FOX: modular approach to structure solution using powder data

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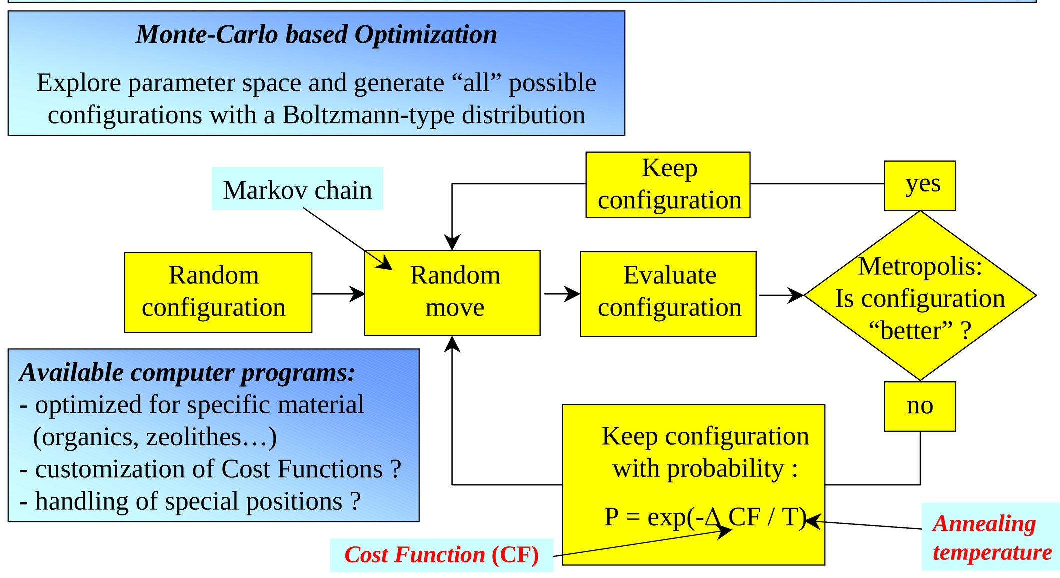
Abstract. Program FOX for *ab initio* crystal structure determination from powder diffraction uses global optimization algorithms to find the correct structure by making trials in the direct space. It is a modular program, capable of using several criteria for evaluating each trial configuration, e.g. combining neutron and X-ray diffraction patterns. The program describes the structural building blocks (polyhedrons, molecules etc.) with their internal coordinates (Z-matrices), thus allowing natural constraints on interatomic distances and angles. Identical atoms shared between neighboring building blocks, and special positions are handled with an automatic, adaptive method (Dynamical Occupancy Correction). Several algorithms (Simulated Annealing, Parallel Tempering) are currently available. The program is based on an object-oriented crystallographic library ObjCryst++ (programming language c++). The program and the library are available for Linux and Windows on *http://objcryst.sourceforge.net*. Inorganic and organic structures with the complexity up to 26 independents atoms are routinely solved from laboratory X-ray, synchrotron or neutron data.

Global Optimization in Direct Space

Direct space methods : locating building units (molecules, polyhedrons, atoms) in the cell.
Global Optimization : evaluating a ***Cost*** of the structural model in parameter space.



