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Hidden complexity in D_2O Ice VII

Wojciech A. Slawinski
wslawinski@chem.uw.edu.pl

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Contributors

Wojciech A. Sławiński
Krzysztof Woźniak
Roman Gajda
Michał Chodkiewicz
Piotr Rejnhardt
Mihails Arhangelskis

Grzegorz Łach

Craig L. Bull

Christopher J. Ridley

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Foundation for Polish Science

- TEAM TECH Core Facility for Crystallographic and Biophysical Research

ISIS Neutron and Muon Source, STFC

- ISIS Beamtime Allocation: RB2310212

Interdisciplinary Centre for Mathematical and Computational Modelling University of Warsaw

- computational allocation no G97-1992

Outline

Introduction

- water molecule in gas phase
- water molecule in liquid state
- solid form of water
  - ✓ phase diagram
  - ✓ ordered / disordered phase of ice
  - ✓ metastable forms

Outline

Disordered ICE VII

- average structure
- neutron experiment at ISIS Neutron and Muon Source UK
- *big box modeling* in RMCProfile7

Results

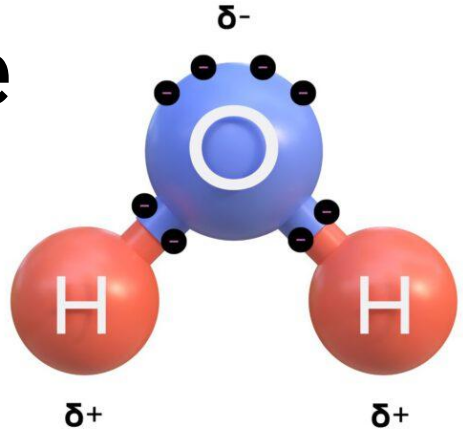
- How does the local structure differes form the average?
- What about molecule geometry in solid?

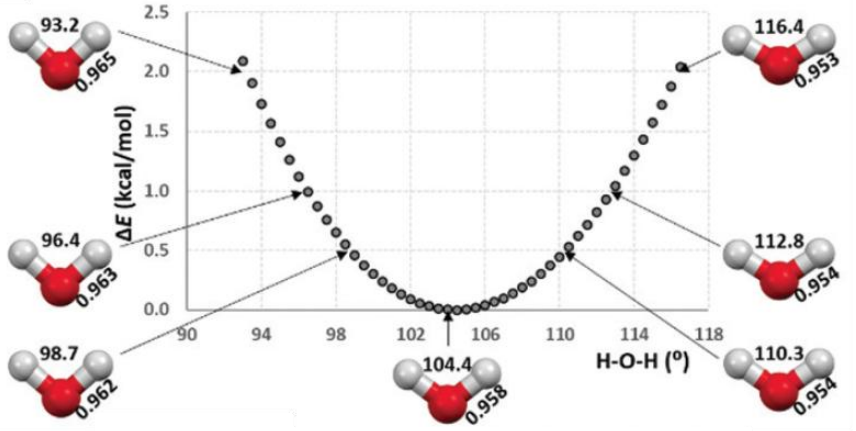
Conclussions

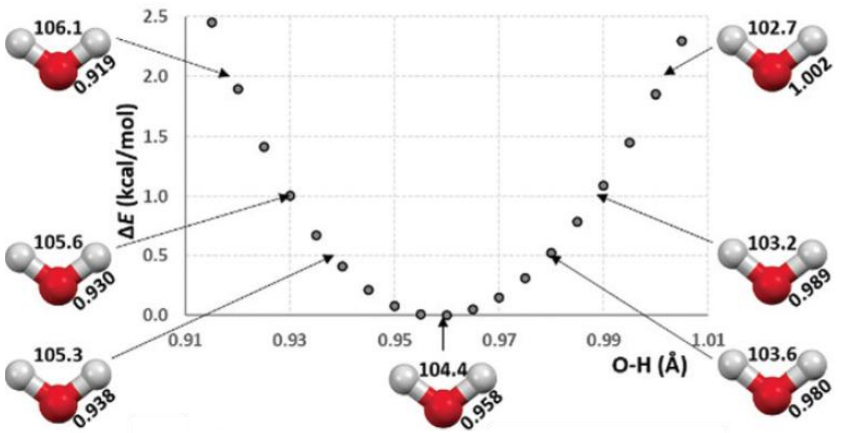
Some more details about *RMCProfile7* modelling

H_2O molecule in gas phase

$d_{O\text{-}H}$ = 0.958 Å
$\alpha_{H\text{-}O\text{-}H}$ = 104.4°





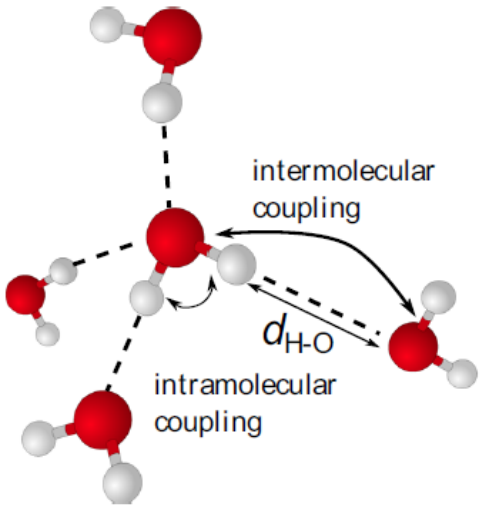


Results of Energy calculations in CCSD(T)/aug-cc-PV6Z potential in Gaussian package

[figs from M. R. Milovanović, J.M. Živković, D.B. Ninković, I.M. Stanković, S.D. Zaric, Phys.Chem.Chem.Phys., 2020, 22, 4138]
[molecule figure from https://www.centralgalaxy.com/what-makes-water-so-special/]

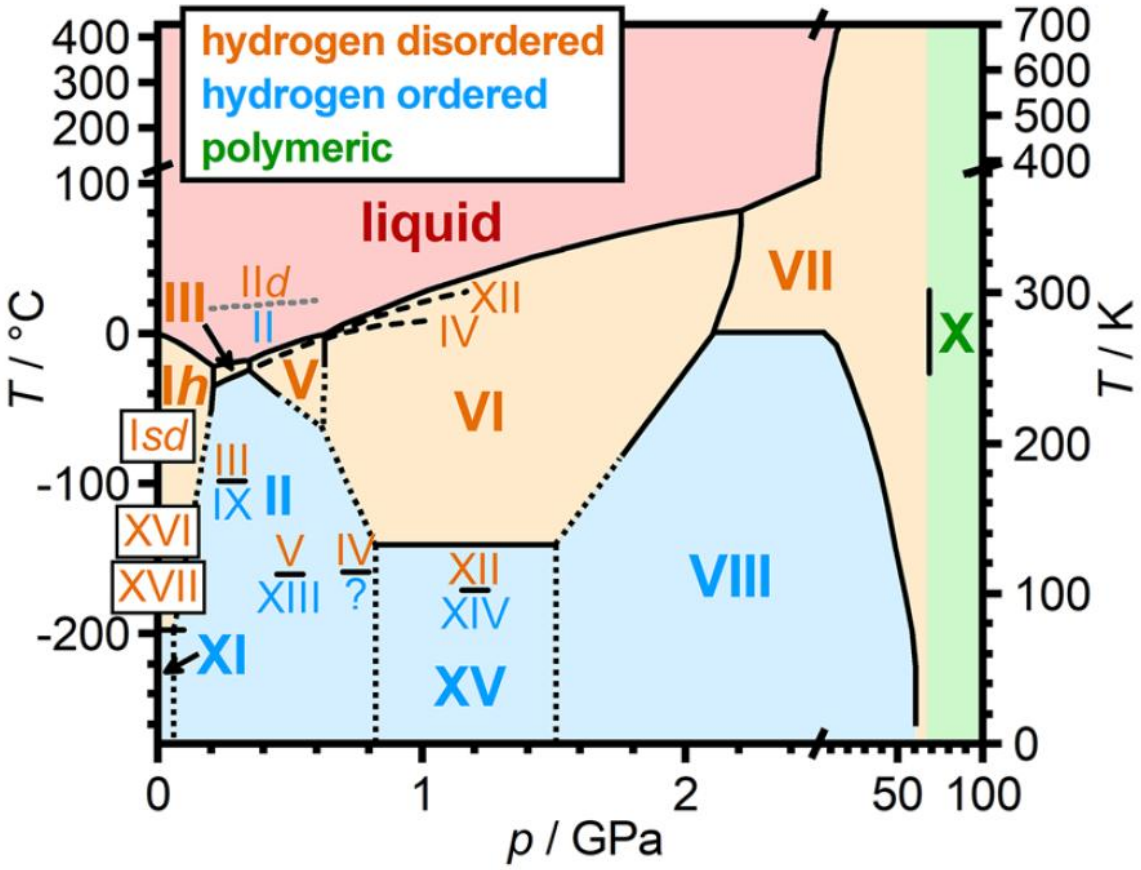
H_2O molecule in liquid phase

- In liqid water H-O-H angle increases to 106.1 ± 1.8° and O-H distance is 0.960 ± 0.005 Å [1]
- H_2O molecules also fom tetrahedral geometry due to extra electron pairs on oxygen [2]
- H_2O molecules in liquid and solid follow *„ice rules”*



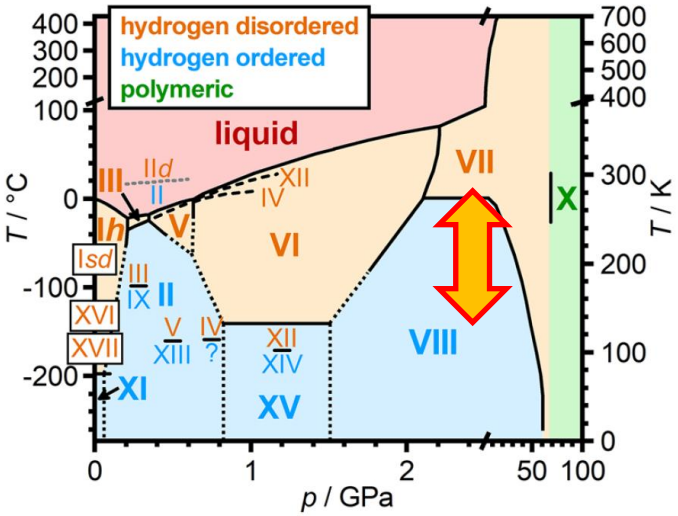
[1] from K. Ichikawa, Y. Kameda, T. Yamaguchi, H. Wakita and M. Misawa, Mol. Phys., 1991, 73, 79
[fig from 2] L. Gunkel, A.A. Ehrhard, C.S. Krevert, B.A. Marekha, M. Bonn, M. Grechko, J. Hunger, Nature Communications, 2024, 1, 5:10453

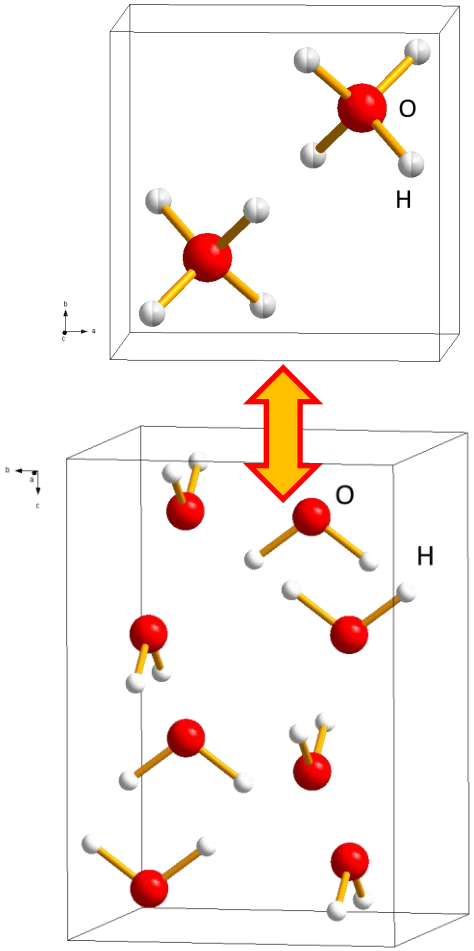
H_2O in solid phase = ice



[fig from] C.G. Salzmann, J. Chem. Phys. 150, 060901 (2019)

