Short Rietveld Course 2001
Introduction to *FullProf*

- **Increasing the knowledge about powder diffraction.**
  Web sites
- **The program *FullProf***
- **Examples: self-tutorials**

Freely available software tools for crystallography

Lachlan M.D. Cranswick (L.Cranswick @dl.ac.uk)
CCP14 Project for Single Crystal and Powder Diffraction
http://www.ccp14.ac.uk ccp14@ccp14.ac.uk

Downloading of Software

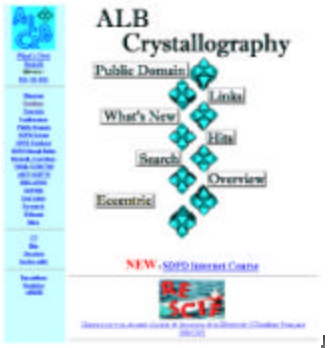
The above software and resources can be downloaded via the CCP14 site:

http://www.ccp14.ac.uk

Graphical tutorial run-through of most of this software is located via **("look before you try"):**

http://www.ccp14.ac.uk/tutorial/

Armel Le Bail page: http://sdpd.univ-lemans.fr



What's *FullProf* ?

- **A program for :**
  Simulation of powder diffraction patterns
  Pattern decomposition⇨ integrated intensities
  Structure refinement
  Powder and single crystal data
- **Crystal and magnetic structures**
- **Multiple data sets: simultaneous treatment of several powder diffraction patterns (CW X-rays & neutrons, Energy dispersive X-rays, TOF neutron diffraction)**
- **Combined treatment of single crystal and powder data**
- **Structure determination capabilities: simulated annealing on integrated intensity data**

A few words of history …(1)

- Origins: DBW program, 1981 in Barcelona (thanks to Ray Young)
- Reorganization towards a structured programming within the FORTRAN 77 language, corrections of bugs, different ways of calculating R-factors, etc. Barcelona/Grenoble (1982-1987)
- Introduction of magnetic scattering, anisotropic broadening, profile matching (now known as Le Bail method), rigid bodies 1988-1992, Institute Laue-Langevin, Grenoble.
  The name *FullProf* is adopted in 1990

"FULLPROF: A Program for Rietveld Refinement and Pattern Matching Analysis"
J. Rodríguez-Carvajal
Powder Diffraction, Satellite meeting of the XV congress of the International Union of Crystallography, Toulouse 16-19 July (1990)

A few words of history …(2)

- Improvements of magnetic scattering options, new peak shapes, single crystal and integrated intensities options, ... Distribution by anonymous ftp in 1993. LLB, Orsay (near Paris)
- Introduction of a rudimentary option for handling Time of Flight neutron powder diffraction data in 1996.
- WinPLOTR and Windows version of FullProf, distribution via the LLB Web site. Progressive conversion to Fortran 90 style and conventions (1998).
- Complete reorganization of the code within the new Fortran 90 language. Programmed in the subset ELF90. Multiple data sets, TOF improvements (Barcelona, Argonne, Orsay, 1999 …)

FullProf Web site:

http://www-llb.cea.fr/fullweb/powder.htm
or
ftp://charybde.saclay.cea.fr/pub/divers

Version 3.5 (FORTRAN 77, most common platforms)
ftp://charybde.saclay.cea.fr/pub/divers/fullp
(single pattern, discontinued version, only action: correction of bugs)

FullProf.9x & FullProf.2k (Fortran 90 subset ELF90)
Windows 9x/2k, Windows NT, MacOS, Linux
ftp://charybde.saclay.cea.fr/pub/divers/ fullprof.98
ftp://charybde.saclay.cea.fr/pub/divers/ fullprof.2k

New features of *FullProf*

New features of *FullProf* (1)

http://www-llb.cea.fr/fullweb/powder.htm

- Full multipattern capabilities: joint refinements of neutron and X-ray patterns, different wavelengths, detector banks, etc.
- Optimization for common or routine problems
- Automatic attribution of code parameters, distances, angles and bond-valence calculations
- Form factor refinements

New features of *FullProf* (2)

http://www-llb.cea.fr/fullweb/powder.htm

- Generalization of anisotropic broadening formulation for micro-strains and size effects.
- Interpretation of micro-structural parameters
- New formulation of T.O.F. versus d-spacing (Jason Hodges, Argonne) fully implemented

