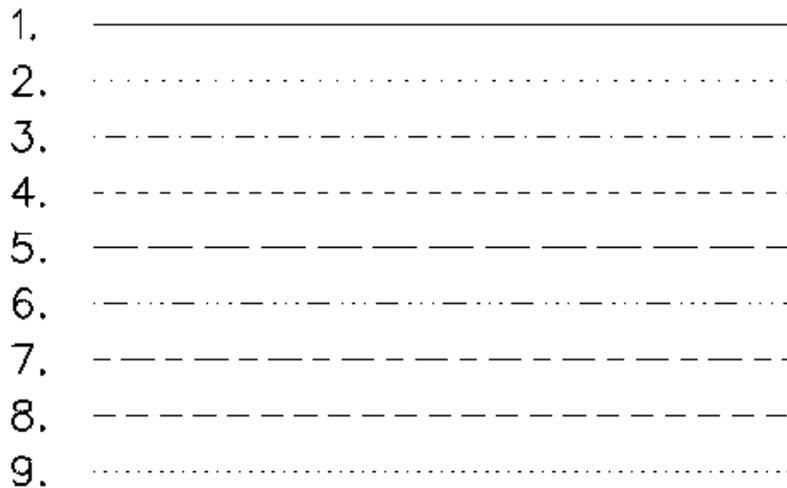
Appendix B: Transforming between unit cells

Suppose we want to change from a unit cell with lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ to a new one with lattice vectors $\mathbf{a}'_1$, $\mathbf{a}'_2$ and $\mathbf{a}'_3$. The transformation between these is given by a transformation matrix $\mathbf{T}$, such that.

$$\mathbf{a}'_i = \sum_j \mathbf{T}_{ij} \mathbf{a}_j \tag{B1}$$

The inverse matrix will transform the lattice vector back:

$$\mathbf{a}_i = \sum_j \mathbf{T}_{ij}^{-1} \mathbf{a}'_j . \tag{B2}$$

Assume that position $\mathbf{r}$ has coordinates α_i in the starting unit cell:

$$\mathbf{r} = \sum_i \alpha_i \mathbf{a}_i . \tag{B3}$$

We want to know the coordinates in the new frame:

$$\mathbf{r} = \sum_i \alpha'_i \mathbf{a}'_i . \tag{B4}$$

The solution for this can be found by substituting (B2) in (B3):

$$\mathbf{r} = \sum_i \alpha_i \mathbf{a}_i = \sum_i \alpha_i \left(\sum_j \mathbf{T}_{ij}^{-1} \mathbf{a}'_j \right) = \sum_j \left(\sum_i \alpha_i \mathbf{T}_{ij}^{-1} \right) \mathbf{a}'_j . \tag{B5}$$

Thus

$$\alpha'_j = \sum_i \alpha_i \mathbf{T}_{ij}^{-1} = \sum_i \left(\mathbf{T}^{-1} \right)^t_{ji} \alpha_i , \tag{B6}$$

where t stands for transpose. Thus the matrix that transforms the coordinates from the old to the new unit cell is given by the transpose of the inverse of matrix $\mathbf{T}$.

The matrix $\mathbf{T}$ itself transforms the diffraction indices $\mathbf{H} = (hkl)$ to the ones corresponding to the new unit cell (see e.g. B.E. Warren, *X-ray diffraction*). In summary, we thus have the following transformations between the two unit cells:

$$\begin{pmatrix} \mathbf{a}'_1 \\ \mathbf{a}'_2 \\ \mathbf{a}'_3 \end{pmatrix} = \mathbf{T} \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{pmatrix} \qquad \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{pmatrix} = \mathbf{T}^{-1} \begin{pmatrix} \mathbf{a}'_1 \\ \mathbf{a}'_2 \\ \mathbf{a}'_3 \end{pmatrix}$$