H_2O in solid phase = ice



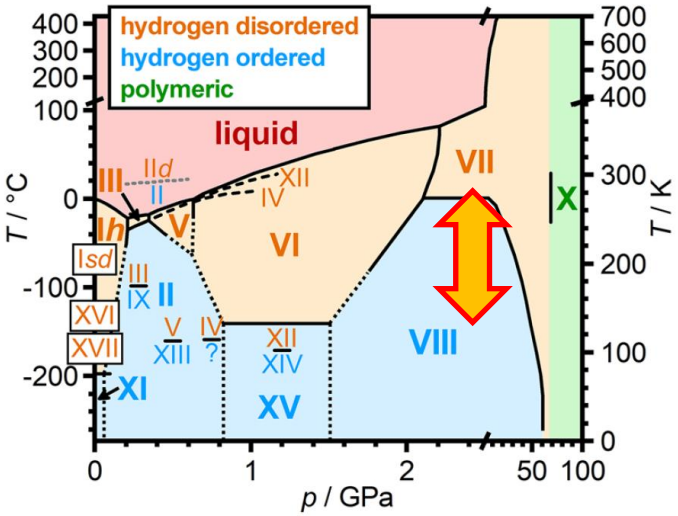


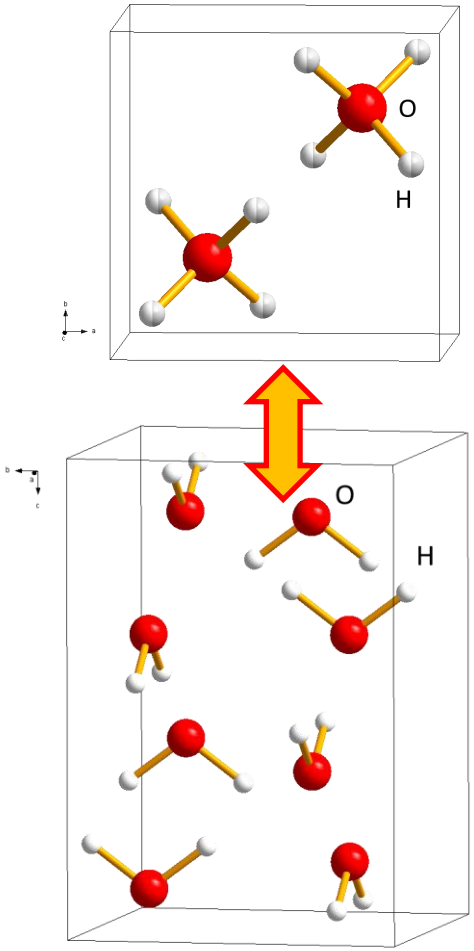
disordered ice VII

ordered ice VIII

[fig from] C.G. Salzmann, J. Chem. Phys. 150, 060901 (2019)

H_2O in solid phase = ice





disordered ice VII

ordered ice VIII

- some crystal forms are metastable
- differen experimental rutes show different phases

[fig from] C.G. Salzmann, J. Chem. Phys. 150, 060901 (2019)

Ice VII structure by HAR (Hirshfeld Atom Refinement)

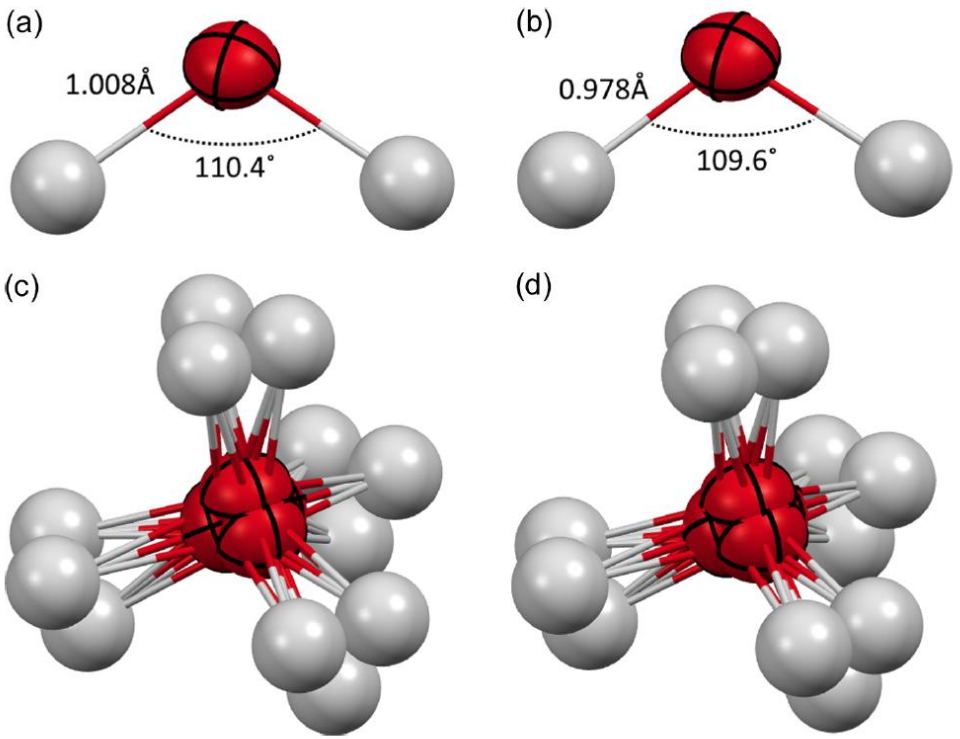
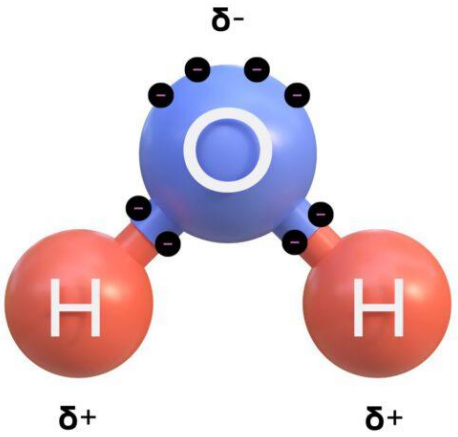


Figure 4
Structures refined with the oxygen atom split in the ⟨111⟩ family of directions. (*a*, *b*) Geometries of selected configurations of the water molecule. (*c*, *d*) Disordered water molecule. Refinements for (*a*) and (*c*) H_2O; (*b*) and (*d*) D_2O.

[fig from] R. Gajda, M. Chodkiewicz, D. Zhang, P. Nguyen, V. Prakapenka, K. Wozniak, IUCRJ, 12(3) (2025) 288-294

H_2O molecule in different Ice phases

Ice	Bond angle[a] (°)	Bond length[a] (Å)
I_h[3]	109.34–109.57	0.999–1.001
Ice 2[4]	82.40–99.88	1.007–1.023
Ice 3[5]	74.00–132.00	0.915–0.958
Ice 4[6]	89.69–118.32	0.840–1.079
Ice 5[7]	82.33–126.09	0.984–1.063
Ice 6[8]	97.97–115.51	0.937–0.986
Ice 7[9]	109.42	0.943
Ice 8[10]	106.80	0.973
Ice 9[11]	97.86	0.915–0.958
Ice 10[12]	109.48	1.180
Ice 11[13]	109.42–109.45	0.961
Ice 12[14]	100.70–119.20	0.917–0.988
Ice 13[15]	100.25–109.31	0.938–1.004
Ice 14[15]	98.29–108.49	1.001–1.083
Ice 15[16]	94.21–107.62	0.887–1.115
Ice 16[17]	106.57	0.993
Ice 17[18]	108.60–113.10	1.006–1.023



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[molecule figure from https://www.centralgalaxy.com/what-makes-water-so-special/]

Results obtained from neutron PDF

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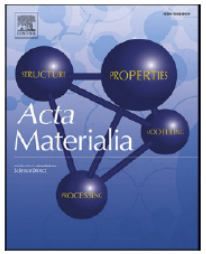
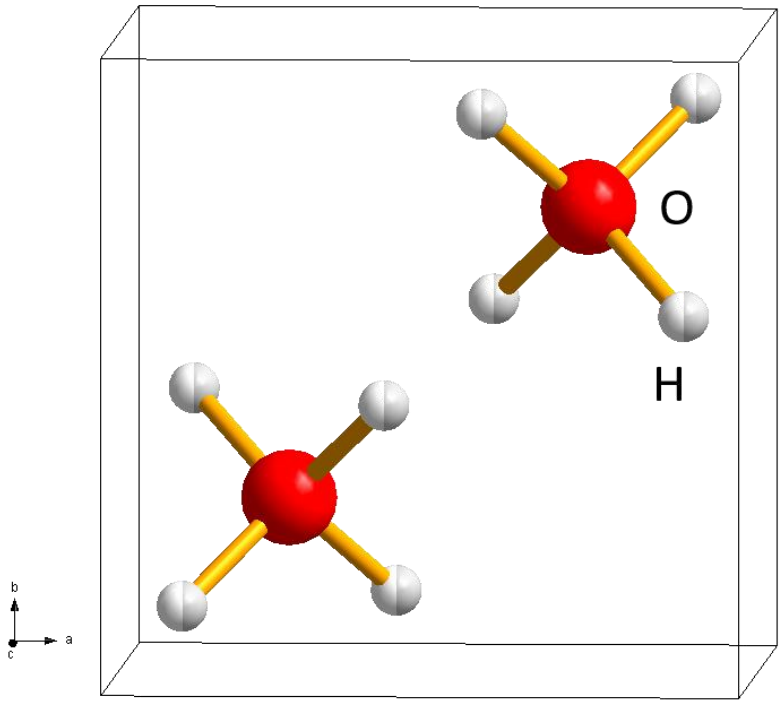


Hidden complexity in D_2O Ice VII

Wojciech A. Sławiński [a,*], Grzegorz Łach [b], Roman Gajda [a], Michał Chodkiewicz [a], Piotr Rejnhardt [a], Mihails Arhangelskis [a], Christopher L. Ridley [c,e], Craig L. Bull [c,d], Krzysztof Woźniak [a,*]

[a] *Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warszawa, Poland*
[b] *Faculty of Physics, University of Warsaw, Pasteura 5, 02-093 Warszawa, Poland*
[c] *STFC, Rutherford Appleton Laboratory, ISIS Neutron and Muon Source, Harwell Campus, Didcot, Oxfordshire, OX11 0QX, United Kingdom*
[d] *EaStCHEM School of Chemistry, University of Edinburgh, Joseph Black Building, Edinburgh EH9 3FJ, Scotland, United Kingdom*
[e] *Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA*

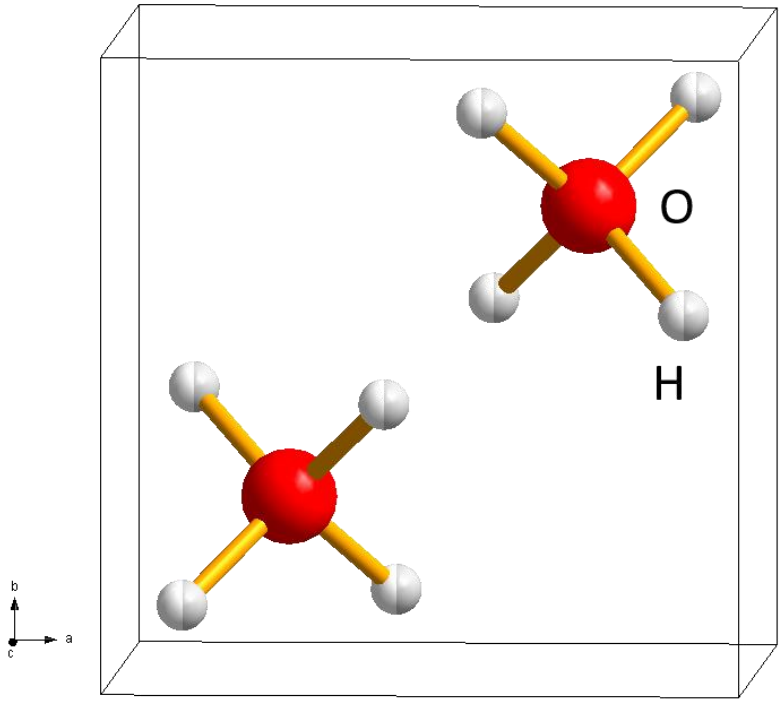
ice VII average crystal structure



spacegroup Pn-3m
a = 3.3738 Å

O at (¼ ¼ ¼) occ = 1.0
H at (0.40834 0.40834 0.40834) occ = 0.5

ice VII average crystal structure and possible moleucle displacements



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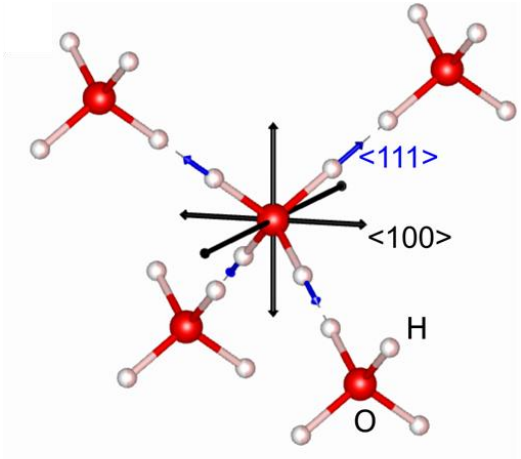

right fig. from K. Yamashitaa, K. Komatsua, S. Klotz, O. Fabelo, M.T. Fernandez-Diaz, J. Abed, S. Machidad, I. Hattorie, I. Irifune, I. Shinmeif, K. Sugiyama, I. Kawamata, H. Kagi, Proc. Natl. Acad. Sci. U. S. A. 119 (2022) e2208717119

