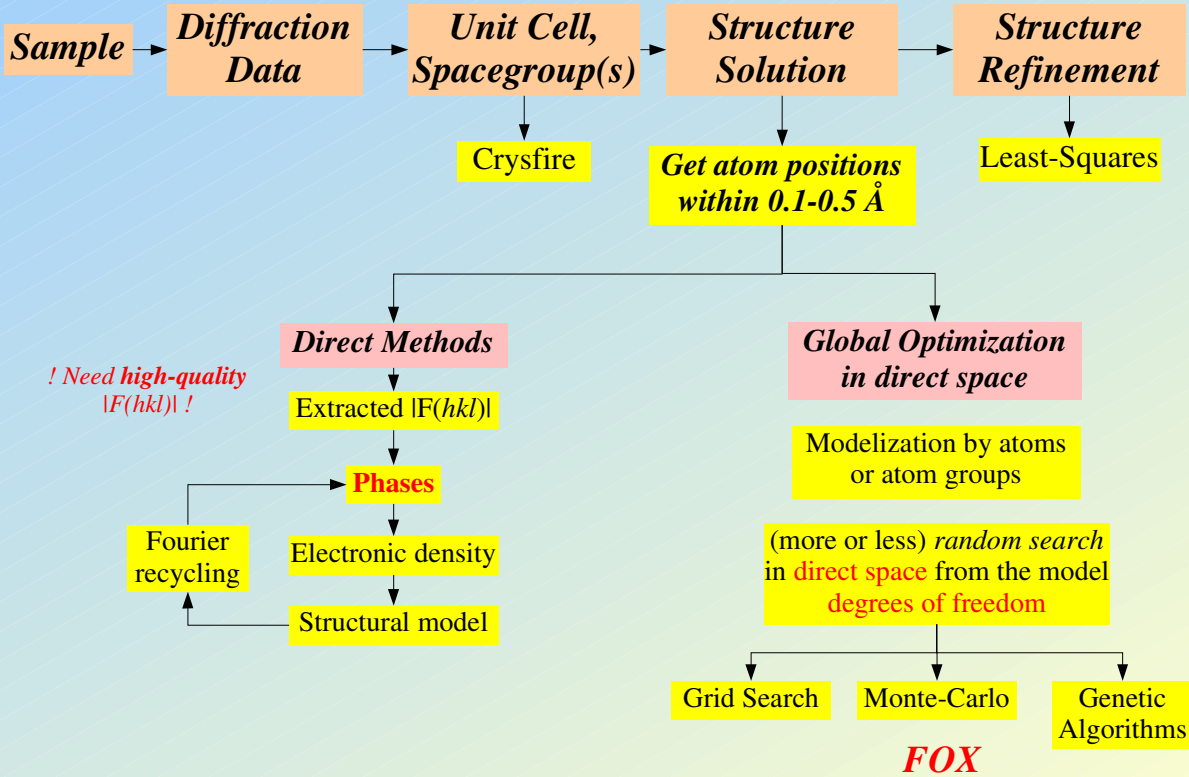
FOX, "Free Objects for Xtallography" a free, modular approach to crystal structure solution