$$\begin{pmatrix} h' \\ k' \\ l' \end{pmatrix} = \mathbf{T} \begin{pmatrix} h \\ k \\ l \end{pmatrix} \qquad \begin{pmatrix} h \\ k \\ l \end{pmatrix} = \mathbf{T}^{-1} \begin{pmatrix} h' \\ k' \\ l' \end{pmatrix} \tag{B7}$$

$$\begin{pmatrix} \alpha'_1 \\ \alpha'_2 \\ \alpha'_3 \end{pmatrix} = \left(\mathbf{T}^{-1} \right)^t \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \end{pmatrix} \qquad \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \alpha_3 \end{pmatrix} = \left(\mathbf{T} \right)^t \begin{pmatrix} \alpha'_1 \\ \alpha'_2 \\ \alpha'_3 \end{pmatrix} .$$

Example: from fcc cubic to (111) surface unit cell

$$\mathbf{H}_{(111)} = \begin{pmatrix} \frac{1}{2} & 0 & -\frac{1}{2} \\ -\frac{1}{2} & \frac{1}{2} & 0 \\ 1 & 1 & 1 \end{pmatrix} \mathbf{H}_{fcc} \qquad \mathbf{H}_{fcc} = \frac{1}{3} \begin{pmatrix} 2 & -2 & 1 \\ 2 & 4 & 1 \\ -4 & -2 & 1 \end{pmatrix} \mathbf{H}_{(111)}$$

$$\alpha_{(111)} = \frac{1}{3} \begin{pmatrix} 2 & 2 & -4 \\ -2 & 4 & -2 \\ 1 & 1 & 1 \end{pmatrix} \alpha_{fcc} \qquad \alpha_{fcc} = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} & 1 \\ 0 & \frac{1}{2} & 1 \\ -\frac{1}{2} & 0 & 1 \end{pmatrix} \alpha_{(111)}$$

Example: from (111) surface unit cell to (√3x √3)R30° surface unit cell

$$\mathbf{H}_{\sqrt{3}} = \begin{pmatrix} 2 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \mathbf{H}_{(111)} \qquad \mathbf{H}_{(111)} = \begin{pmatrix} \frac{1}{3} & -\frac{1}{3} & 0 \\ \frac{1}{3} & \frac{2}{3} & 0 \\ 0 & 0 & 1 \end{pmatrix} \mathbf{H}_{\sqrt{3}}$$

$$\alpha_{\sqrt{3}} = \begin{pmatrix} \frac{1}{3} & \frac{1}{3} & 0 \\ -\frac{1}{3} & \frac{2}{3} & 0 \\ 0 & 0 & 1 \end{pmatrix} \alpha_{(111)} \qquad \alpha_{(111)} = \begin{pmatrix} 2 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \alpha_{\sqrt{3}}$$

Appendix C. Examples of input files

Below are listed examples of valid input files. The example is from the Ag(111)-(√3x√3)R30°-Sb surface. For details about this particular reconstruction, see S.A. de Vries, W.J. Huisman, P. Goedtkindt, M.J. Zwanenburg, S.L. Bennett, I.K. Robinson and E. Vlieg, Surface Sci. 414 (1998) 159.

A bulk model file (*.bul).
```
Ag(111) bulk unit cell in root3 frame:
5.0039 5.0039 7.0766 90 90 120
Ag      0.00000 0.00000  0.00000 1
Ag      0.66667 0.33333  0.00000 1
Ag      0.33333 0.66667  0.00000 1
Ag      0.33333 0.33333 -0.33333 1
Ag      0.66667 0.00000 -0.33333 1
Ag      0.00000 0.66667 -0.33333 1
Ag      0.33333 0.00000 -0.66667 1
Ag      0.66667 0.66667 -0.66667 1
Ag      0.00000 0.33333 -0.66667 1
```