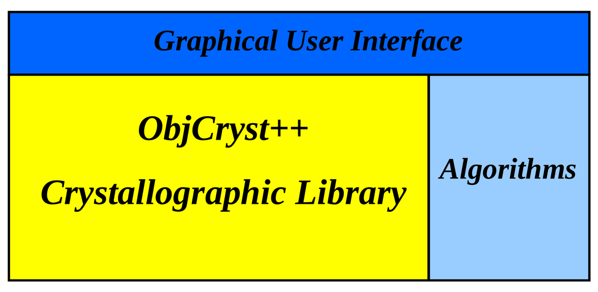
Applications

Compound	Atoms[c]	Space group	DOF	Modelization	Data[d]	Cost Function[e]	Success [%]	Trials×10^3 (time [s])
$PbSO_4$[b]	5	*Pnma*	18	free atoms (6)	Xl+N	iR_{wp}	100	<40(<30)
			9	Pb + (SO_4)	Xl+N	iR_{wp}	100	<50(<30)
$CsOH{\cdot}H_2O$[a]	2	*$I4_1/amd$*	9	free atoms (3)	Xl	iR_{wp}	100	<20(<30)
$LiBH_4$ - RT[a]	5	*Pnma*	9	Li + (BH_4)	Xs	iR_{wp} + AB	100	<50(<30)
$LiBH_4$ - HT[a]	4	*$P6_3mc$*	9	Li + (BH_4)	Xs	iR_{wp} + AB	100	<50(<30)
$NdNi_4MgD_{3.6}$[a]	5M,	*$Pmn2_1$*	15,	free atoms (5M)	Xs,	iR_{wp} + AB	100	100(60)
	3D		15	free atoms (5D)	N	iR_{wp}	100	100(60)
$Zr_3NiO_{0.6}D_{6.32}$[a]	4D	*Cmcm*	15	free atoms (5D)	N	iR_{wp}	100	100(60)
$LaNi_2Mn_3D_{5.5}$[a]	5D	*P6/mmm*	15	free atoms (5D)	N	iR_{wp}	100	100(60)
$ErFe_2D_{4.72}$	10D	*$Pmn2_1$*	60	free atoms (20D)	N	iR_{wp} + AB	100	500(300)
$LaMg_2NiD_7$[a]	8M,	*$P2_1/c$*	24,	free atoms (8M)	Xs,	iR_{wp}	100	100(60)
	14D		42	free atoms (14D)	N	iR_{wp} + AB	100	400(900)
MgIr[a]	23	*Cmca*	69	free atoms (23)	Xs+N	iR_{wp} + AB	50	500(12000)
			20	4[Ir(Ir,Mg)$_{12}$]	Xs+N	iR_{wp}	75	100(7000)
K-tartrate	11	*$P2_12_12_1$*	14	K + (C_4O_6)	Xl	iR_{wp}	95	1200(720)
Cimetidine[b]	17	*$P2_1/c$*	14	($C_{10}N_6S$)	Xs	iR_{wp}	90	4000(2800)
$Al_2(CH_3PO_3)_3$[a]	26	*P*-1	24	2Al + $3H_3CPO_3$	Xl	iR_{wp} +AB	100	750(750)

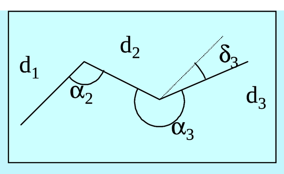
[a] new crystal structure; [b] test data available on web; [c] M=metal atom, D=deuterium
[d] Xl=laboratory X-ray, Xs=synchrotron, N=neutron, Xl(s)+N=joint use, Xl(s),N=successive use
[e] iR_{wp} (weighted, integrated profile), AB (anti-bump)

FOX: Free Objects for Xtallography

(i) The crystal structure can be described using ***any*** combination of ***building blocks***: isolated atoms, molecules, polyhedrons.
(ii) The correct structure can be found without ***any*** assumption on the actual ***connectivity*** between building blocks, nor ***any*** *a priori* knowledge about atoms on ***special positions***.
(iii) Several ***optimization algorithms*** can be used, with ***easy*** path from one to another and with ***easy*** upgrade of algorithm. All optimized objects (crystal structure, powder pattern) can define their ***Cost Function*** (CF) and ***any*** combination of CF can be used as a criterion.
(iv) It is possible to use ***jointly*** all available diffraction data sets.
(v) Any modification or upgrade of the program is ***easy***.

