**Rigid body**

**Rigid body approach**

“Model molecule” is a fragment, which is placed arbitrarily and does not contribute to structure factors.

Model molecule is transformed to “Actual positions” by translation vector and three rotation angles:

\[ x_i = R_1 \cdot (x_m - x_0) + t_1 \]

- \( x_m \) is position in the model molecule.
- \( x_0 \) is a reference point.
- Reference point determines the symmetry.

Rotations can be combined with an inversion.

Molecule can have its own local symmetry.
The parameters of atoms of the model molecule (coordinates, ADP ...) can be refined. Thus the model molecule is less rigid than an object fixed by “Keep geometry rigid”
Model molecule

Actual position #1

Actual position #2
Model molecule

Actual position #1

Actual position #2
TLS tensors

Instead of individual ADP of the model molecule we can assume that all atoms have amplitudes appropriate to a rigid body and that all atoms are moving in phase. Then we can refine TLS tensors (20 parameters) for each actual position. Symmetry restrictions will be done according to the reference point.
Rigid body approach applied to structure of cyclodextrin

β-Cyclodextrin duplex connected by two disulfide bonds


a=b=21.04 Å, c=26.69 Å, α=β=γ=90°

V=11833 Å³

Symmetry I4
Some of glucose units are disordered, the others not. The disordered part could not be described reliably by splitting of atoms because of low data quality. Fixing geometry by restraints would be extremely laborious.
One of not disordered glucose units was taken as a model molecule.

The model molecule is indicated in yellow and suffix “a”.

O1, O2 and C1a were refined freely.
The model molecule enters to ten actual positions. The pairs g-f, h-l, e-d describe disordered glucose units, with total occupancy 1. Because all actual position have common geometry refined only for the model molecule, disorder can be reliably refined.

Introduction of rigid bodies did not affect R value. This is a prove that the glucose unit is the same in all position within our data precision.

Advantages for visualization: minor actual position can be easily removed.
Modulated structures

very short explanation what does it mean
Sodium carbonate
View along c

z from 0 to 1
Sodium carbonate
View along c
z from 1 to 2
Sodium carbonate
View along c
z from 2 to 3
Is there some translation periodicity?
Probably yes because the diffraction pattern looks like usually
…. but we cannot describe all peak positions with a lattice
The remaining spots can be described with q-vector, which has irrational components.

Indices $h \ k \ l \ m$
Four-dimensional reciprocal lattice
Modulated and composite crystals can be described in a (3+d) dimensional superspace. The theory has developed by P.M. DeWolff, A. Janner and T. Janssen (Aminoff prize 1998). The basic idea: real diffraction pattern is a projection from the (3+d) dimensional superspace. The basic assumption: all satellites are clearly separated. (the intensities diminish for large satellite index).
The atom is displaced from its basic position by a periodic modulation function that can be expressed as a Fourier expansion. In the first approximation intensities of satellites reflections up to order $m$ are determined by modulation waves of the same order.

\[
\mathbf{r} = \mathbf{\bar{r}} + \mathbf{u}
\]

\[
\mathbf{u}(\bar{x}_4) = \sum_{n=1}^{m} A_{s,n} \sin(2\pi n \bar{x}_4) + \sum_{n=1}^{m} A_{c,n} \cos(2\pi n \bar{x}_4)
\]
Example 5.2: Anhydrous Sodium carbonate
Structure with strong harmonic modulation of positions and ADP.
Chemical formula: Na$_2$CO$_3$

3d $\rightarrow$ incommensurate $\rightarrow$ commensurate

<table>
<thead>
<tr>
<th>Phase</th>
<th>Lattice Parameters</th>
<th>Temperature</th>
</tr>
</thead>
</table>
| Alpha | $9.02, 5.21, 6.50$ | $757K$      
$90, 90, 90$ | $90, 90.33, 90$ | $90, 101.35, 90$ |
| Beta  | $8.98, 5.25, 6.21$ | $628K$, P6$_3$/mmm | $C2/m(\alpha 0 \gamma)$ |
| Gamma | $8.92, 5.25, 6.05$ | $170K$, $8.90, 5.24, 6.00$ | $90, 101.87, 90$ |
| Delta | $8.90, 5.24, 6.00$ | $628K$, P6$_3$/mmm | $C2/m(\alpha 0 \gamma)$ |