A surface model file (*.sur)
```
Sb/Ag(111) surface cell in root3 frame:
5.0039 5.0039 7.0766 90 90 120
Sb      0.33333 0.33333  1.33333 1
Ag      0.66667 0.00000  1.33333 1
Ag      0.00000 0.66667  1.33333 1
Ag      0.00000 0.00000  1.00000 1
Ag      0.66667 0.33333  1.00000 1
Ag      0.33333 0.66667  1.00000 1
Ag      0.33333 0.33333  0.66667 1
Ag      0.66667 0.00000  0.66667 1
Ag      0.00000 0.66667  0.66667 1
Ag      0.33333 0.00000  0.33333 1
Ag      0.66667 0.66667  0.33333 1
Ag      0.00000 0.33333  0.33333 1
```

A fit model file (*.fit)
```
!in new file format
 5.0039 5.0039 7.0766  90.000  90.000 120.000
Sb 0.33333  1.0000  0  0.0000  0  0.33333  1.0000  0  0.0000  0  1.33333  1.0000  2  0.0000  0 2 0 0
Ag 0.66667  1.0000  0  0.0000  0  0.00000  1.0000  0  0.0000  0  1.33333  1.0000  3  0.0000  0 1 0 0
Ag 0.00000  1.0000  0  0.0000  0  0.66667  1.0000  0  0.0000  0  1.33333  1.0000  3  0.0000  0 1 0 0
Ag 0.00000  1.0000  1  0.0000  0  0.00000  1.0000  1  0.0000  0  1.00000  1.0000  0  0.0000  0 1 0 0
Ag 0.66667 -1.0000  1  0.0000  0  0.33333  0.0000  1  0.0000  0  1.00000  1.0000  0  0.0000  0 1 0 0
Ag 0.33333  0.0000  1  0.0000  0  0.66667 -1.0000  1  0.0000  0  1.00000  1.0000  0  0.0000  0 1 0 0
Ag 0.33333  1.0000  0  0.0000  0  0.33333  1.0000  0  0.0000  0  0.66667  1.0000  0  0.0000  0 1 0 0
Ag 0.66667  1.0000  0  0.0000  0  0.00000  1.0000  0  0.0000  0  0.66667  1.0000  0  0.0000  0 1 0 0
Ag 0.00000  1.0000  0  0.0000  0  0.66667  1.0000  0  0.0000  0  0.66667  1.0000  0  0.0000  0 1 0 0
Ag 0.33333  1.0000  0  0.0000  0  0.00000  1.0000  0  0.0000  0  0.33333  1.0000  0  0.0000  0 1 0 0
Ag 0.66667  1.0000  0  0.0000  0  0.66667  1.0000  0  0.0000  0  0.33333  1.0000  0  0.0000  0 1 0 0
Ag 0.00000  1.0000  0  0.0000  0  0.33333  1.0000  0  0.0000  0  0.33333  1.0000  0  0.0000  0 1 0 0
```

A parameter file (*.par)

```
!best-fit parameter values for Ag(111)-sqrt3-Sb
!Goto set parameter menu
set par
scale           0.6821    0.0500    2.0000  YES
beta            0.0000    0.0000    0.5000  NO
surffrac        0.7546    0.5000    1.0000  YES
displace  1     0.0122   -0.2000    0.2000  YES
displace  2     0.0238   -0.2000    0.2000  YES
displace  3     0.0193   -0.2000    0.2000  YES
b1        1     0.6600    0.0000    0.0000  NO
return return
```