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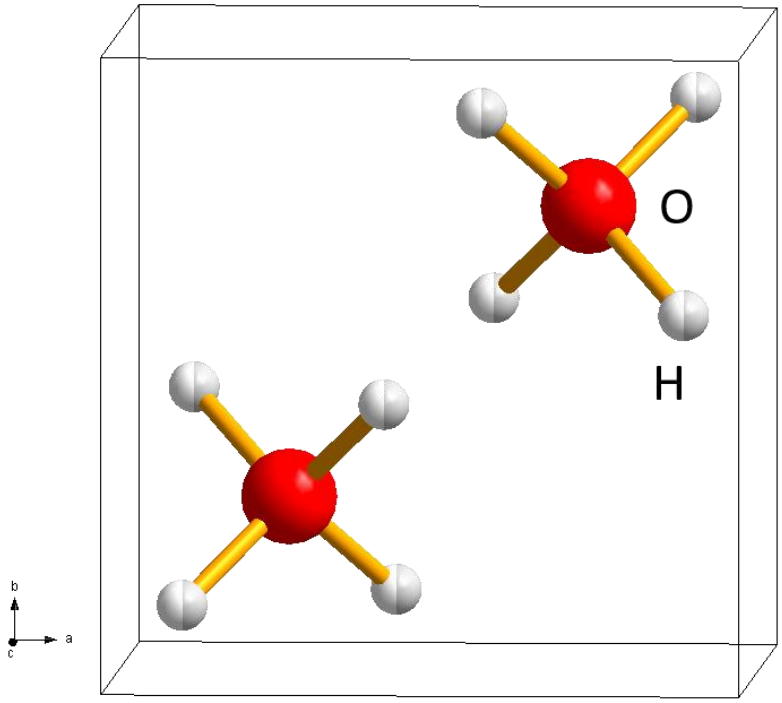

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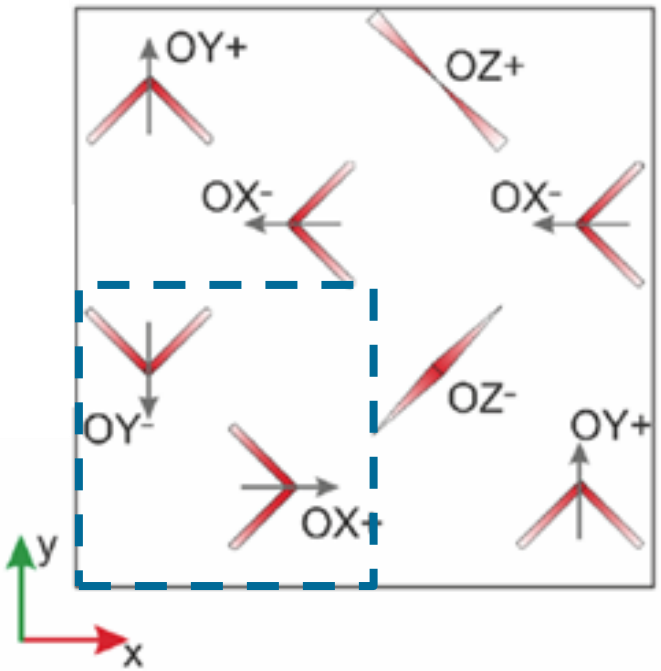
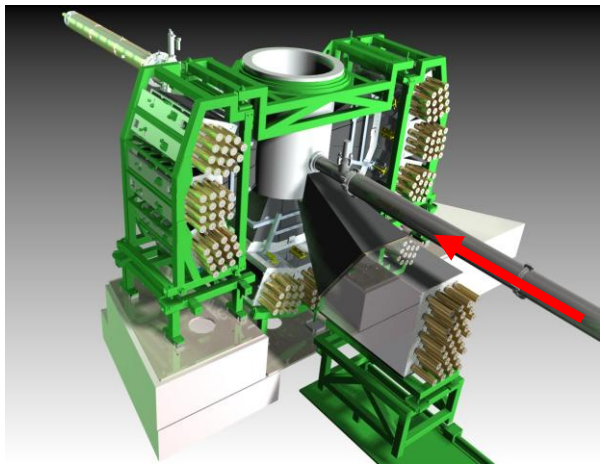


High Pressure experiment at ISIS neutron and muon source

Science and Technology Facilities Council | ISIS Neutron and Muon Source



- pure D_2O between two zirconia-toughend alumina anvils within a null scattering TiZr gascet and placed in a Paris-Edinburgh press
- maximum load was 40 tonnes
- measurement time was 23 h at 290 K at RT

The Paris-Edinburgh press

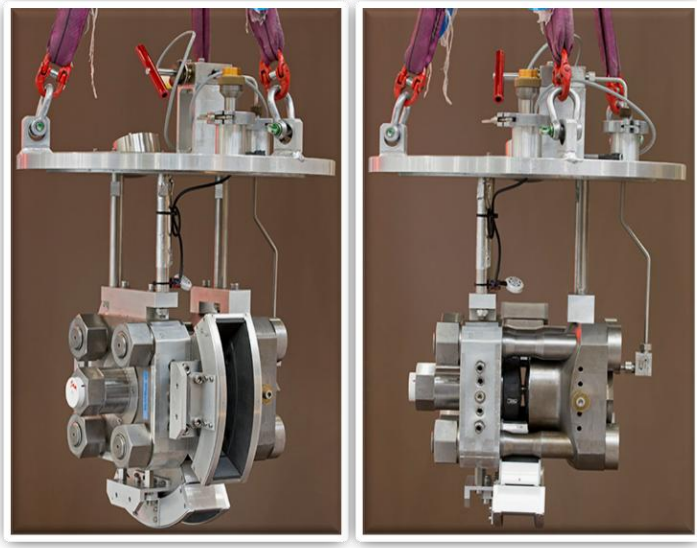


fig from https://www.isis.stfc.ac.uk/Pages/pearl.aspx

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High Pressure experiment at ISIS neutron and muon source

- In order to avoid Preffered Orientation and increase sample crystallinity the following route was used:

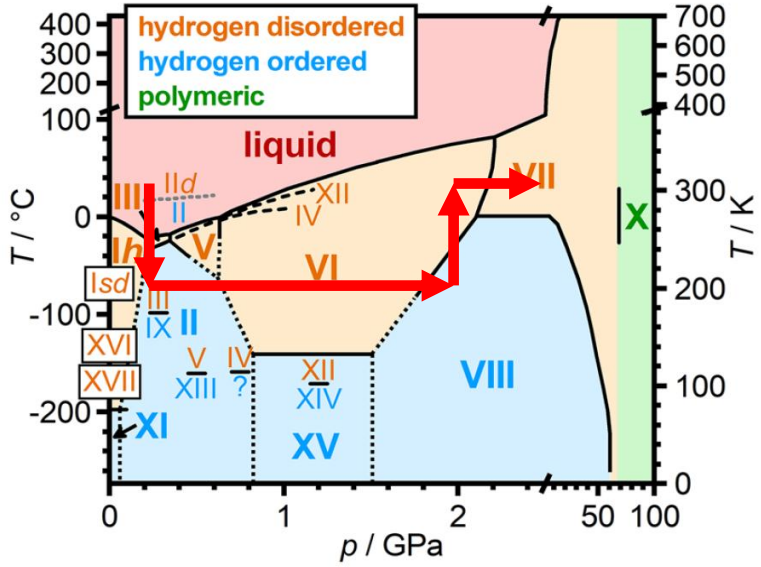
290 K, 3 tonns →

→ 200 K, 3 tonns →

→ 200 K, 32.5 tonns →

→ 290 K, 32.5 tonns →

→ 290 K, 37.5 tons



[fig from] C.G. Salzmann, J. Chem. Phys. 150, 060901 (2019)

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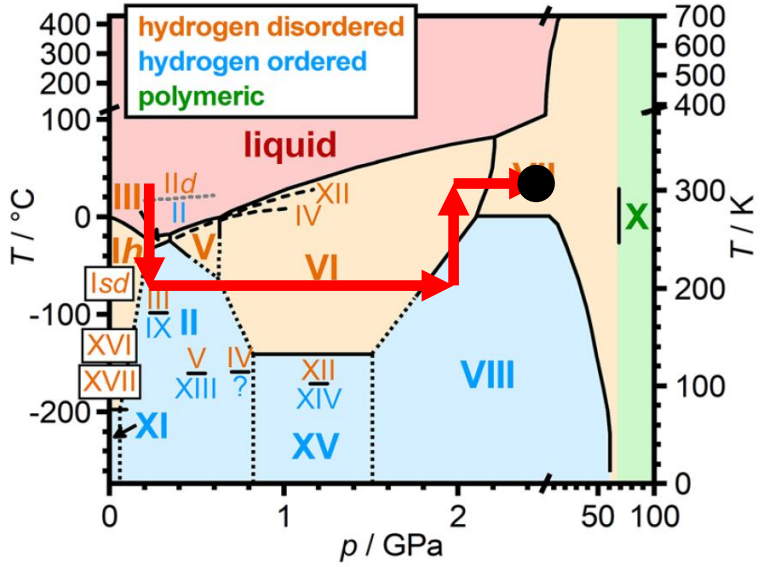

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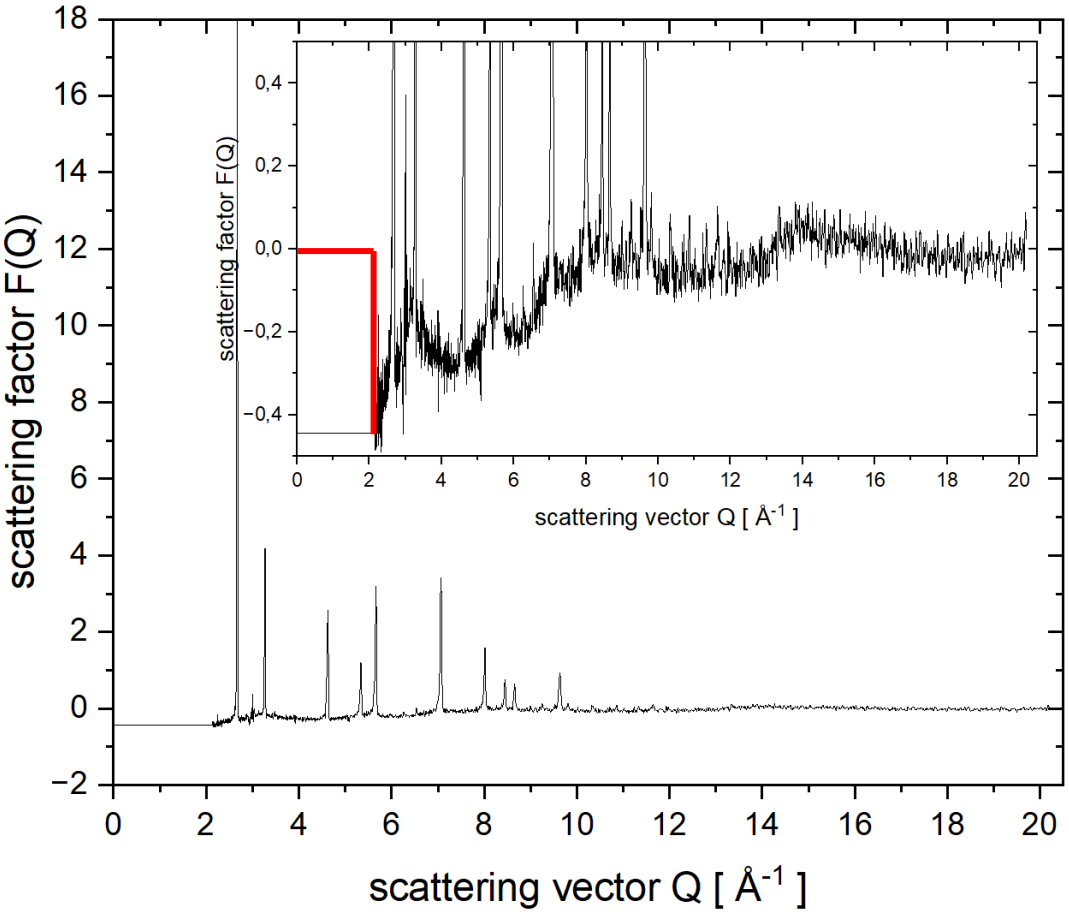