New features of *FullProf* (3)

http://www-llb.cea.fr/fullweb/powder.htm

- Superstructures treated within the basic subcell and Fourier coefficients of displacement vectors
- Simulated annealing for solving crystal and magnetic structures.
- New formulation for rigid bodies: Z-matrices (only partially implemented at present)

Refinement of multiple data sets...

```
COMM  MultiPattern: PbSO4 D1A(ILL) + RX
NPATT      2
W_PAT   0.500 0.500
!Nph Dum Ias Nre Cry Opt Aut
   1   0   0   0   0   1   1
!Job Npr Nba Nex Nsc Nor Iwg Ilo Res Ste Uni Cor Asym
   1   7   0   2   0   0   0   0   0   0   0   0   0
   0   5   0   2   0   0   0   0   0   0   0   0   0
!File names of data(patterns) files
pbso4
pbsox
!
!Mat Pcr Syo Rpa Sym Sho
   0   2   0   0   0   0
!Ipr Ppl Ioc Ls1 Ls2 Ls3 Prf Ins Hkl Fou Ana
   0   0   1   0   0   0   1   6   1   1   0
   0   0   1   0   0   0   1   0   1   1   0
!
! lambda1 Lambda2    Ratio   Bkpos    Wdt    Cthm     muR   AsyLim   Rpolarz ->Patt1
 1.913615 1.913615  1.0000 70.0000  6.0000  0.0000  0.0000  160.00    0.0000
!
! lambda1 Lambda2    Ratio   Bkpos    Wdt    Cthm     muR   AsyLim   Rpolarz ->Patt2
 1.540500 1.544400  0.5000 50.0000  6.0000  0.8000  0.0000  160.00    0.0000
!
```



```
!NCY  Eps  R_at  R_an  R_pr  R_gl
  3  0.10  1.00  1.00  1.00  1.00
!     Thmin      Step      Thmax    PSD    Sent0  -> Patt#: 1
    10.0000    0.0500   155.4500   0.000   0.000
!     Thmin      Step      Thmax    PSD    Sent0  -> Patt#: 2
    10.0000    0.0250   160.0000   0.000   0.000
! Excluded regions (LowT  HighT) for Pattern#  1
       0.00      10.00
     154.00     180.00
! Excluded regions (LowT  HighT) for Pattern#  2
       0.00      10.00
     154.00     180.00
!
     50    !Number of refined parameters
!
!  Zero    Code    Sycos    Code   Sysin    Code  Lambda     Code MORE ->Patt# 1
-0.0864   81.00  0.0000    0.00  0.0000    0.00 1.913615  161.00    0
!   Background coefficients/codes  for Pattern#  1
  207.53      40.752      45.464      -26.893      -42.644      14.787
    501.000     31.000      41.000      51.000      61.000      71.000
!
!  Zero    Code    Sycos    Code   Sysin    Code  Lambda     Code MORE ->Patt# 2
  0.0062   91.00  0.0000    0.00  0.0000    0.00 0.000000    0.00   0
!   Background coefficients/codes  for Pattern#  2
  128.66      35.422     -65.957     -23.530      88.944     -29.782
    101.000     111.000     121.000     131.000     141.000     151.000
```



```
!-------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:     4.23
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  2:     4.79
!-------------------------------------------------------------------------------
 PbSO4
!Nat Dis Mom Jbt Isy Str Furth      ATZ    Nvk More
   5   0   0   0   0   0   0     0.0000    0   1
!Jvi Jdi Hel Sol Mom Ter
   0   3   0   0   0   0
!Contributions (0/1) of this phase to the  2 patterns
 1 1
!Irf Npr Jtyp  for Pattern#  1
   0   7   1
! Pr1    Pr2    Pr3   Brind.   Rmua   Rmub   Rmuc     for Pattern#  1
  0.000  0.000  1.000  1.000  0.000  0.000  0.000
!Irf Npr Jtyp  for Pattern#  2
   0   5   0
! Pr1    Pr2    Pr3   Brind.   Rmua   Rmub   Rmuc     for Pattern#  2
  0.000  0.000  1.000  1.000  0.000  0.000  0.000
!
! Max_dst(dist) (angles)  Bond-Valence Calc.
      3.5000      0.0000        BVS
!  N_cations   N_anions      Tolerance(%) / Name or cations/ and Anions
       2           1                0.00
PB+2 S+6
O-2
P n m a                  <--Space group symbol
```