Part of a data file (*.dat)

```
Ag(111)-sqrt3xsqrt3-Sb data first run
    1    0   0.200     3.67      0.42       0
    1    0   0.400     3.04      0.51       0
    1    0   0.600     3.42      0.53       0
    1    0   0.800     3.65      0.60       0
    1    0   1.005     3.25      0.62       0
    1    0   1.200     3.19      0.68       0
    1    0   1.400     2.13      0.91       0
    1    0   1.600     1         5          0
    1    0   1.800     1         5          0
    1    0   2.005     6.18      0.85       0
    1    0   2.200     5.30      0.89       0
    1    0   2.400     5.52      0.91       0
    1    0   2.600     4.14      1.02       0
    1    1  -2.600    64.13      6.42       2
    1    1  -2.500    69.08      6.92       2
    1    1  -2.400    72.67      7.28       2
    1    1  -2.300    77.81      7.79       2
    1    1  -2.200    81.48      8.16       2
    1    1  -2.050    90.52      9.06       2
    1    1  -1.700   114.09     11.41       2
    1    1  -1.500   133.15     13.32       2
    1    1  -1.400   157.08     15.71       2
    1    1  -1.300   171.53     17.16       2
    1    1  -1.200   273.63     27.37       2
    1    1  -0.900   250.59     25.06       2
    1    1  -0.800   149.52     14.96       2
    1    1  -0.700    96.07      9.62       2
    1    1  -0.600    82.07      8.21       2
    1    1  -0.500    75.89      7.60       2
    1    1  -0.400    80.05      8.01       2
    1    1  -0.300    78.38      7.85       2
    1    1  -0.200    92.03      9.21       2
    1    1   0.200    87.75      8.78       2
    1    1   0.300    84.85      8.49       2
    1    1   0.400    81.40      8.15       2
    1    1   0.500    87.63      8.77       2
    1    1   0.600    92.58      9.26       2
    1    1   0.700    93.41      9.34       2
    1    1   0.800    94.27      9.43       2
    1    1   0.900   101.10     10.11       2
    1    1   0.980   109.64     10.97       2
    1    1   1.100   106.93     10.70       2
    1    1   1.200   111.40     11.14       2
```