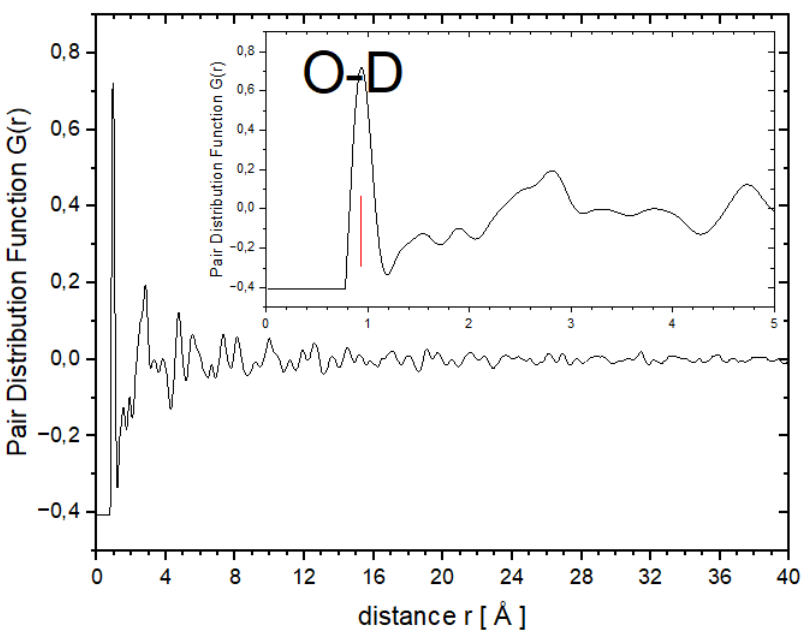
- Q_{MAX} = 20.5 Å^{-1}
- Q_{MIN} = 1.55 Å^{-1}

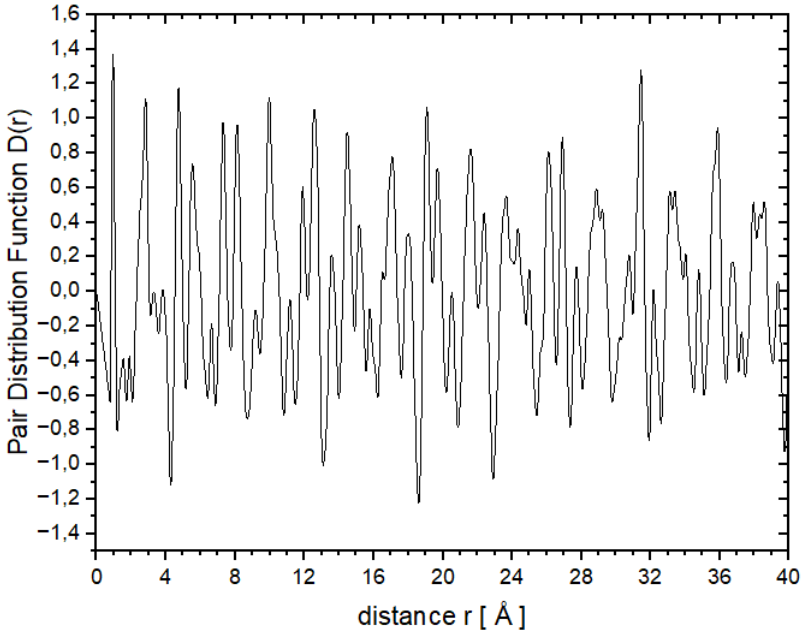
$$F(Q \to 0) = -\sum_{i=1}^{n} c_i \bar{b}_i^2 + \eta,$$

RMCProfile7 hint

see equations in D. Keen, J. Appl. Cryst. (2001). 34, 172

High Pressure experiment at ISIS neutron and muon source





see equations in D. Keen, J. Appl. Cryst. (2001). 34, 172

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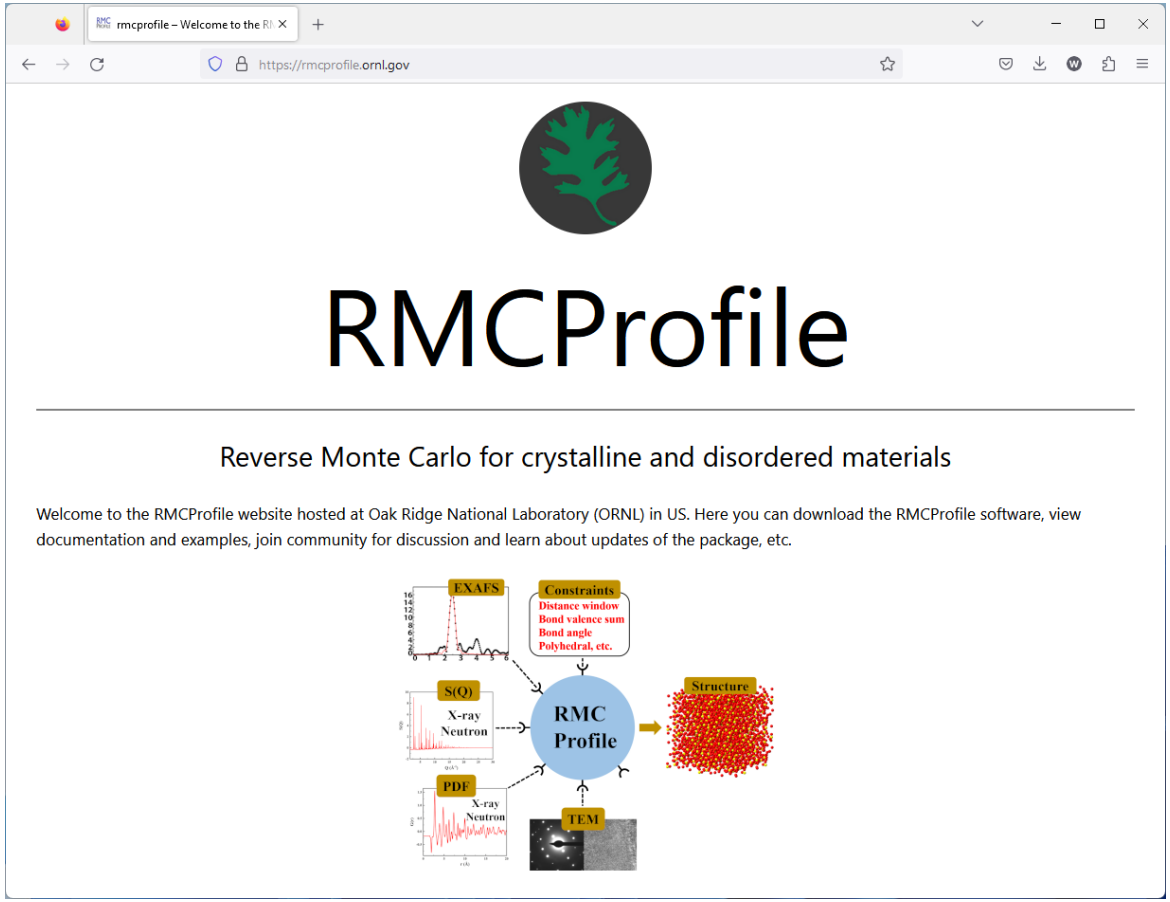
RMCProfile in brief



https://rmcprofile.ornl.gov/

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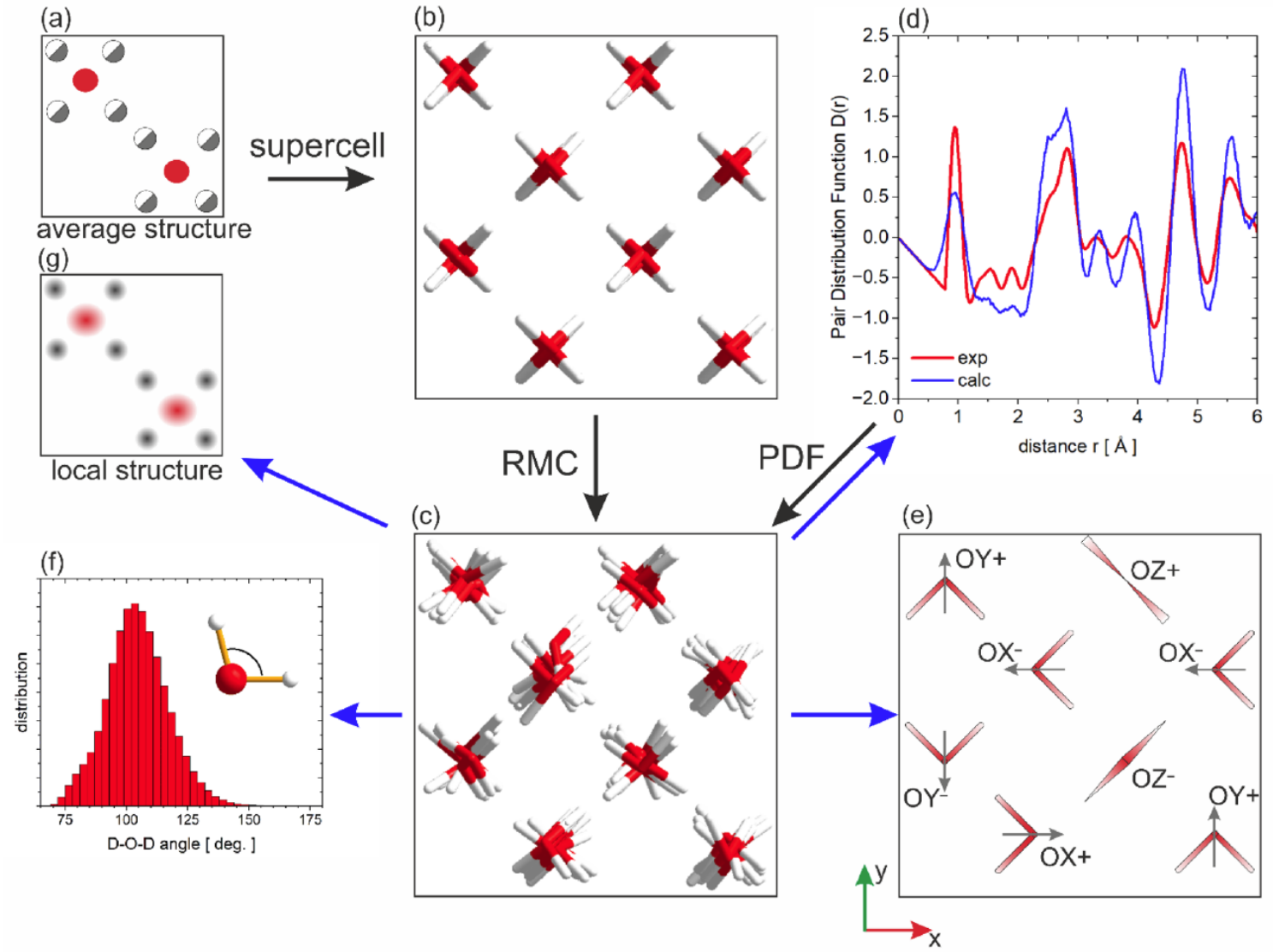
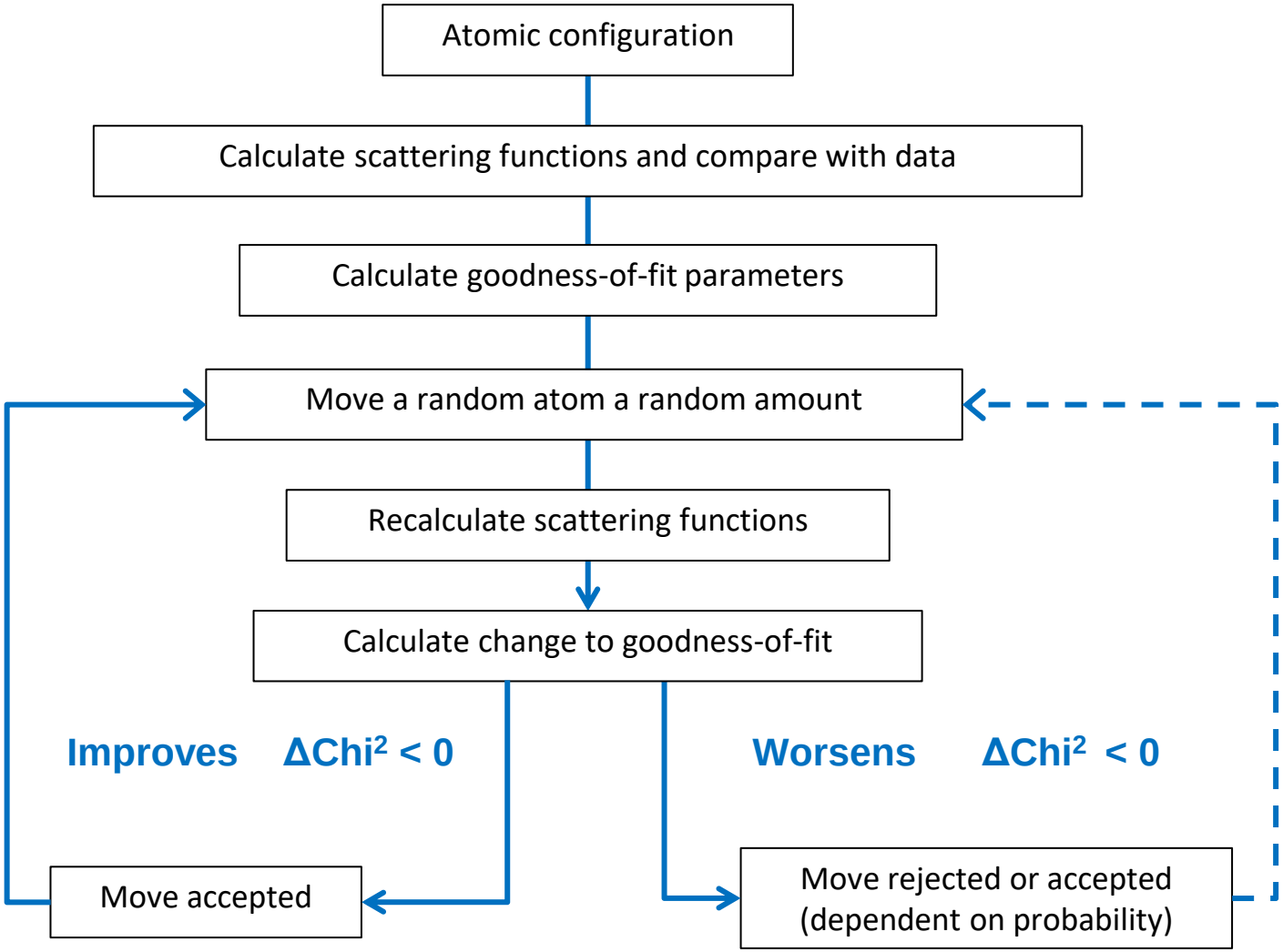
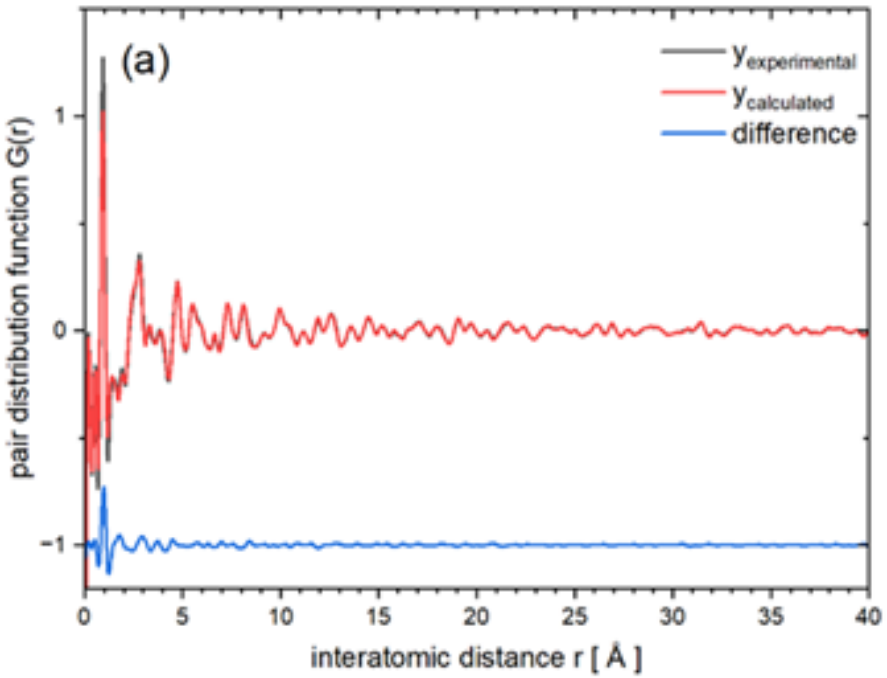
RMCProfile in brief