The main change of the structure occurs during the alpha $\rightarrow$ beta transition which changes rotation symmetry. Although modulations in gamma and delta phase are very strong they only modify the beta structure keeping the rotation symmetry unchanged.
Data for the phase gamma

Single crystal data measured with KUMA four-circle diffractometer
Input files: naco.hkl, naco.cif_od
Frame scaling, absorption correction: done with software of diffractometer

Unit cell: $a=8.9338$, $b=5.2678$, $c=6.0565$, $\alpha=90.1018$, $\beta=101.551$, $\gamma=89.7404$
$q$ vector: $(0.1776, 0, 0.3252)$
# Import wizard

## Data reduction file from:

<table>
<thead>
<tr>
<th>File name</th>
<th>naco.hkl</th>
</tr>
</thead>
</table>

### Options:
- CAD4
- Nonius-CCD
- Siemens P4
- Bruker-CCD
- Oxford Diffraction-CCD
- Oxford Diffraction-PD
- Rigaku-CCD
- IPDS Stoe
- D9-ILL
- ILL-Vivaldi
- ISIS SXD
- Hasylab F1
- Hasylab HUBER
- Hasylab XDS

## Define basic input file:

- input from "sum" file
- input from "cif_od" file

File name: naco.cif_od

## Complete/correct experimental parameters:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Cell parameters</td>
<td>8.9338 5.2678 6.0565 60.1018 101.551 89.7404</td>
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<tr>
<td>Number of input indices</td>
<td>4</td>
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<tr>
<td>1st modulation vector</td>
<td>0.1776 0.3252</td>
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</table>

## X-ray tube

<table>
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<th>Value</th>
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<tbody>
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<tr>
<td>Temperature</td>
<td>293</td>
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</table>

## Polarization correction:

- Circular polarization
- Perpendicular setting
- Parallel setting
Symmetry wizard

Tolerances for crystal system recognition:

Original cell parameters: 11.306 6.690 10.068 89.97 97.28 90.03
Maximal deviation for cell lengths in [Å] 0.02
Maximal deviation for cell angles in deg 0.2

Tolerances for space group recognition:

Maximal ave(I/sig(I)) for centering 10
Maximal ave(I/sig(I)) for extinctions 20

Search for higher symmetrical supercell (recommended)

Check non-standard centering:

- look for centering vectors composed from 0 and 1/2
- look for centering vectors composed from 0, 1/3 and 2/3

Select Laue symmetry

<table>
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<tr>
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<th>Rint(obs/all)</th>
<th>#averaged</th>
<th>Redundancy</th>
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<tr>
<td>Triclinic</td>
<td>-1</td>
<td>3.17/6.42</td>
<td>3555/15796</td>
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<tr>
<td>Monoclinic</td>
<td>2/m</td>
<td>3.67/7.19</td>
<td>2112/8061</td>
</tr>
</tbody>
</table>

Averages made from 8852/46822 reflections
Data processing was done with C centering.
Symbol C2/m(0b0)s0 means:
- 3d symmetry C2/c
- q vector (0 β 0)
- shift by ½ in x4

M50:
**symmetry** x1 x2 x3 x4
**symmetry** -x1 x2 -x3 -x4+1/2
**symmetry** -x1 -x2 -x3 -x4
**symmetry** x1 -x2 x3 x4+1/2
The only reason for the random seed is compatibility with the text of Jana Cookbook.