Appendix D. List of all commands

```
******************************** MAIN MENU ********************************
 Read      : Read data/model files
 List      : List data/model
 RESet     : Reset all parameters
 Calculate : Calculate structure factors
 Plot      : Goto plotting menu
 Set       : Set parameters
 Fit       : Fit experimental structure factors
 FITPlus   : Extensive asa fit
 Energy    : Goto lattice energy menu
 Macro     : Run macro file
 :         : Execute an operating system command
 Help      : Display menu
 QUIT      : Quit program
ROD>
***************************** INPUT FILE TYPES *****************************
 Data      : Structure factor data
 SURface   : Coordinates of surface atoms
 Bulk      : Coordinates of bulk atoms
 Fit       : File with fit model of surface atoms
 Molecule  : File with coord. of surface molecule n
 Liquid    : File with liquid model
 PArameters: File with fit parameters (macro)
 FAtomic   : File with atomic scatt. factors (macro)
 COnstraints: File with parameter constraints
 Help      : Display menu
 Return    : Return to main menu
File type:
******************************** LIST MENU ********************************
 Bulk      : Bulk contribution
 SURface   : Surface contribution
 MOlecules : Molecule(s) contribution
 LIQuid    : Liquid layer contribution
 Sum       : Interf. sum of bulk, surface & molecules
 All       : Above three values
 Data      : Structure factor data
 SModel    : Surface model
 BModel    : Bulk model
 Fit       : Fitting model for surface structure
 Mmodel    : Molecule model in fractional format
 Lmodel    : Liquid film model
 Compare   : Comparison between data and theory
 ROdcompare: Data-theory comparison for selected rod
 PArameters: Values of fit parameters
 FAtomic   : Coefficients atomic scattering factors
 SYmmetry  : Symmetry-equivalent reflections of data
 BOnds     : Bond lengths of surface structure
 Zdensity  : Z-proj. electron density (plot first!)
 CONstraint: Fitting parameter constraints
 Help      : Display menu
 Return    : Return to main menu
ROD.LIST>
***************************** CALCULATION MENU ****************************
 ROd       : Calculate rod profile
 RAnge     : Calculate f's for range of h and k
 Qrange    : Calculate f's within q-max
 Data      : Calculate f's for all data points
 DIstance  : Calculate the distance between two atoms
 Angle     : Calculate bond angle between three atoms
 ROUghness : Calculate roughness in atomic layers
 Help      : Display menu
 Return    : Return to main menu
ROD.CALC>
******************************** PLOT MENU ********************************
 Bulk      : Bulk contribution (against l)
```

```
 SURface   : Surface contribution (against l)
 MOLecules : Contribution of molecules (against l)
 LIQuid    : Contribution of liquid layer (against l)
 Sum       : Interference sum of bulk and surface
 All       : Above 5 curves if present (against l)
 Data      : Data (against l)
 RData     : Data of specific rod (against l)
 BOth      : Data plus calculated interference sum
 FTheory   : Theoretical structure factors (hk plane)
 FData     : Experimental structure factors (hk plane)
 FBoth     : Theor. and exp. f's (hk plane)
 ALLData   : All data rods in multiplot
 ALLBoth   : All data rods & model sum in multiplot
 MOriginal : Original structure model
 MRefined  : Refined structure model
 MBoth     : Original + refined structure model
 MLarge    : Several unit cells of refined model
 XYZ       : Refined model, XYZ output file
 RES       : Model with vibration param., RES output file
 DPatterson: Patterson function of experimental data
 TPatterson: Patterson of theoretical structure f's
 DIfference: Electron density difference map
 ELectron  : Electron density map of model
 ZDensity  : Z-projected electron density
 Errors    : Set error bar plotting on/off
 Unit      : Set drawing of unit cell on/off
 Help      : Display menu
 Return    : Return to main menu
ROD.PLOT>
********************************* SET MENU *********************************
 Calculate : Parameters for rod calculation
 PArameters: Values of fit parameters
 Domain    : Parameters describing the domains
 Plot      : Plotting parameters
 SYmmetry  : Plane group symmetry of model
 FAtomic   : Atomic scattering factors
 Help      : Display menu
 Return    : Return to main menu
ROD.SET>
*********************** SET ROD CALCULATION PARAMETERS ***********************
 STructure : Use structure factors or intensities
 LStart    : Start value of l
 LEnd      : End value of l
 Npoints   : Number of points on rod
 Atten     : Attenuation factor of beam
 Beta      : Roughness parameter beta
 LBragg    : l-value of nearest Bragg peak
 Fractional: Fractional rod calculation yes/no
 Energy    : Serial number of X-ray energy
 NLayers   : Number of layers in bulk unit cell
 SCale     : Scale factor of theory
 SUbscale  : Serial number active subscale parameter
 SFraction : Fraction of surface with 1st unit cell
 S2fraction: Fraction of surface with 2nd unit cell
 NSurf2    : Number of atoms in 2nd unit cell
 ROUghness : Roughness mode calculation
 BWeight   : Decrease weight near Bragg peaks
 SWeight   : Relative weight of specular rod
 DYNamical : Flag to denote dynamical corr. for specular
 POScrangle: Positive critical angle yes/no
 List      : List parameters
 Help      : Display menu
 Return    : Return to main menu
ROD.SET.CALC>
*************************** SET ROUGHNESS MODE ***************************
 Approx    : Approximated beta model