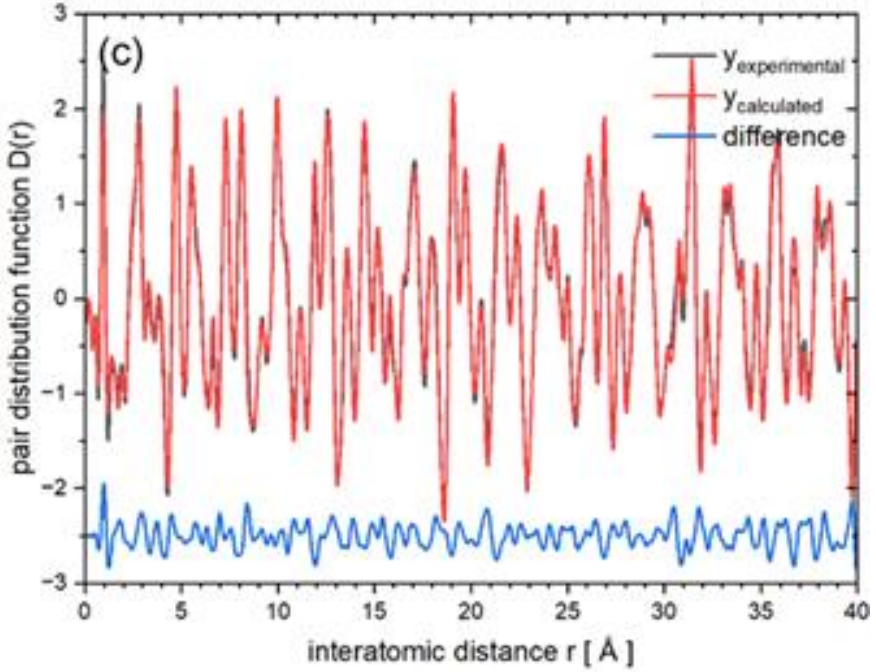


Reversed Monte Carlo in brief

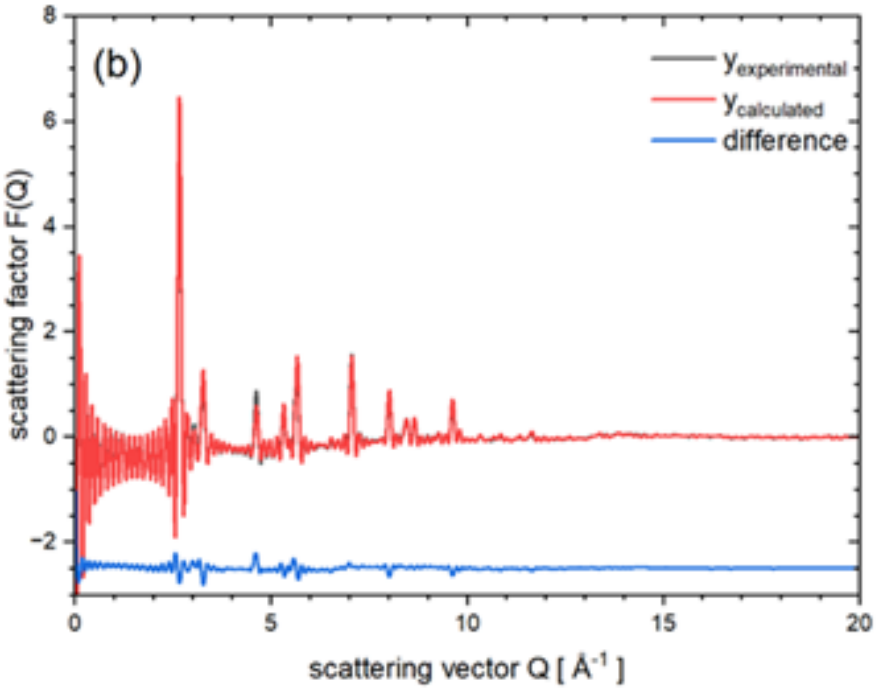


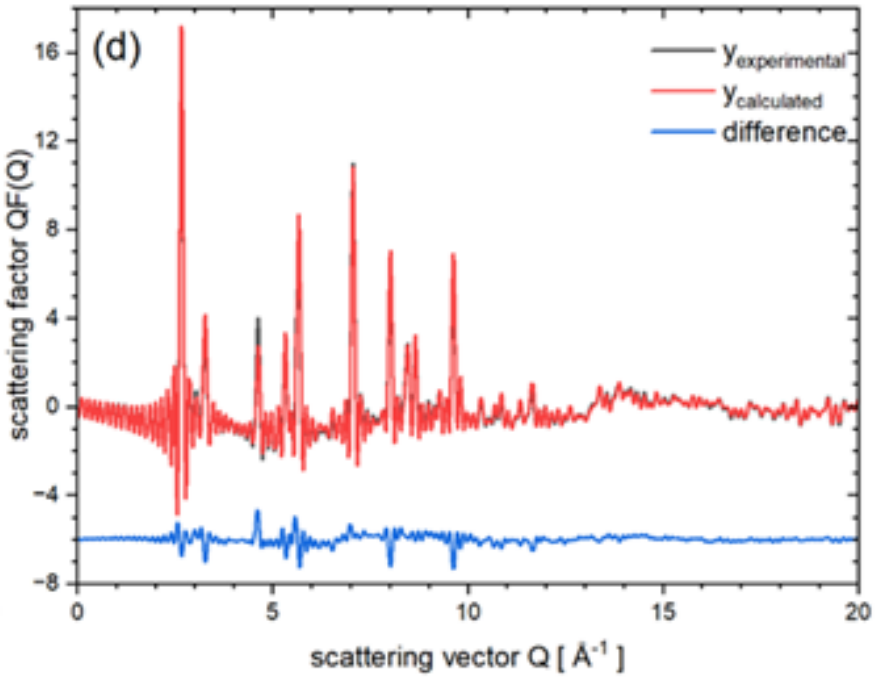
RMCProfile results





RMCProfile results





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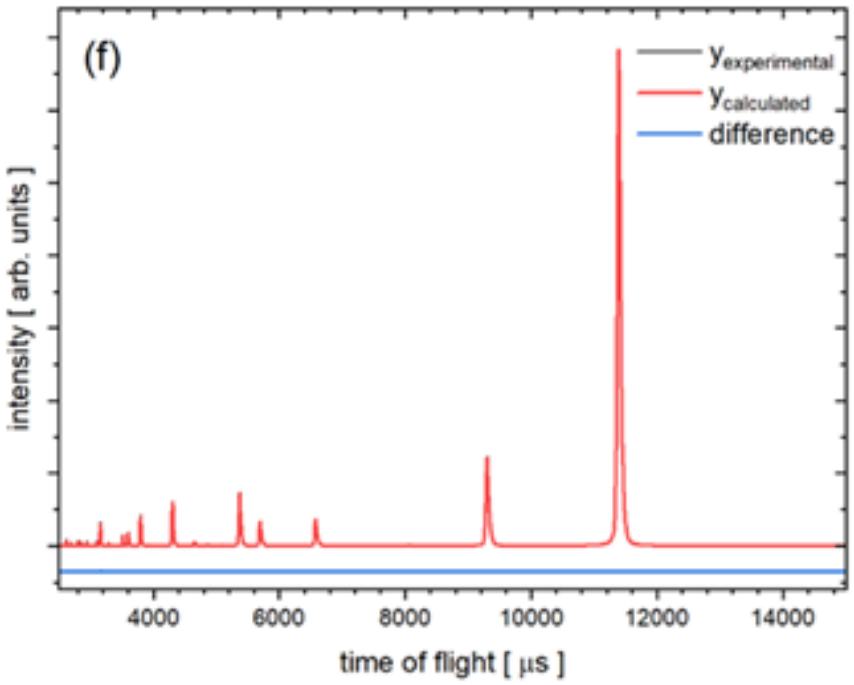