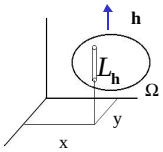
```
!Atom Typ       X         Y         Z      Biso      Occ     In Fin N_t Poi /Codes
Pb   PB      0.18771   0.25000   0.16728  1.37185  0.50000   0   0   0     1
               171.00      0.00    181.00    281.00      0.00
S    S       0.06516   0.25000   0.68359  0.49027  0.50000   0   0   0     2
               191.00      0.00    201.00    291.00      0.00
O1   O       0.90771   0.25000   0.59525  1.94953  0.50000   0   0   0     3
               211.00      0.00    221.00    301.00      0.00
O2   O       0.19359   0.25000   0.54312  1.44874  0.50000   0   0   0     3
               231.00      0.00    241.00    311.00      0.00
O3   O       0.08099   0.02719   0.80898  1.29124  1.00000   0   0   0     3
               251.00    261.00    271.00    321.00      0.00
!-------> Profile Parameters for Pattern #  1
!  Scale       Shape1      Bov      Str1      Str2      Str3    Strain-Model
  1.4742       0.0000   0.0000   0.0000   0.0000   0.0000       0
    11.00000      0.00      0.00      0.00      0.00      0.00
!       U         V         W         X         Y       GauSiz   LorSiz Size-Model
   0.15742  -0.46171   0.41993   0.00000   0.09353   0.00000   0.00000   0
    381.00    391.00    401.00      0.00    411.00      0.00      0.00
!      a         b         c        alpha      beta       gamma
   8.485911   5.401731   6.964305  90.000000  90.000000  90.000000
 351.00000  361.00000  371.00000    0.00000    0.00000    0.00000
!  Pref1  Pref2    Asy1     Asy2     Asy3     Asy4
 0.00000 0.00000 0.36082 0.03665-0.30050 0.00000
    0.00    0.00  421.00  431.00  441.00    0.00
!-------> Profile Parameters for Pattern #  2
!  Scale       Shape1      Bov      Str1      Str2      Str3    Strain-Model
 0.47250E-03   0.0000   0.0000   0.0000   0.0000   0.0000       0
    21.00000      0.00      0.00      0.00      0.00      0.00
```


Microstructural effects
Anisotropic peak broadening

Anisotropic broadening due to size effects

Scherrer formula: $b_{\mathbf{h}} = \dfrac{l}{D_{\mathbf{h}} \cos q}$

$$D_{\mathbf{h}} = \frac{1}{V} \iiint_{\Omega} L_{\mathbf{h}}(x, y)\, d^3\mathbf{r}$$



$D_{\mathbf{h}}$: **volume average of column lengths along h=(*hkl*) for all crystallites in the sample**

Microstructural effects are simulated in the Rietveld Method using the Voigt approximation (Langford & Louër).

Special expressions for anisotropic broadening due to size effects:

- **Infinite needles**
- **Infinite platelets**
- **Finite cylinders**

Spherical harmonics to simulate the average form of crystallites

$$\frac{1}{D_{\mathbf{h}}} = \sum_{lmp} a_{lmp} P_{lm}\left(\cos\Theta_{\mathbf{h}}\right) \begin{Bmatrix} \cos m\Phi_{\mathbf{h}} \\ \sin m\Phi_{\mathbf{h}} \end{Bmatrix}; \quad p = +/-$$

$\left(\Theta_{\mathbf{h}}, \Phi_{\mathbf{h}}\right)$: Polar angles of reciprocal vector **h** w.r.t. crystal frame

$$FWHM = \frac{k\,l}{\cos q} \sum_{lmp} a_{lmp} P_{lm}\left(\cos\Theta_{\mathbf{h}}\right) \begin{Bmatrix} \cos m\Phi_{\mathbf{h}} \\ \sin m\Phi_{\mathbf{h}} \end{Bmatrix}$$

Anisotropic strain broadening

Phenomenological model: strains considered as fluctuations and correlation between metric parameters
J. Rodríguez-Carvajal *et al* (J. Phys. Cond. Matt. **3**, 3215 (1991)

$$M_{hkl} = \frac{1}{d_{hkl}^2} = M\left(a_i; hkl\right)$$

The metric parameters a_i (direct, reciprocal or any combination) are considered as stochastic variables with a Gaussian distribution characterized by :