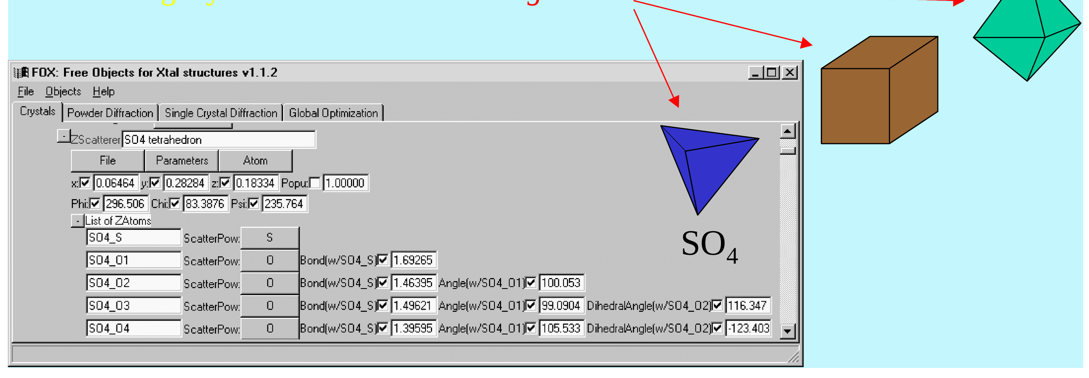


Building Blocks : Polyhedrons, Molecules described by Z-matrix



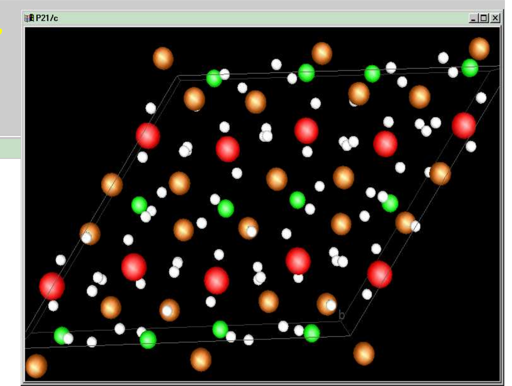
Z-Matrix: describe atom positions using ***relevant*** parameters:
Bond lengths, bond angles and dihedral angles
- give ***'natural' constraints*** to the model
- keep some ***flexibility*** (limit parameters)
- reduce the *n*-dimensional ***parameter space***

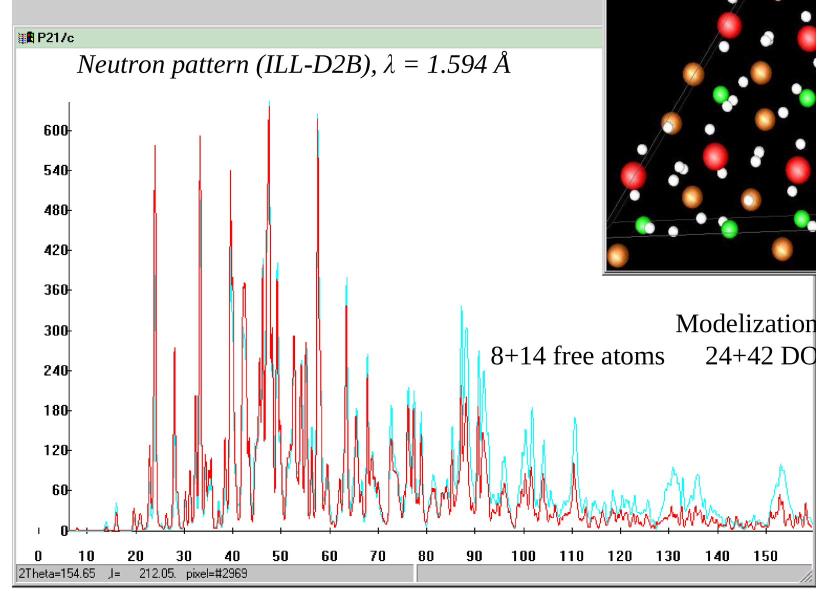
*Describing cryst. from "known" **building blocks** :*