Convergence with $R \sim 21\%$
Output of Superflip confirms the symmetry

Space group derived from the symmetry operations:

Tentative HM symbol: C12/m1(a0g)0s
Fingerprint: 431222C0R960028dXM1 (0,0,0,0)
Centering vectors:
  0.000  0.000  0.000  0.000
  0.500  0.500  0.000  0.000
Symmetry operations:
  1:  x1   x2   x3   x4
m|s(0,1,0):  x1 -x2  x3  1/2+x4
2|0(0,1,0): -x1  x2 -x3  1/2-x4
-1:  -x1  -x2 -x3  -x4

Position of the origin in the CF map:
  0.9099  0.6324  0.6417  0.9031
Agreement factors of individual generators:
Number smb agreement
  4  m|s  0.13
  2  2|0  0.78
The initial structure model

Step #1: Select atoms to be used -> 6 selected

Na1  
Na2  
Na3  
C1   
C2   
C3

1

Step #2: Select action by right mouse click or by this button: Action

Left mouse double click starts the Edit/Define action

2

Delete selected atoms  
Merge selected atoms  
Transform selected atoms  
Expand selected atoms  
Atoms from molecule to atomic part  
Adding of hydrogen atoms  
Rename selected atoms to "atom_type"+number  
Make symmetrically contiguous motifs  
Split atomic position

Edit/Define atoms

3

Define

Type

ADP parameter(s):

- isotropic
- harmonic
- anharmonic
- Use TLS

Modulation waves:

- Occupancy
- Position

Use:

- Use: none

- Use: none
Individual atoms
Structure plots

- Draw average structure
- Draw supercell structure
- Draw approximant structure

- Cutoff occupancy
- tzero
- Check short distances in the approximant
- Min. distance

- Keep atom names (duplicity could appear)
- Change atom names to "atom_type"+number

- Draw+return
- Quit
- Draw+continue

-or-

- Draw average structure
- Draw supercell structure
- Draw approximant structure

- Cutoff occupancy: 0.5
- tzero: 0
- Check short distances in the approximant
- Min. distance

- Keep atom names (duplicity could appear)
- Change atom names to "atom_type"+number

- Draw+return
- Quit
- Draw+continue
The plot helps to identify oxygens
C1 and C2 will be changed to oxygens with “Edit atoms” tool of Jana
Structure refinement

Refinement of the initial structure model

Adding position modulation waves
Refinement with harmonic ADP and four position modulation waves for all atoms

<table>
<thead>
<tr>
<th>Factor</th>
<th>Value</th>
<th>Factor</th>
<th>Value</th>
<th>Factor</th>
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<td>9.67</td>
<td>R(all)</td>
<td>14.12</td>
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<tr>
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<td>9.67</td>
<td>R(all)</td>
<td>14.12</td>
<td>wR(all)</td>
<td>10.18</td>
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<td>R factors for main reflections</td>
<td>1147=904+243</td>
<td>R factors for satellites order 1</td>
<td>2068=1436+632</td>
<td>R factors for satellites order 2</td>
<td>2294=1220+1074</td>
</tr>
<tr>
<td>R(obs)</td>
<td>5.79</td>
<td>wR(obs)</td>
<td>8.02</td>
<td>R(all)</td>
<td>6.81</td>
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<tr>
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<td>R(all)</td>
<td>6.81</td>
<td>wR(all)</td>
<td>8.14</td>
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<td>R factors for satellites order 1</td>
<td>2049=719+1330</td>
<td>R factors for satellites order 3</td>
<td>2285=358+1927</td>
<td>R factors for satellites order 4</td>
<td>21.07</td>
</tr>
<tr>
<td>R(obs)</td>
<td>7.20</td>
<td>wR(obs)</td>
<td>8.55</td>
<td>R(all)</td>
<td>9.59</td>
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<tr>
<td>wR(obs)</td>
<td>8.55</td>
<td>R(all)</td>
<td>9.59</td>
<td>wR(all)</td>
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<td>R factors for satellites order 2</td>
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<td>R factors for satellites order 3</td>
<td>2049=719+1330</td>
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<td>8.91</td>
<td>wR(obs)</td>
<td>10.31</td>
<td>R(all)</td>
<td>16.35</td>
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<tr>
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<td>10.31</td>
<td>R(all)</td>
<td>16.35</td>
<td>wR(all)</td>
<td>10.81</td>
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<tr>
<td>R factors for satellites order 3</td>
<td>2049=719+1330</td>
<td>R factors for satellites order 4</td>
<td>2285=358+1927</td>
<td>R(obs)</td>
<td>13.69</td>
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<td>R(obs)</td>
<td>13.69</td>
<td>wR(obs)</td>
<td>16.69</td>
<td>R(all)</td>
<td>33.21</td>
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<tr>
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<td>R(all)</td>
<td>33.21</td>
<td>wR(all)</td>
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<tr>
<td>R factors for satellites order 4</td>
<td>2285=358+1927</td>
<td>R(obs)</td>
<td>21.07</td>
<td>wR(obs)</td>
<td>27.68</td>
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<tr>
<td>wR(all)</td>
<td>64.88</td>
<td>R(all)</td>
<td>64.88</td>
<td>wR(all)</td>
<td>32.04</td>
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<tr>
<td>Last wR(all)</td>
<td>16.20</td>
<td>10.38 10.18</td>
<td>10.18 10.18</td>
<td>10.18</td>
<td></td>
</tr>
<tr>
<td>Maximum change/s.u.</td>
<td>-0.0076 for xsin2[O2]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fourier maps and Contour plots