V. Favre-Nicolin & R. Černý

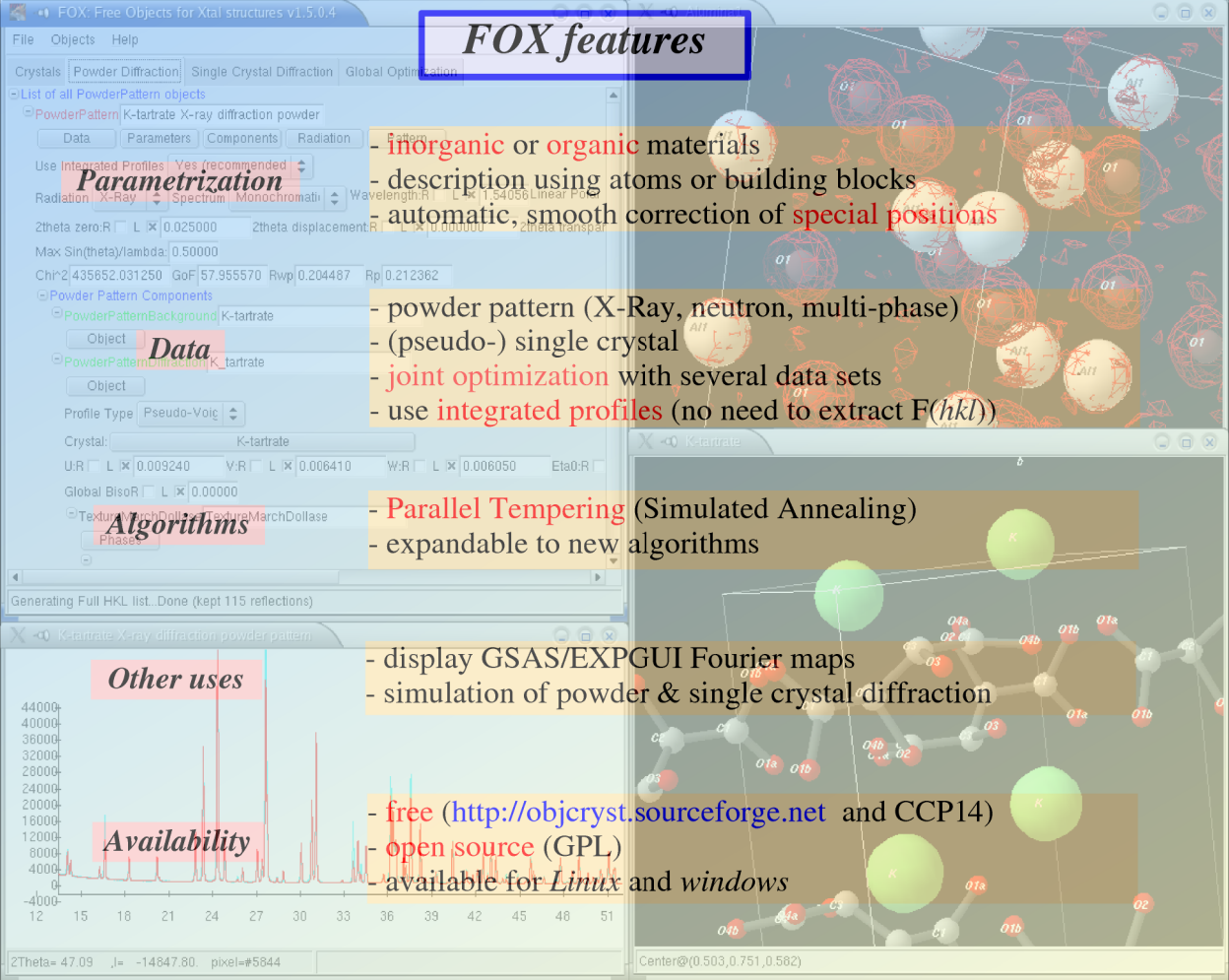
I Purpose & Algorithms
II Inorganic Structures
III Organic Structures

UNIVERSITÉ DE GENÈVE

Structure Determination Overview



FOX features



Parametrization

- inorganic or organic materials
- description using atoms or building blocks
- automatic, smooth correction of special positions

Data

- powder pattern (X-Ray, neutron, multi-phase)
- (pseudo-) single crystal
- joint optimization with several data sets
- use integrated profiles (no need to extract F(*hkl*))

Algorithms

- Parallel Tempering (Simulated Annealing)
- expandable to new algorithms

Other uses

- display GSAS/EXPGUI Fourier maps
- simulation of powder & single crystal diffraction

Availability

- free (http://objcryst.sourceforge.net and CCP14)
- open source (GPL)
- available for *Linux* and *windows*

Monte-Carlo Algorithm

Parametrization -> Degrees Of Freedom

starting sonfiguration

random change of parameters

evaluation of the new configuration: ***Cost (C)***

is configuration better ?
$C_n < C_{n-1}$

yes

keep configuration

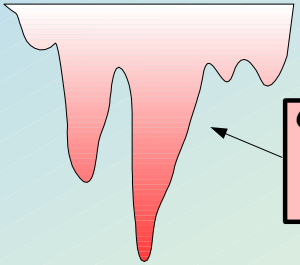
no

keep configuration with probability:

$$P = e^{\frac{-\Delta C}{T}}$$

Temperature of the algorithm

Hypersurface Cost = f (DOF)