Isolated atoms : $LaMg_2NiD_7$

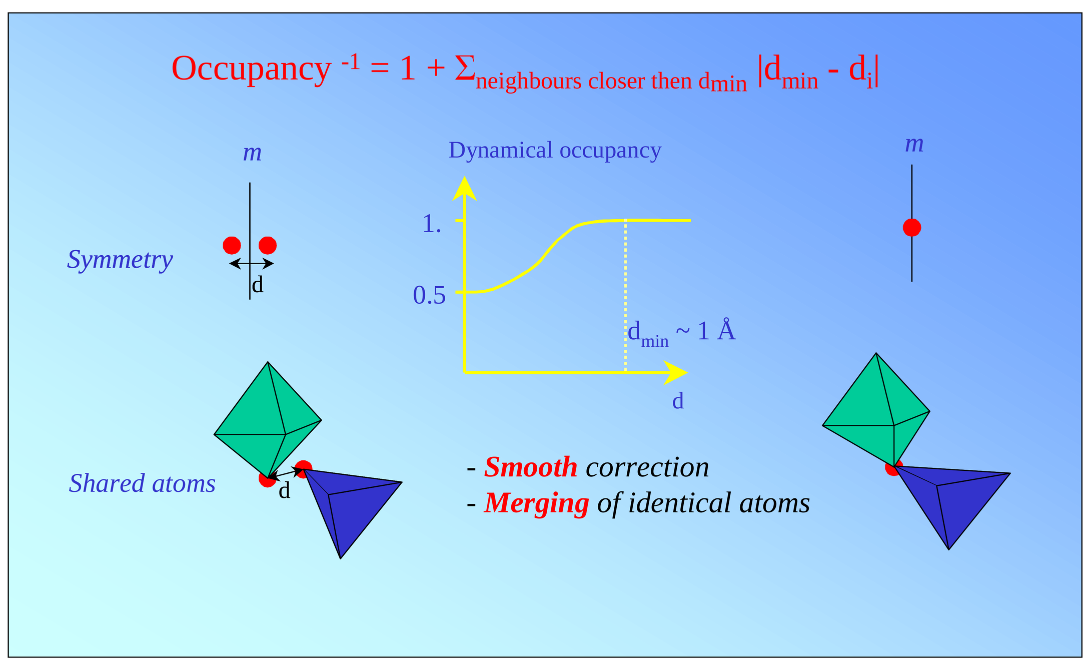
a = 13.9785 ***b*** = 4.7025 ***c*** = 16.0244 **β** = 125.238, **sg** *$P2_1/c$*, metal atoms pseudosymmetry *Cmcm*
8 metal and 14 deuterium atoms





Modelization
8+14 free atoms 24+42 DOF solution in 60+900 s

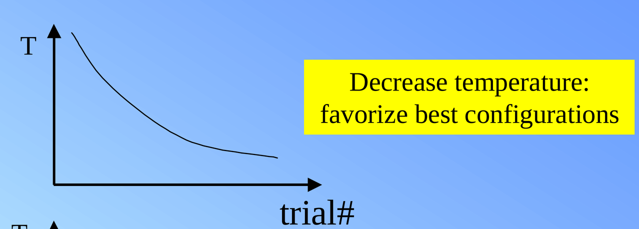
Special Positions and Connectivity : Dynamical Occupancy Correction



Algorithms and Cost Functions

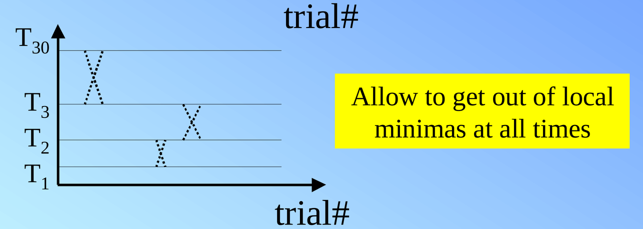
Cost Functions are defined for each kind of object : R, R_w, AntiBump, …
Use a ***weighted sum*** of Cost Functions: $f = w_1 R_1 + w_2 R_2 + w_3$ AntiBump+…