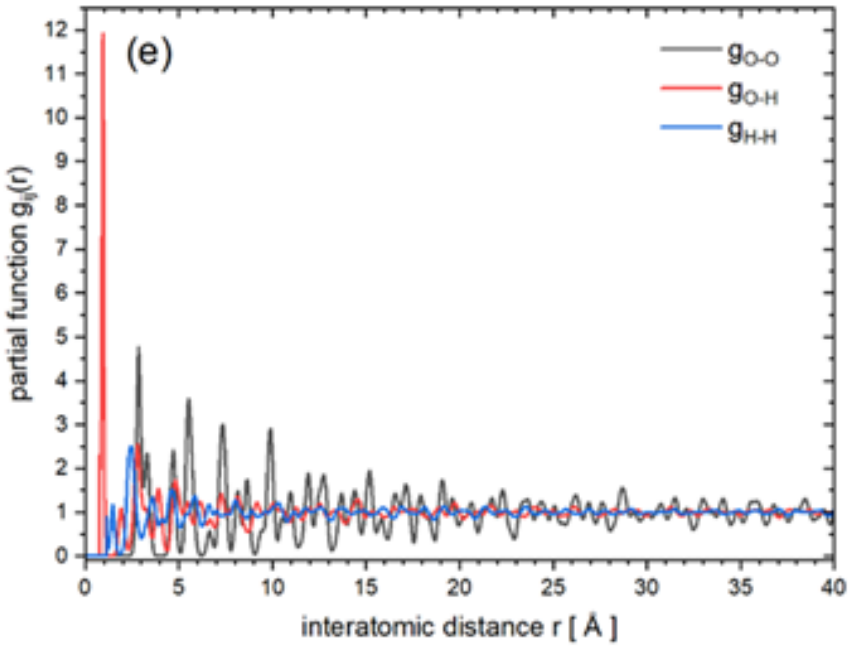

due to Preffered Orientation for RMC refinement
corrected and simulated powder pattern was used

RMCProfile7 hint

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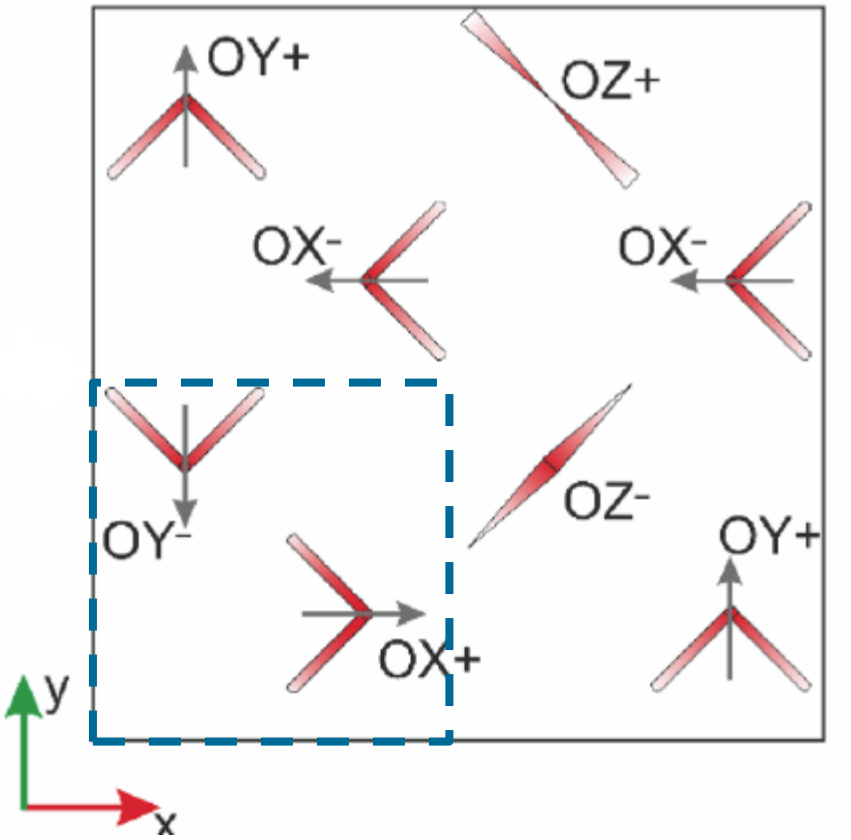
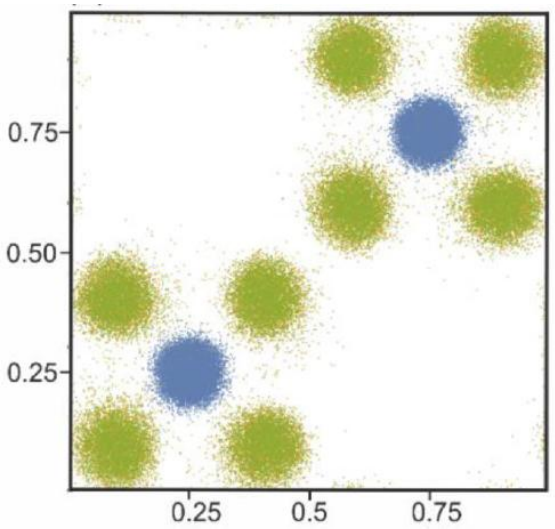
RMCProfile results





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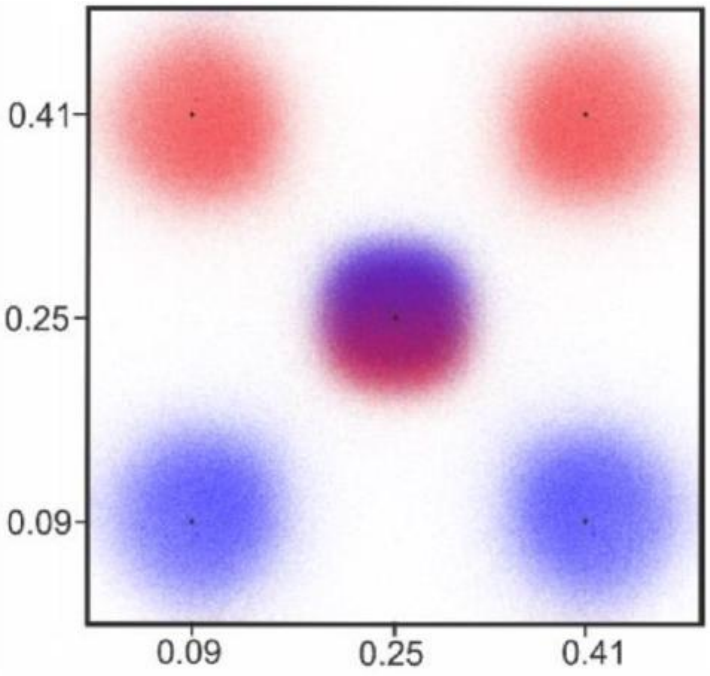

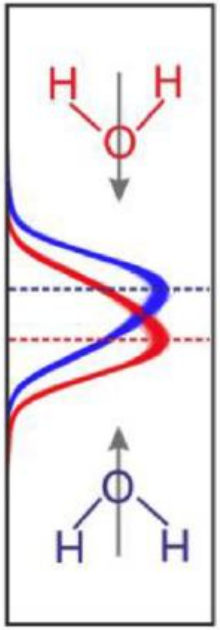

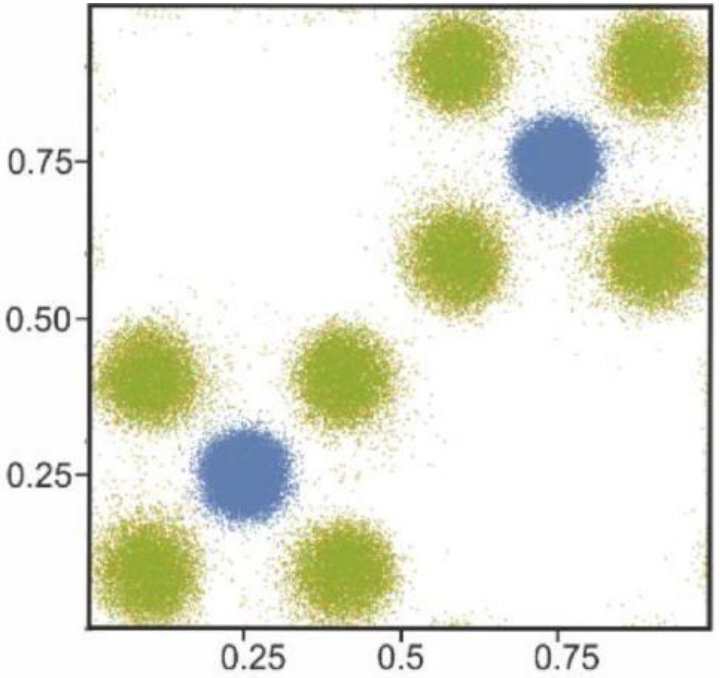

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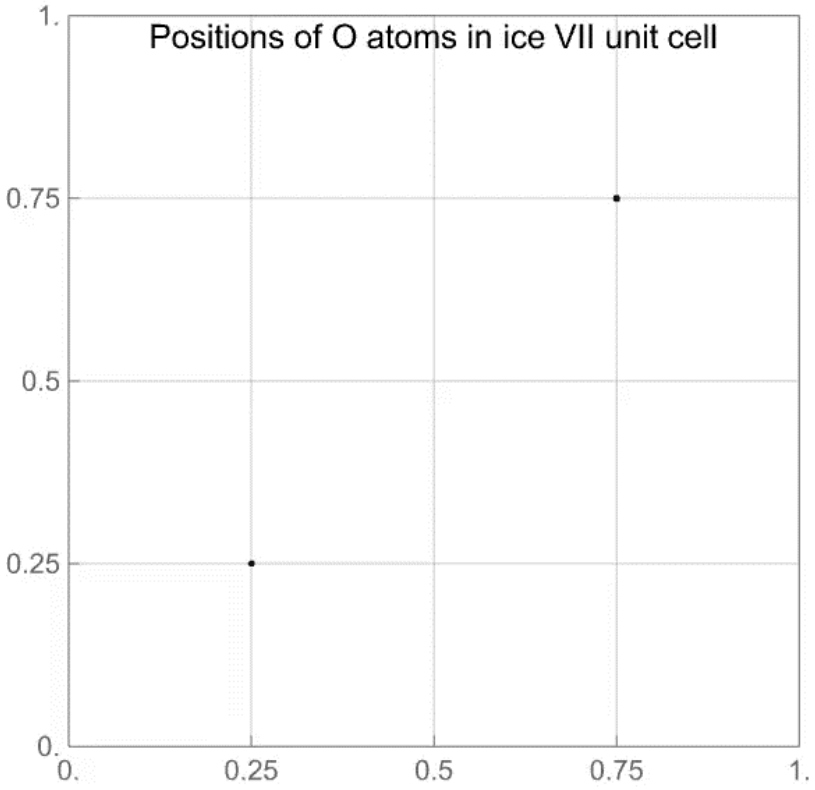
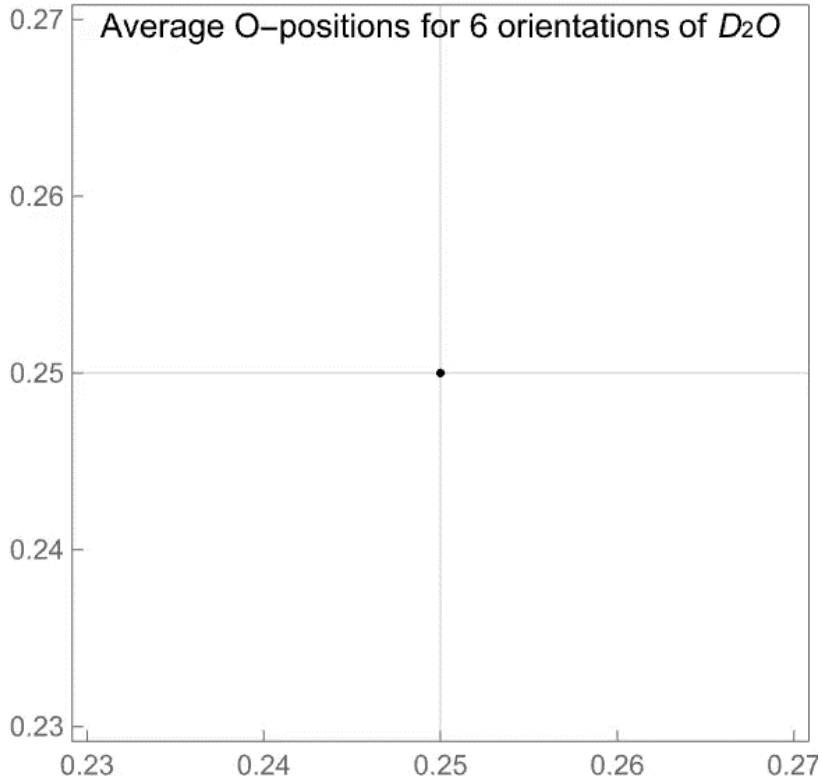
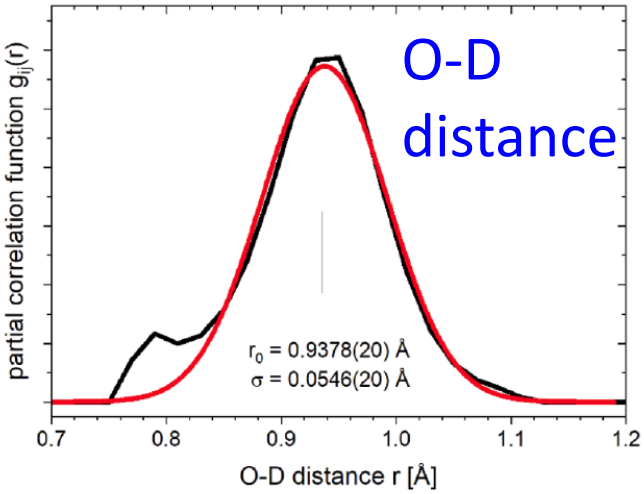
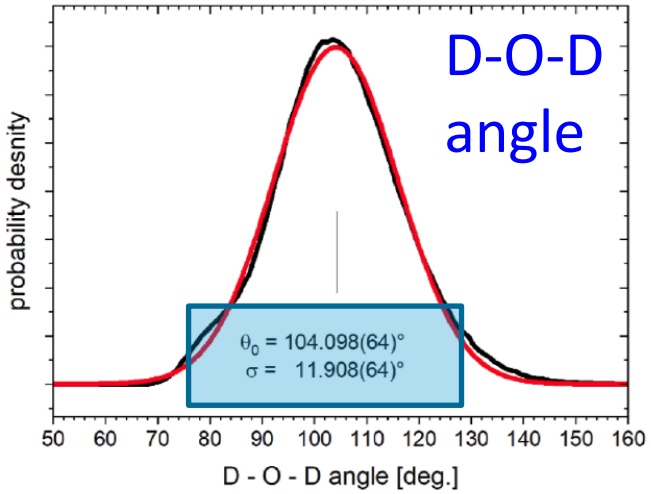
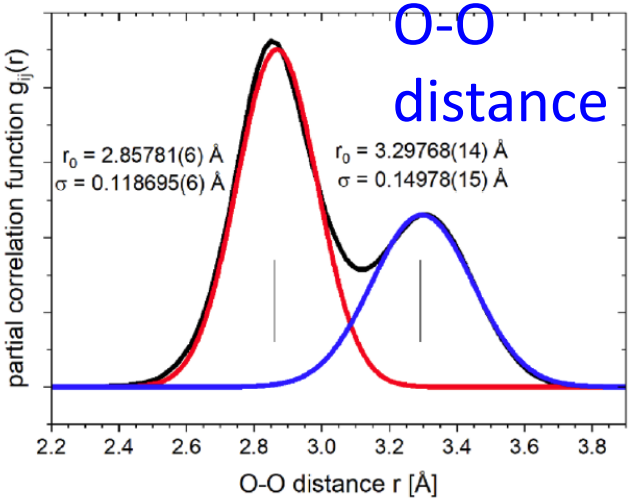