 Beta      : Numerical beta model
 Poisson   : Poisson model
```

```
 Gaussian  : Gaussian model
 LINear    : Linear model
 Cosine    : Cosine model
 Twolevel  : Two-level model
 Help      : Display menu
 Return    : Return to last menu
ROD.SET.CALC.ROUGH>
****************************** SET PARAMETERS ******************************
 SCale     : Scale factor of theory
 Beta      : Roughness parameter beta
 SUrffrac  : Reconstructed-surface fraction
 Displace  : Value of displacement parameter
 B1        : Value of parallel Debye-Waller parameter
 B2        : Value of perpend. Debye-Waller parameter
 Occupancy : Value of occupancy parameter
 SUBscale  : Value of subscale parameter
 Molpar    : Position/rotation parameters of molecule n
 LIQpar    : Parameters of liquid model
 List      : List parameters
 Help      : Display menu
 Return    : Return to main menu
ROD.SET.PAR>
*************************** SET DOMAIN PARAMETERS ***************************
 Ndomains  : Number of rotational surface domains
 Matrix    : Matrix elements of domain n
 Fractional: Include fractional coordinates yes/no
 Equal     : All domains equal occupancy yes/no
 Occupancy : Set occupancy parameters of domain n
 Coherent  : Add rotational domains coherently yes/no
 FItoccup  : Include domain occupancy in fit yes/no
 List      : List parameters
 Help      : Display menu
 Return    : Return to main menu
ROD.SET.DOMAIN>
*************************** SET PLOT PARAMETERS ***************************
 Size      : Size of circles in plot of f's
 Threshold : Plotting threshold for f's
 RAdius    : Radius of atom in plot of model
 XMIncont  : Lower bound on x value in patterson
 XMAxcont  : Upper bound on x value in patterson
 NXcontour : Number of steps along x in patterson
 YMIncont  : Lower bound on y value in patterson
 YMAxcont  : Upper bound on y value in patterson
 NYcontour : Number of steps along y in patterson
 MInlevel  : Minimum contour level in patterson
 MAxlevel  : Maximum contour level in patterson
 Nlevel    : Number of contour levels in patterson
 List      : List parameters
 Help      : Display menu
 Return    : Return to main menu
ROD.SET.PLOT>
************************* SET PLANE GROUP SYMMETRY *************************
 P1        : Plane group no. 1
 P2        : Plane group no. 2
 PM        : Plane group no. 3
 PG        : Plane group no. 4
 CM        : Plane group no. 5
 P2MM      : Plane group no. 6
 P2MG      : Plane group no. 7
 P2GG      : Plane group no. 8
 C2MM      : Plane group no. 9
 P4        : Plane group no. 10
 P4MM      : Plane group no. 11
 P4GM      : Plane group no. 12
 P3        : Plane group no. 13
 P3M1      : Plane group no. 14
 P31M      : Plane group no. 15
 P6        : Plane group no. 16
```

```
 P6MM       : Plane group no. 17
 List       : List current plane group
 Help       : Display menu
 Return     : Return to main menu
ROD.SET.SYMMETRY>
*********************** SET ATOMIC SCATTERING FACTORS ***********************
 Fatomic    : Atomic scattering factor f0
 Dispersion: Dispersion corrections f1 and f2
 List       : List scattering factors
 Help       : Display menu
 Return     : Return to main menu
ROD.SET.FATOMIC>
************************** SET FITTING PARAMETERS **************************
 Value      : Set parameter value
 LOWer      : Set lower parameter limit
 Upper      : Set upper parameter limit
 Fix        : Fix a parameter value
 FRee       : Make parameter free
 Center     : Center parameter within range
 AFIx       : All parameters fixed
 AFRee      : All parameters free
 ACenter    : Center all free parameters
 COntrol    : Set control parameters
 List       : List parameter values
 Help       : Display menu
 RUn        : Start fit (Levenberg Marquardt)
 ASa        : Start fit (adaptive simulated annealing)
 Return     : Return without fitting
ROD.FIT>
************************* SET CONTROL PARAMETERS **************************
 COvariance: Use covariance matrix for error estimate
 CHisqr     : Use chi^2 for error estimate
 ITermax    : Max. number of iterations (LM fit)
 CONv       : chi^2 convergence criterion
 OPen       : Open fit summary file
 CLose      : Close fit summary file
 ANNeal     : ASA: Temperature anneal scale
 LIMit      : ASA: Limit in number of acceptances
 Time       : ASA: Time limit of run (min)
 RATio      : ASA: Temperature ratio scale
 COSt       : ASA: Cost parameter scale
 REAnneal   : ASA: Reannealing interval
 NPrint     : ASA: printing inverval
 USerinit   : ASA: user initial values (yes/no)
 List       : List parameters
 Help       : This list
 Return     : Return to main menu
ROD.FIT.CONTROL>
*************************** LATTICE ENERGY MENU ***************************
 Alpha      : Set bond length deformation par.
 Beta       : Set bond angle deformation par.
 RAdius     : Set atomic radius (angstrom)
 EQuangle   : Set equilibrium bond angle
 Keating    : Use Keating potential
 LEnnard    : Use Lennard-Jones potential
 Include    : Include atom in energy calculation
 Exclude    : Exclude atom in energy calculation
 REMove     : Remove a bond from calculation
 ADdbond    : Add bond to calculation
 Findbonds : Find all bonds between atoms
 CHisqr     : Include energy in chi^2 minimization
 ENergy     : Calculate lattice energy
 Minimize   : Minimize lattice energy
 List       : List parameter values
 BOndlist   : List bonds between atoms
 ANglelist : List angles between atoms
 LENGthlist: List length of all included bonds
 Help       : Display menu
```

```
 Return     : Return to main menu
ROD.ENERGY>
```