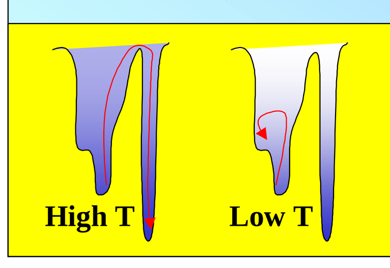
Simulated Annealing :



Parallel Tempering :

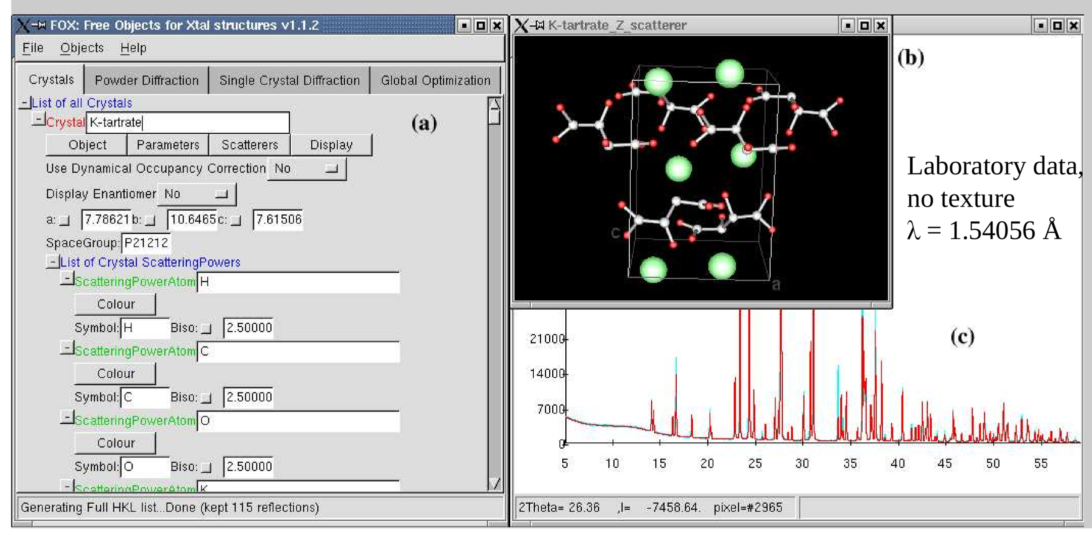
$$P = e^{-\frac{\Delta CF}{T}}$$





Molecule : Potassium Hydrogen 2R, 3R (+) Tartrate ($C_4H_5O_6K$)

a = 7.7954, ***b*** = 10.6516, ***c*** = 7.6166, **sg** *$P2_12_12_1$* — Modelization: K + (C_4O_6)
11 non-hydrogen atoms — 14 DOF solution in 720 s



Tuned for Global Optimization

Avoid useless recalculations (auto. store profiles, scattering factors, …)

Performance : up to 5000 trial structures / s (Athlon 1.4 Ghz, Linux)

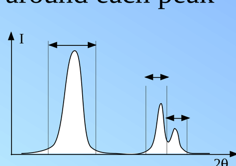
Cimetidine : up to 2500 trials/s for 150 reflections in single-crystal mode, 40 % slower in powder-mode.

'Smart' annealing temperature : automatic adaptative tuning of the temperature to keep the acceptance rate between 10 and 30 %

'Smart' moves for molecules : local minimization after a random move, increase the success rate

Cimetidine : success increases from 80 to 90 %

Integrated R-factor : summing more than 90% of intensity around each peak using full observed and calculated patterns :



Conclusions

ObjCryst++ — ***versatile***, ***expandable*** Crystallographic library; *not* a "finished" product (add your code!)