- the mean $\langle a_i \rangle$ and
- the variance-covariance matrix C_{ij}

The mean and the variance of the function M_{hkl} are given by (JRC *et al* , J. Phys. Cond. Matt. **3**, 3215 (1991) **):**

$$\langle M_{hkl} \rangle = M\left(\langle a_i \rangle; hkl\right)$$

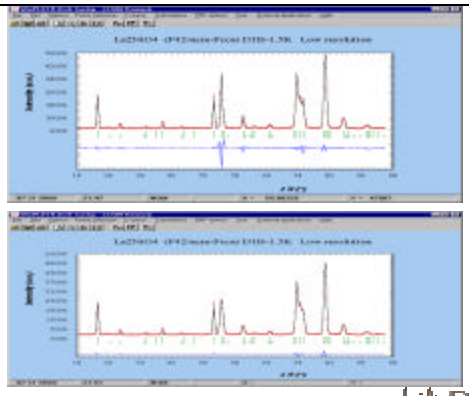
$$s^2\left(M_{hkl}\right) = \sum_{i,j} C_{ij} \frac{\partial M}{\partial a_i} \frac{\partial M}{\partial a_j}$$

C_{ij} contains 21 parameters, 15 independent

If the metric parameters are taken as the coefficients of the quadratic form: $\frac{1}{d_{hkl}^2} = Ah^2 + Bk^2 + Cl^2 + Dkl + Ehl + Fhk$ $\{a_i\} = \{A,B,C,D,E,F\}$

$$s^2\left(M_{hkl}\right) = \sum_{\substack{HKL \\ \{H+K+L=4\}}} S_{HKL} h^H k^K l^L$$

P. W. Stephens, J. Appl. Cryst. 32, 281 (1999)



Simulated Annealing ….

Classically, crystal structure determination is considered as a process to determine the "phases" of the structure factors

$$r(\mathbf{r}) = \sum_{\{\mathbf{h}\}} F_{\mathbf{h}}\, exp\{-2p\; i\mathbf{hr}\}$$

$$r(\mathbf{r}) = \sum_{\{\mathbf{h}\}} |F_{\mathbf{h}}|\, exp\{-2p\; i(\mathbf{hr} + \Phi_{\mathbf{h}})\}$$

For a centrosymmetric structure $\Phi_{\mathbf{h}}$ is 0 or 1/2

The knowledge of all phases for the measured structure factors provides a density map from which the structure is derived (chemically recognised).

The resolution of the "phase problem" is the goal of the crystal structure determination methods

Direct Methods tackle the problem looking for phase relations (tangent formula) between structure factors of different reflections

Direct methods need a high number of reflections and good resolution (powders)

Direct methods are generally very efficient

But …
sometimes direct methods fail in solving particular structures
or
cannot be applied because poor data quality (low resolution)

Structure factor calculation

$$F(\mathbf{h}) = \sum_{j=1}^{n} O_j\, f_j(\mathbf{h})\, T_j \sum_{s} exp\,\{2p\; i[\mathbf{h}\{S|\mathbf{t}\}_s \mathbf{r}_j]\}$$

If the chemical composition and the space group are known we have to determine just the 3n variables

$$F_{obs}(\mathbf{h})_r \approx \left| \sum_{j=1}^{n} O_j\, f_j\, T_j \sum_{s} exp\,\{2p\; i[\mathbf{h}\{S|\mathbf{t}\}_s \mathbf{r}_j]\} \right|_r$$

$$\mathbf{h}_r = (h, k, l)_r \quad (r = 1, 2, \ldots N)$$

$$\mathbf{r}_j = (x_j, y_j, z_j) \quad (j = 1, 2, \ldots n)$$

Direct space methods:

- **Look directly for atom positions explaining the experimental data**
- **Minimize a reliability factor with respect to the "configuration vector" or "chromosome"**

$$| \qquad \rangle$$

$$R(v) = c \sum^{N} \left| F^2_{obs}(\mathbf{h}_r) - F^2_{calc}(\mathbf{h}_r, v) \right|$$

Solving Crystal structures by Powder diffraction and direct space methods

(1) *Indexing the powder diffraction pattern:* ***DICVOL, TREOR, ITO,…*** (**WinPLOTR**)

(2) *Extracting integrated intensities* ***(FullProf)*** Space Group determination

(3) Use ***ExPo*** to solve the structure

(4) If ***ExPo*** fails then Use Simulated Annealing ***(FullProf)*** or Genetic Algorithms

Simulated Annealing (SA):

The SA method is a general purpose optimization technique for large combinatorial problems introduced by:

Kirpatrick, Gelatt and Vecchi, *Science* **220**, 671-680 (1983).