Appendix E. Changes in ROD

Changes and modifications in version of August 2018
- Add starting position and rotation of molecule to molecule file; change default extension of molecule file to .moc (instead of .mol).

Changes and modifications in version of March 2018
- Add SHELX .res output format that allows plotting of disorder ellipsoids.

Changes and modifications in version of Dec 2017
- Extend fit parameter constraints to two input parameters and allow both multiplication and division of input parameters.

Changes and modifications in version of Nov/Dec 2016
- Add liquid layer to model. Four forms implemented for the moment: step, film, double-film or layered. This layer only contributes to the specular rod.
- Add option to include dynamical (refraction) effects for specular beam.
- Add option to change the relative weight of specular data.

Changes and modifications in version of May 2016
- Extend fit parameter constraints to position (molx, moly, molz) and orientation (molxr, molyr, molzr) of molecules.

Changes and modifications in version of March 2015
- Allow constraints between fitting parameters. For the time being, this is only implemented for occupancy parameters of atoms or molecules.

Changes and modifications in version of September 2013
- Allow more than one molecule to be fitted. When reading a molecule file (with unchanged format), the serial number of the molecule needs to be provided. Molecule(s) calculation now includes different domains.
- Add option for extended automated fitting (still being tested).

Changes and modifications in version of June 2012
- Add optional serial number of atoms as first column in model fit file.
- Use element symbol rather than a serial number to select element for parameter setting.

Changes and modifications in version of January/February 2012

- Include full fitting features of the *z*-coordinate, just as for the *x* and *y* coordinates. This is in particular handy when treating films with variable height and layer spacing. The old .fit files can still be read in.

- Add two new automated plotting commands to the ROD.PLOT> menu: ALLDATA and ALLBOTH that automatically plot all rods in a data file. For ALLBOTH the theoretical structure factors are *automatically* calculated for the different rods. This also works for a single rod, and thus this can be a convenient alternative to the BOTH command.

- Remove option to set a fit model in ROD, because separate editor is far more convenient.

- Remove range checking flag in fitting: when range is specified (i.e. not both lower and upper limit equal to zero) the range is always checked.

- Add flag to fix or free a parameter to parameter file (.par). (This used to be the range checking parameter).

- Allow domain occupancies as fitting parameters.

- List comparison between data and model calculation for selected rod.

Changes and modifications in version of November 2011

- Include molecule in structure factor calculation. This is treated as separate object, characterized by position, rotation and coverage. Only single molecule possible at the moment.

Changes and modifications in version of September 2011

- Include dispersion corrections. All atomic scattering factors can be set or modified in a new menu SET.ROD.FATOMIC>.

- Include many subscale factors. This replaces the old 'scale2' factor. This is part of the *dataflag* label (that replaces the old 'LBRAGG') in data files.

- Allow different energies in one data set. Also set using the *dataflag* label.

- New command in plot menu, RDATA, that plots the subset of the data file with the most recently used values of *h* and *k* and the specified values for the serial energy parameter and subscale parameter and the fractional rod flag. With this command, there is no need to make data files for each rod. The command BOTH now also uses the same selected rod data. Thus the sequence 'ROD>CA RO 1 1 PL BO' will make a graph of model and data for the 11 rod (and the corresponding energy, subscale and fractional labels as specified in ROD.SET.CALC>).