Coordinates of Na1: x, y, z
Sections to plot: x2-x4

Range of x2: from \((y - 2Å/b)\) to \((y + 2Å/b)\) step 0.02Å
Range of x4: from 0 to 2, step 0.02

Stacking of sections: x2-x4 x3(1) x1(1)
......
x2-x4 x3(n) x1(1)
x2-x4 x3(1) x1(2)
......
x2-x4 x3(n) x1(m)

Range of x1: from \((x - 1Å/a)\) to \((x + 1Å/a)\) step 0.02Å
Range of x3: from \((z - 1Å/c)\) to \((z + 1Å/c)\) step 0.02Å
Observed and difference Fourier map for Na1 indicates modulation of ADP. Similar features can be seen in difference maps of other atoms except carbon.
Adding ADP modulation waves

Final refinement

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position waves</th>
<th>ADP waves</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na1</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Na2</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Na3</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>O1</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>O2</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Cl</td>
<td>3</td>
<td>0</td>
</tr>
</tbody>
</table>
Final difference maps

Contour step 0.1
Interpretation of structure model using Grapht

Internal coordinate $t$
Interpretation of structure model using Dist

***************
* List of distances *
***************

Full coordination of atoms will be printed
The results will be printed in columns without symmetry codes

Distances will be calculated from d(min)= 0.000 to specific maximal distances as listed below expanded by 5%:

Na-Na 2.820 R  Na-C 2.680 R  Na-O 2.336 T
C-C 1.560 T  C-O 1.360 T
O-O 1.480 R

T ... typical distances taken either from the file distributed with Jana program or defined by user
R ... distance as derived from atomic radii

<table>
<thead>
<tr>
<th>Atom type</th>
<th>Atom radius</th>
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<tr>
<td>Na</td>
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</tr>
<tr>
<td>C</td>
<td>0.770</td>
</tr>
<tr>
<td>O</td>
<td>0.740</td>
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</table>

The calculation will run for t from the interval <0.000,1.000> at 131 equidistant steps
Each 10th step will be printed

---------
* atom Na
---------

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<th>0.400</th>
<th>0.500</th>
<th>0.600</th>
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<td>4.183(3)</td>
<td>4.334(3)</td>
<td>4.259(3)</td>
<td>4.066(3)</td>
<td>3.901(3)</td>
<td>3.891(3)</td>
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<tr>
<td>min</td>
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Interpretation of structure model using plots