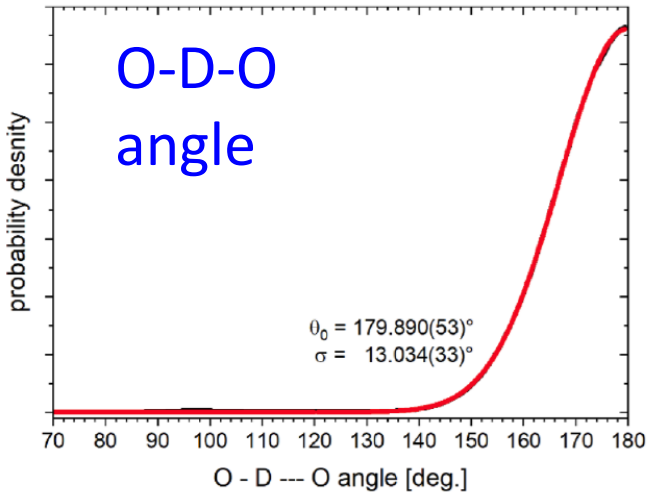


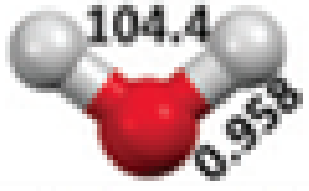
RMCProfile results











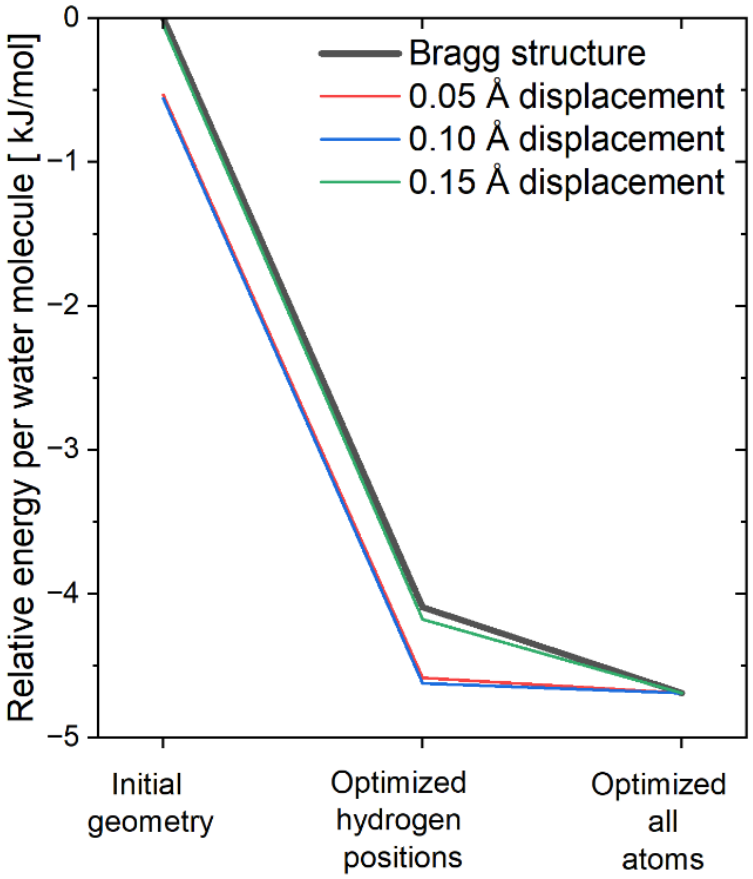
[from M. R. Milovanović, J.M. Živković, D.B. Ninković, I.M. Stanković, S.D. Zaric, Phys.Chem.Chem.Phys., 2020, 22, 4138]

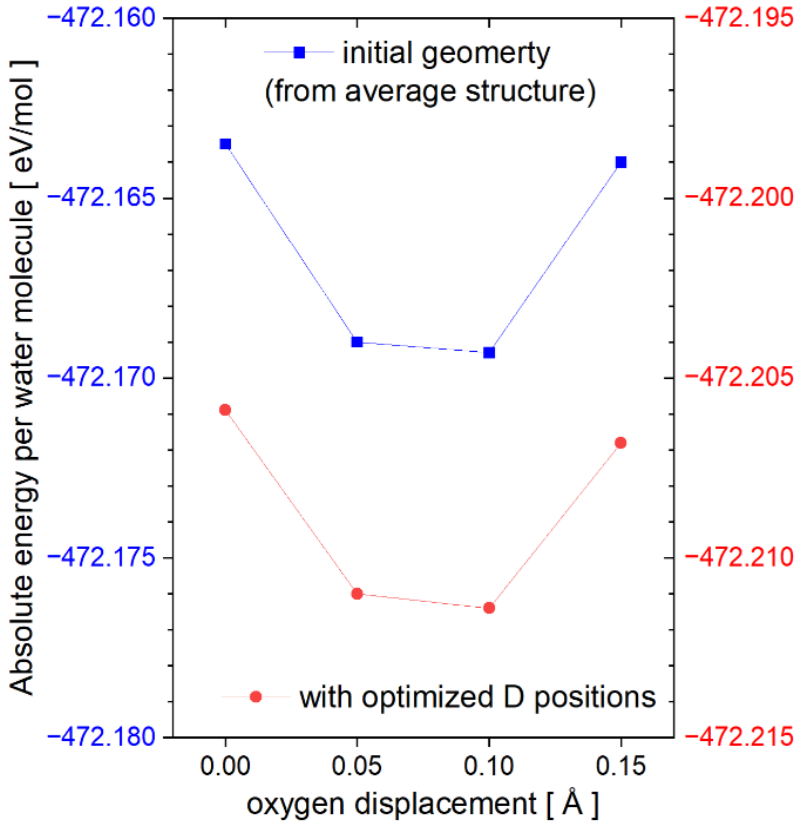
$d_{O\text{-}D}$ = 0.896(1) Å

$\alpha_{D\text{-}O\text{-}D}$ = 109.47°

from average structure Rietveld refineemnt (our data)

DFT results





Displacements of D_2O molecules by 0.05 Å stabilizes the structure by 0.536 kJ mol^{-1} per water molecule with respect to the average structure

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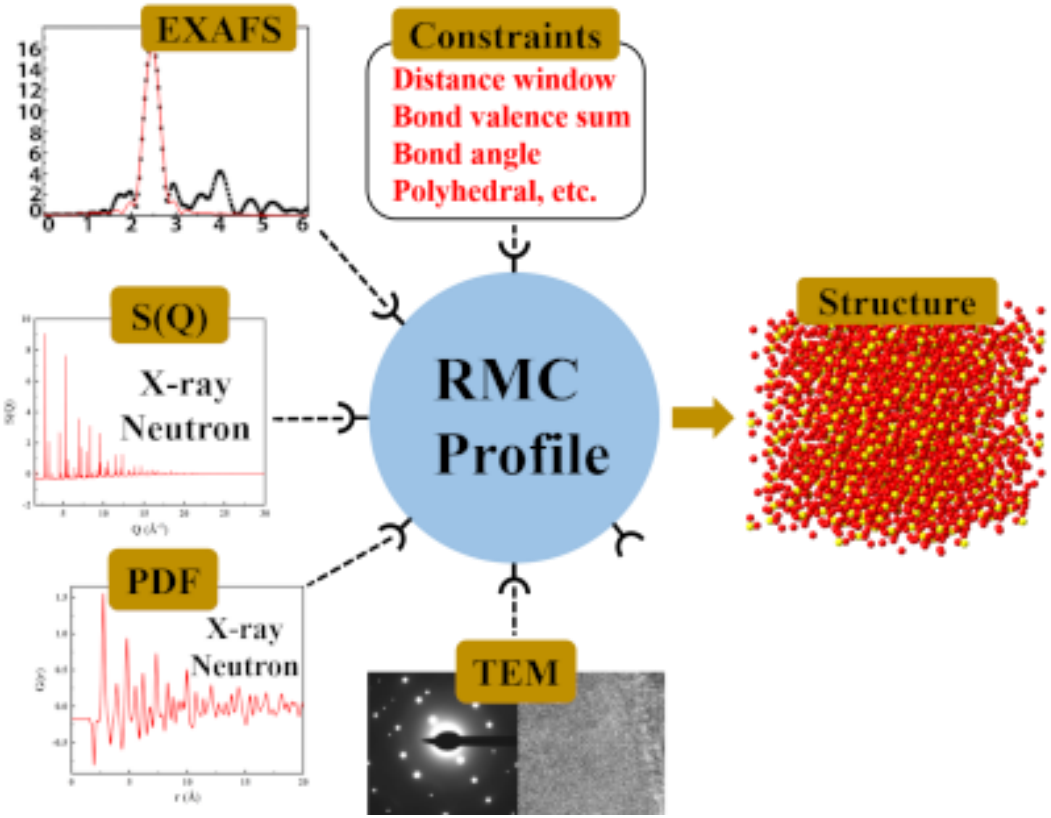
Summary

- High quailty PDF data can be measured at high pressure and analized with big box approach by RMCProfile7
- Pair Distribution Function studies allow:

  - get the local structures of ice VII with well defined positions of water molecules,
  - identify distributions of water molecules deviating from the average positions,
  - obtain reliable geometrical parameters,
  - identify subtle structural effects hidden within the average structure.