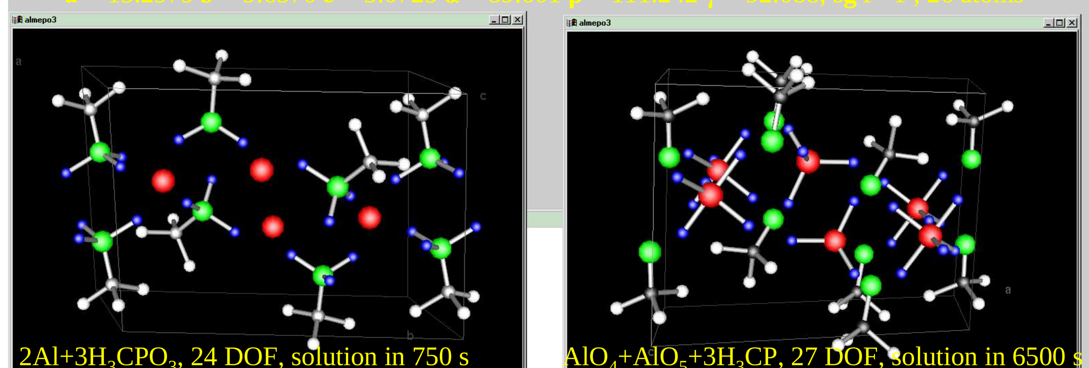
FOX — program for the global optimization of crystal structures (powder diffraction)
- ***any*** combination of ***building blocks*** : isolated atoms, molecules, polyhedrons
- ***no*** assumption on the actual ***connectivity***
- ***no*** *a priori* knowledge about ***special positions***
- ***joint*** use of diffraction data sets
- ***easy*** modifications

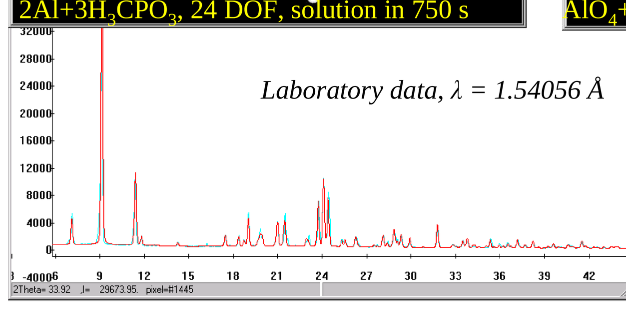
Future developments :
- ***smart modelization*** of molecules (restraints)
- ***new*** Cost Functions (energy, atomic coordination)
- ***guided optimization*** (structure envelopes, parameter space modification)
- ***other algorithms*** (genetic)

Availability (Windows, Linux): ***http://objcryst.sourceforge.net***

Hybrid : $Al_2(CH_3PO_3)_3$

Edgar *et al.* (2002) submitted to *Chem. Commun.*
a = 13.2979 ***b*** = 9.6570 ***c*** = 5.0725 **α** = 89.601 **β** = 111.242 **γ** = 92.088, **sg** *P*-1, 26 atoms





Buildings blocks deduced from $_{27}$Al, $_{13}$C and $_{31}$P NMR spectra :
3 C-PO3 units and 2 Al atoms

Favre-Nicolin V. and Černý R.; submitted to *J. Appl. Cryst. - computer programs*;
see also : *http://objcryst.sourceforge.net/*
and
Book of Abstract of the ECM 20, Krakow 2001, p. 135

Acknowledgements

Samples or powder patterns
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Polyhedrons : MgIr

a = 18.4648 ***b*** = 16.1701 ***c*** = 16.8175, **sg** *Cmca*
11 Ir and 12 Mg atoms
Frank-Kasper intermetallic compound

Modelization
23 free atoms — 69 DOF solution in 12000 s
4 icosahedrons — 20 DOF solution in 7000 s