The function, E($\mathbf{w}$) to be optimized with respect to the configuration described by the vector state $\mathbf{w}$ is called the "cost" function.

Simulated Annealing (SA):

The SA method applied to structural problems:

- J. Pannetier, J. Bassas-Alsina, J. Rodríguez-Carvajal and V. Caignaert, *Nature* **346**, 343-345 (1990)
- J.M. Newsam, M.W. Deem and C.M. Freeman, Accuracy in Powder Diffraction II. NIST Special Publ. No. **846**, 80-91 (1992)
- J. Rodríguez-Carvajal, Physica B **192**, 55-69 (1993)

The Simulated Annealing Algorithm

begin
  Initialise (set to zero useful quantities, do preliminary calculations)
  $\tau = 1$
  do
    do
      Perturb the system:
      $\mathbf{w}_{old} \rightarrow \mathbf{w}_{new}$, $\Delta = E(\mathbf{w}_{new}) - E(\mathbf{w}_{old})$
      if $\Delta \leq 0$ then **accept**, else
      if $\exp(-\Delta/T_\tau) >$ random[0,1] then **accept**
      if **accept** then **Update** (replace $\mathbf{w}_{old}$ by $\mathbf{w}_{new}$)
    until equilibrium is approached closely enough (Ncyc)
    $T_{\tau+1} = f(T_\tau)$ (decrease temperature, usually $T_{\tau+1} = q\, T_\tau$, q≈0.9)
    $\tau = \tau + 1$
  until stop criterion is true (maximum τ, convergence, low % accepted...)
end


```
COMM Ab initio structure solution of PbSO4 (Simulated Annealing, data D1A-ILL)
! Files => DAT-file: pb_san,   PCR-file: pb_san
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
   1   0   1   0   0   0   0   0   0   0   0   0   0  12   3   0   0   0   0
!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 Syo Prf Ins Rpa Sym Hkl Fou Sho Ana
   0   0   1   0   1   0   0   0   0   1   0   0   0   0   0   0   0
!
!NCY  Eps  R_at  R_an  R_pr  R_gl     Thmin       Step       Thmax     PSD    Sent0
  1  0.10  1.00  1.00  1.00  1.00     15.0000     0.0200   120.0400   0.000   0.000
!
   12    !Number of refined parameters
!-------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:      7.86
!-------------------------------------------------------------------------------
 PbSO4
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth      ATZ    Nvk Npr More
   5   0   0 0.0 0.0 1.0   0   4   0   0   0         0.00   0   7   0
!
P n m a                  <--Space group symbol
!Atom Typ       X         Y         Z      Biso       Occ     In Fin N_t Poi /Codes
Pb   PB      0.81174  0.23348  0.83479  1.42124  0.50000   0   0   0   0
               11.00    21.00    31.00     0.00     0.00
S    S       0.93358  0.23348  0.32454  0.41603  0.50000   0   0   0   0
 . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .
```



```
!  Sc1       Sc2       Sc3       Sc4       Sc5       Sc6
  1.531     0.000     0.000     0.000     0.000     0.000
    0.00      0.00      0.00      0.00      0.00      0.00
!     a         b         c        alpha      beta       gamma
   8.485130   5.402066   6.964059  90.000000  90.000000  90.000000
   0.00000    0.00000    0.00000   0.00000    0.00000    0.00000
! Limits for selected parameters (+ steps & BoundCond for SA):
   1       0.0000       1.0000       0.0500   1       x_Pb
   2       0.0000       1.0000       0.0500   1     y_Pb_SO1
   3       0.0000       1.0000       0.0500   1       z_Pb
   4       0.0000       1.0000       0.0500   1        x_S
   5       0.0000       1.0000       0.0500   1        z_S
   6       0.0000       1.0000       0.0500   1       x_O1
   7       0.0000       1.0000       0.0500   1       z_O1
   8       0.0000       1.0000       0.0500   1       x_O2
   9       0.0000       1.0000       0.0500   1       z_O2
  10       0.0000       1.0000       0.0500   1       x_O3
  11       0.0000       1.0000       0.0500   1       y_O3
  12       0.0000       1.0000       0.0500   1       z_O3
! T_ini    Anneal   Accept NumTemps NumThCyc InitConf
   8.000    0.900    0.008       60        0        0
! NCyclM    Nsolu Num_Ref Nscalef   Algor
     150        1      71       1       2
```