RMCProfile in brief



- big box of atoms
- many datasets
- many constraints
- support from theory

https://rmcprofile.ornl.gov/

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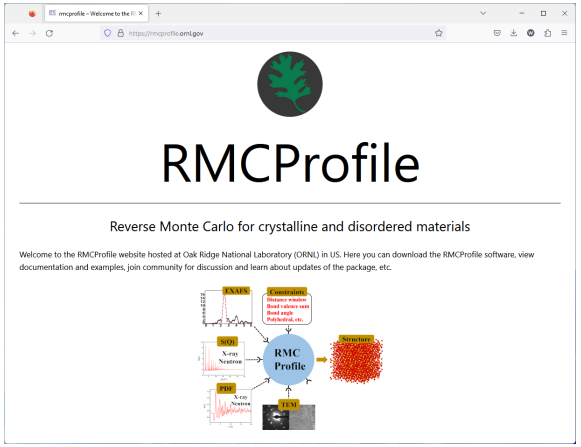
RMCProfile7 in brief



Basic steps

1. Create a starting supercell (called a configuration)
2. Create and normalize experimental data files G(r), D(r), F(Q)
3. Prepare Bragg profile data file
4. Run RMCProfile7 with 0 moves
5. Check initially calculated functions and partials
6. Run RMCProfile7, wait and be patient
7. Check final functions and partials
8. Analyze refined configuration

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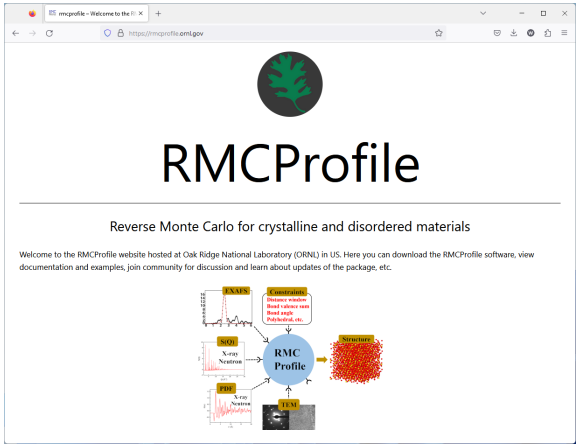
RMCProfile7 in brief



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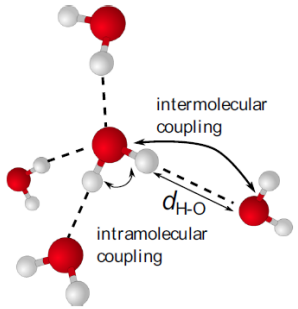
ICE RULES (2 in, 2 out)



https://rmcprofile.ornl.gov/

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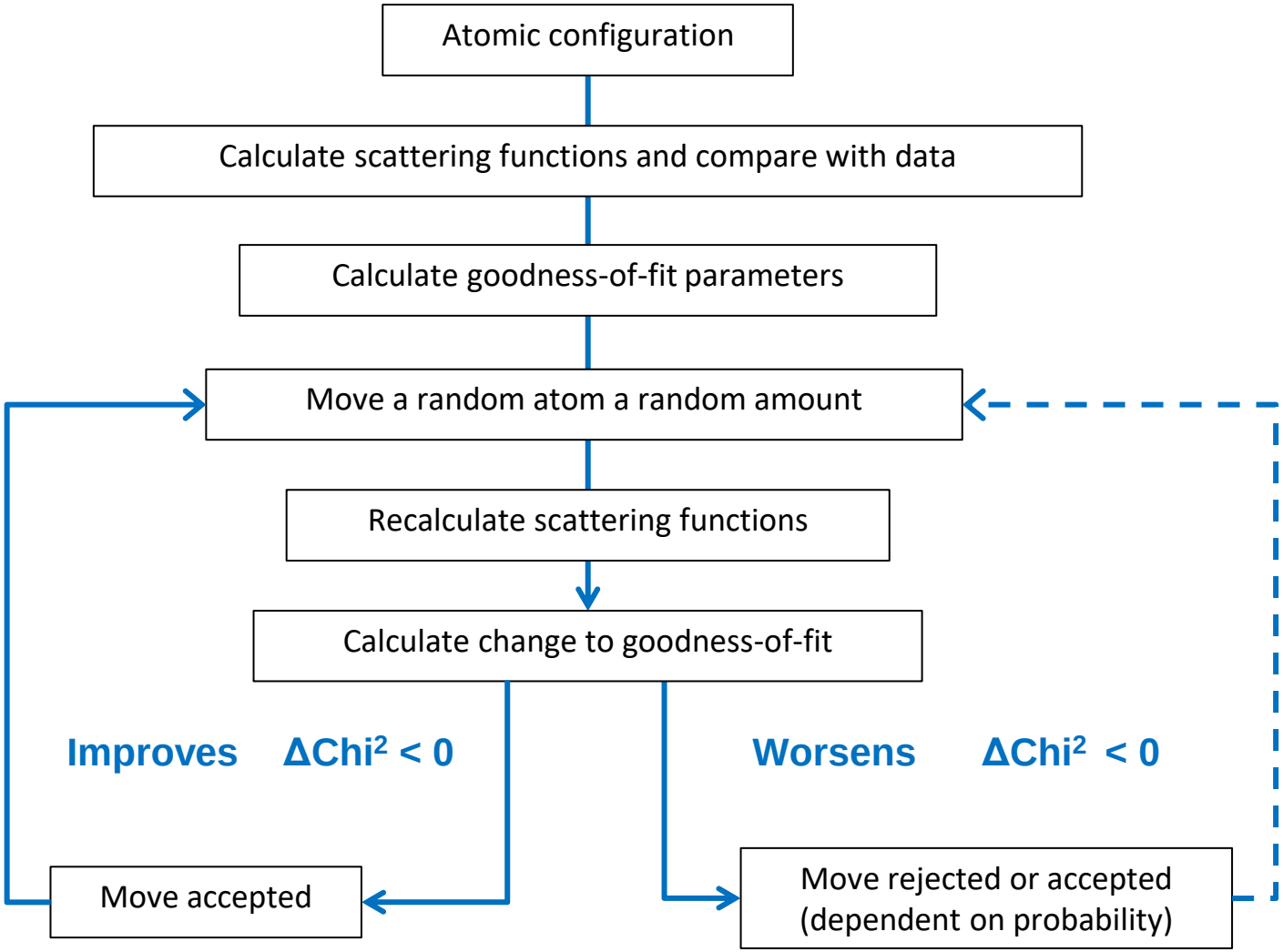
Reversed Monte Carlo in brief



RMCProfile7 in more details

- **Atomic configuration**
  - usually a supercell of the crystallographic unit cell
  - 10 000 – 1 000 000 atoms
- **RMCProfile7 can fit**
  - real space data , i.e. G(r), D(r), G_PDFGUI(r), T(r)…
  - reciprocal space data, i.e. F(Q), QF(Q), S(Q)
  - Bragg data (instrumental parameters from GSAS, GSAS-II and Topas)
  - magnetic scattering in reciprocal space
  - EXAFS (k- and/or r-space)
  - (Electron) single crystal diffuse
- **Variety of additional constraints**
  - minimum distance “hard sphere Monte Carlo”
  - distance window
  - molecular potentials

RMCProfile7 in more details

- **Multiphase refinement**
  - calculation of all dataset types can be done for multiple phases*
- **RMCProfile7 can fit**
  - real space dataset (X-Ray and neutron) can be calculated as a back Fourier Transform of reciprocal space dataset
  - full GSAS-II compatibility (easy Bragg data extraction)
- **Variety of additional constraints**
  - molecular potentials (distances, angles, torsion angle, inversion angle, planarity + variants)
  - potentials and swaps are now compatible
- **Molecule (rigid body) move type**
  - **molecule (rigid body) type move**
  - swap between atoms and atoms, atoms to molecules and molecules to molecules

*W. Sławiński, J. Appl. Cryst. (2018). **51**, 919–923

Some more details about *RMCProfile7*

RMC7_ice_VII.dat

```
TITLE :: ICE VII
R_SPACING    :: 0.02
PRINT_PERIOD :: 10000
SAVE_PERIOD  :: 10000
VERBOSITY    :: STANDARD
%%TIME_LIMIT   ::  10800 SECONDS
%%ITERATION_LIMIT :: 0

CONFIGURATION  :: D2O
  > MAXIMUM_MOVES      ::   0.1 0.1 Angstrom
  > CONFIGURATION_FILE :: ice_vii_24_24_24.rmc7
  > ATOMS :: O 2H
  > PROPORTION :: 1.0
  %%> RESOLUTION_CORRECTION_X :: 0.002
  > MOVEOUT
  > WRITE_HISTORY
  > NO_IGNORE_HISTORY


MINIMUM_DISTANCES ::  1
  > MINIMUM_DISTANCES :: 2.38 0.78 1.16 Angstrom

DISTANCE_WINDOWS ::  1
  > NEIGH_FILE        :: ice_VII.neigh
  > MINIMUM_DISTANCES :: 0.00 0.78 0.00  Angstrom
  > MAXIMUM_DISTANCES :: 0.00 1.12 0.00  Angstrom

MOLECULE ::
  > NO_UPDATE
  > TRANSLATION_PROBABILITY :: 0.2
  > MAXIMUM_MOVES :: 0.1
  > ROTATION_PROBABILITY :: 0.2
  > ROTATION :: euler  0 10 0 10 0 10
  > MOLECULE_FILE :: H2O.list
  > ATOM :: O
  > ATOM :: 2H 1 0.76 1.18 Angstrom
  > ATOM :: 2H 1 0.76 1.18 Angstrom

```

24x24x24 unit cells => 82 944 atoms

isotop definition 2H = D

Minimum distance constrain

Distance windos constrain

D_2O molecule definition

molecule rotation definitione:

- Euler angle
- xyz direction
- uvw direction
- interatomic vector direction

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RMCProfile7 results

```
74  NEUTRON_RECIPROCAL_SPACE_DATA :: 1
75    > FILENAME :: 118473_rmc_low_q_rescale.fq
76    > REBIN :: 0.02
77    > LOW_R_CUT_OFF :: 0.74
78    > START_POINT :: 1
79    > END_POINT :: 4038
80    > WEIGHT ::   0.01
81    > NO_FITTED_OFFSET
82    > NO_FITTED_SCALE
83    > DATA_TYPE :: F(Q)
84    > FIT_TYPE ::  F(Q)
85    > CONVOLVE
86    > REAL_SPACE_FIT :: 1 2000 0.01
87    > REAL_SPACE_FIT_TYPE :: G(r)
88    > REAL_SPACE_QMAX :: 20.180
89    > REAL_SPACE_QMIN ::  0.005
90    > REAL_SPACE_QSTEP :: 0.005
91    > NO_REAL_SPACE_FITTED_SCALE
92    > NO_REAL_SPACE_FITTED_OFFSET
```

real and reciprocal space correction
=> subtraction of ripples below 0.74 Å

internal data type converion

calculation of real space data as a back Fourier transform also for neutron data

```
129 BRAGG ::
130   > BRAGG_SHAPE :: 1 GSASII_TOF
131   > WEIGHT ::   0.0001
132   > DMIN :: 0.515
133   > FILENAME :: 118473_tt70_subtracted_cell_ice_VII_no_abs_calc_no_preferred_for_rmc_1.txt
134   > BACKGROUND_TYPE :: 1
135   > BACKGROUND_FILE :: 118473_tt70_subtracted_cell_ice_VII_no_abs_calc_no_preferred_for_rmc.pwdrbck
136   > RECALCULATE
137   > INSTRUMENT_FILE :: 118473_tt70_subtracted_cell_ice_VII_no_abs_calc_no_preferred_for_rmc.instprm
138   > NO_FITTED_SCALE
139   > NO_FITTED_BACKGROUND
140   > NUMBER_OF_POINTS_PER_PEAK :: 2001
```

GSAS-II input files for Bragg data

RMCProfile developers

- Wojciech A. Slawinski, University of Warsaw, Poland
- Chris Kerr, Queen Mary University of London, UK

- Matt Tucker, Oak Ridge National Laboratory, US
- Yuanpeng Zhang, Oak Ridge National Laboratory, US

- Helen Playford, ISIS Neutron and Muon Source, UK

- Marin Dove, Queen Mary University of London, UK
- Anthony Phillips, Queen Mary University of London, UK

RMCProfile7 plans for the future

- **Magnetism**
  - calculation of magnetic contribution to F(Q) and/or mPDF
- **EXAFS**
  - implementation of EXAFS calculation
- **single crystal diffuse scattering**
  - 2D planes and 3D volumes of diffuse scattering calculations
- **better speed optimization and possibly GPU optimization**
- **encourage more Users to switch from RMCProfile6 to RMCProfile7**
  - more examples and tutorials using RMCProfile7
  - more bug testing
  - more user friendly preparation and analysis of configurations