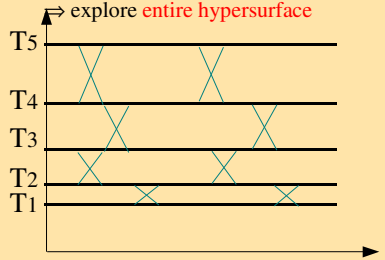


Generate a distribution of configurations following ***Boltzmann****'s law*

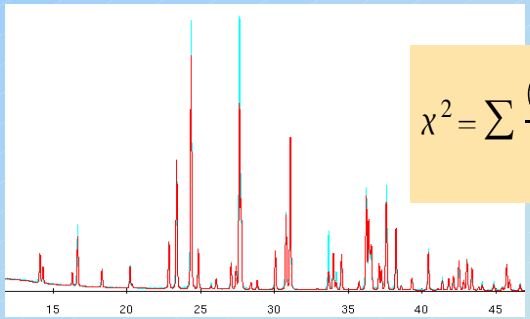
Parallel Tempering

simultaneous optimization at different temperatures

⇒ explore entire hypersurface

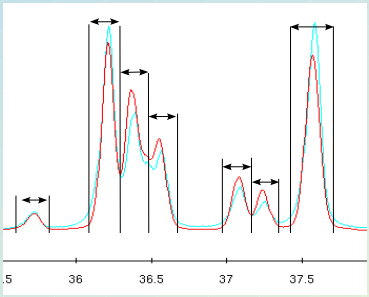


Evaluation of Trial Configurations

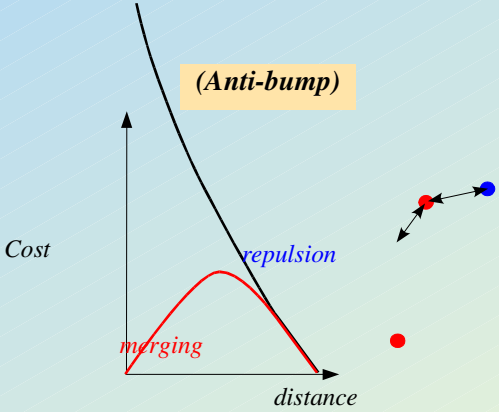


$$\chi^2 = \sum \frac{(y_i^{obs} - y_i^{calc})^2}{\sigma_i^2}$$

integrated profiles



(Anti-bump)

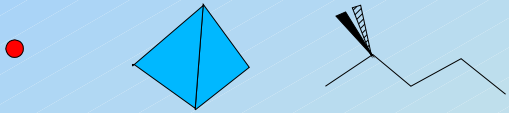


Use any combination of criteria

$$Cost = \sum \chi_j^2$$

Crystal Structure Components

***Building blocks* for the crystal structure**



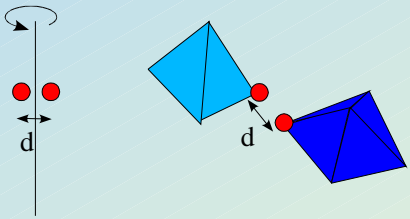
atom ***Polyhedron*** ***molecule***

Description from bond lengths, bond angles and dihedral angles

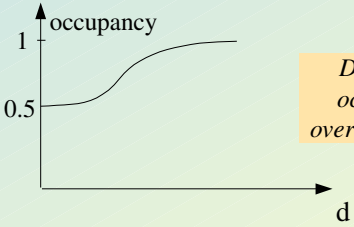
⇒ Use the maximum *a priori* information about the atoms coordination

Less **degrees of freedom**
⇒ More efficient search

Special positions* & *Shared atoms



Overlap of identical atoms using a ***Dynamical Occupancy Correction***



Diminish the occupancy of overlapping atoms

$PbSO_4$-Preparation

Prerequesite

Unit Cell: 8.482 5.398 6.959 90 90 90
Spacegroup: Pnma

Diffraction data:
- X-Ray powder diffraction pattern @ Cu tube
- Neutron powder diffraction @1.909 Å

(profile parameters: optional)

Crystal contents

Formula: Pb SO_4

⇒ ***Building blocks***: Pb atom + SO_4 tetrahedron
S-O distance = 1.5 ± 0.1Å

Unit Cell volume =319 $Å^3$
General multiplicity = 8

=> Probably ***one Pb*** and ***one SO_4*** in the asymmetric unit
(and atoms are probably on a special position)

PbSO4
Post-Global Optimisation

Crystal Object -> Export structure as text

*in FOX 1.5, **export as CIF** is available*

crystal : PbSO4-Tetrahedron(Pnma)
Cell dimensions : 8.48200 5.39800 6.95900 89.99999 89.99999 89.99999
List of scattering components (atoms): 6

Pb at : 0.8126 **0.7613** 0.3315 , Occup=1.0000 * **0.5063** ,ScattPow:Pb , Biso= 1.0000
SO4_S at : 0.0611 **0.2521** 0.1834 , Occup=1.0000 * **0.5000** ,ScattPow:S , Biso= 1.5000
SO4_O1 at : -0.0936 **0.2425** 0.0939 , Occup=1.0000 * **0.5000** ,ScattPow:O , Biso= 1.5000
SO4_O2 at : **0.0852** **0.4595** **0.3060** , Occup=1.0000 * **0.5248** ,ScattPow:O , Biso= 1.5000
SO4_O3 at : **0.0745** **0.0131** **0.3151** , Occup=1.0000 * **0.5248** ,ScattPow:O , Biso= 1.5000
SO4_O4 at : 0.1909 **0.2353** 0.0463 , Occup=1.0000 * **0.5170** ,ScattPow:O , Biso= 1.5000

Occupancy = occ * dyn, where:
- occ is the 'real' occupancy
- dyn is the **dynamical occupancy correction**, indicating either an atom on a special position, or several identical atoms overlapping (dyn=0.5 -> atom on a symetry plane / 2fold axis.. -> OR 2 atoms strictly overlapping)

atoms on special positions
atoms to merge (symetrical)

Total number of components (atoms) in one unit cell : 24.5827

Table of ***minimal distances between all components (atoms)***

	Pb	SO4_S	SO4_O1	SO4_O2	SO4_O3	SO4_O4
Pb	0.000	3.542	2.606	2.874	2.906	2.629
SO4_S	3.542	0.000	1.452	1.422	1.568	1.458
SO4_O1	2.606	1.452	0.000	2.380	2.436	2.435
SO4_O2	2.874	1.422	2.380	0.000	**0.185**	2.274
SO4_O3	2.906	1.568	2.436	**0.185**	0.000	2.431
SO4_O4	2.629	1.458	2.435	2.274	2.431	0.000

⇒ to refinement (least squares) program...

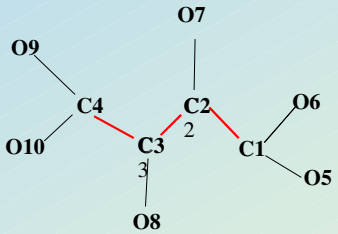
Potassium Tartrate Preparation

Prerequesite

Unit Cell: 7.786 10.647 7.615 90 90 90
Spacegroup: $P2_12_12_1$

Diffraction data:
- X-Ray powder diffraction pattern @ Cu $K\alpha_1$

(profile parameters: optional)



Crystal contents

Formula: HOOC-C*(OH)-C*(OH)-COO⁻ K⁺
⇒ ***Building blocks***: K atom + C_4O_6 molecule

Unit Cell volume = 631Å^3
General multiplicity = 4

=> Probably ***one formula*** per asymmetric unit

Z-Matrix (number of atoms)

```
10
C   1
C   1 1.5
C   2 1.5  1 110
C   3 1.5  2 110   1 0
O   1 1.2  2 120   3 0
O   1 1.2  2 120   5 180
O   2 1.4  1 110   3 180
O   3 1.4  2 110   4 180
O   4 1.2  3 120   2 0
O   4 1.2  3 120   9 180
```

free torsion angles

atom type

bond ***length*** with atom #

bond ***angle*** with atom #

dihedral angle with atom #

Solution requires approx. 400 000 trials (<5 min on a 1.4 GHz athlon)

M. Edgar (St Andrews, Scotland)

$Al_2(H_3CPO_3)_3$

a=13.297 b=9.657 c=5.072 (89.6° 111.2° 92.1°) ***P-1***
17 atoms + 9 H

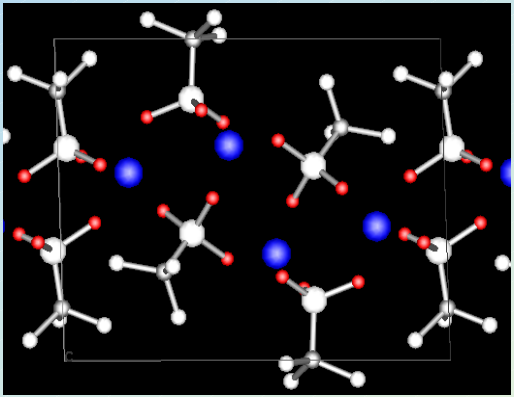
Solving through direct methods : failed

RMN ^{13}C ^{27}Al ^{31}P : identification of 5 building blocks
- 3 non-equivalent H_3C-PO_3 fragments
- 2 Al non-equivalent, one in tetrahedral and one in trigonal bypiramid

2 possible modelization in Fox

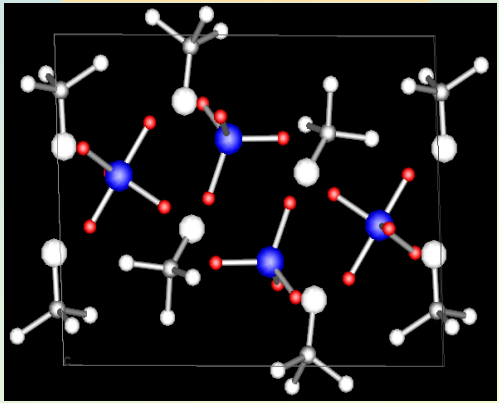
including the hydrogens improves the search, by steric effect

3 H_3C-PO_3 + 2 Al atoms
(24 Degrees of Freedom)



500.000 trials /8 min

3 H_3C-P + AlO_4 + AlO_5
(27 Degrees of Freedom)



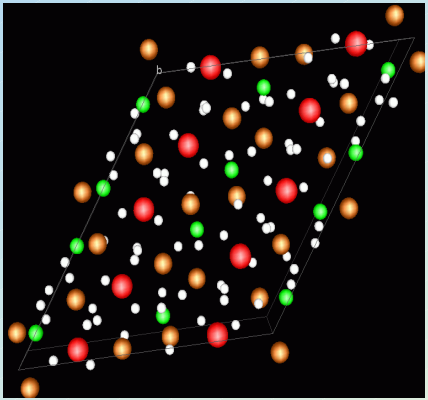
5 million trials /80 min

Structures Solved Using Fox

FOX: has been used to solve new structures:

inorganic

- $CsOH.H_2O$
- $NdNi_4MgD_{3.6}$
- $Zr_3NiO_{0.6}D_{6.32}$
- $LaNi_2Mn_3D_{5.5}$
- $LaMg_2NiD_7$
- $Mg_{12}Ir_{13}$

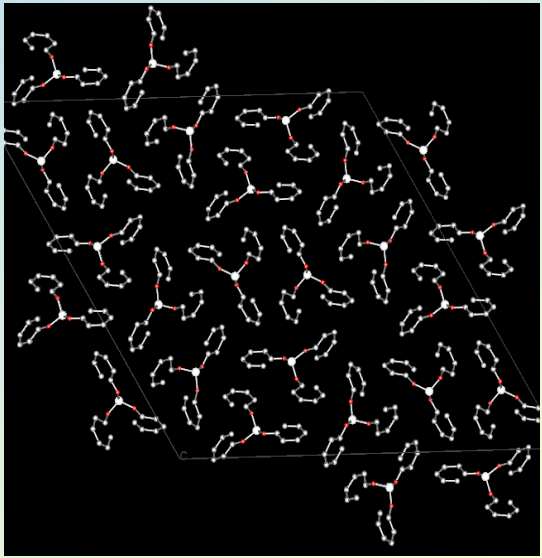


hybrid

- $Al(CH_3PO_3)_2$

...and has been tested on organic structures

- potassium tartrate
- cimetidine
- TriPhenylPhosphite
- ...



Conclusion

FOX features:

- modelize structure from any combination of building blocks *(use chemist's* a priori *knowledge)*
- automatic handling of special positions and building blocks connectivity
- flexible decription of Molecules and Polyhedra for a more efficient search
- multi-pattern joint optimization & multi-phase powder data
- does not require individual structure factor extraction

- expandable (new algorithms, structure modelization, criteria...) : object-oriented library ObjCryst++

- Free for Linux & windows

- not a "black box"

Future of FOX :

- See presentation in the SDPD microsymposium, tuesday morning

Get FOX at http://objcryst.sourceforge.net and from CCP14 mirrors

Acknowledgements

Radovan Černý (Université de Genève)

Anders Markvardsen – Maximum Likelihood help *(ugly approximations are mine),...*

Brian Toby (& Michael Polyakov) – display of GSAS/EXPGUI Fourier maps,...

Lachlan Cranswick – CCP14, suggestions...

Users of Fox

Fox is not my research subject anymore, I continue as a hobby
⇒ help me if you want Fox to go on & improve !

Users advice counts *! Send suggestions, bug reports, interesting data !*
⇒ Get on the ***Fox Mailing list*** *to know when beta versions are released*