Pair Distribution Function
PDF

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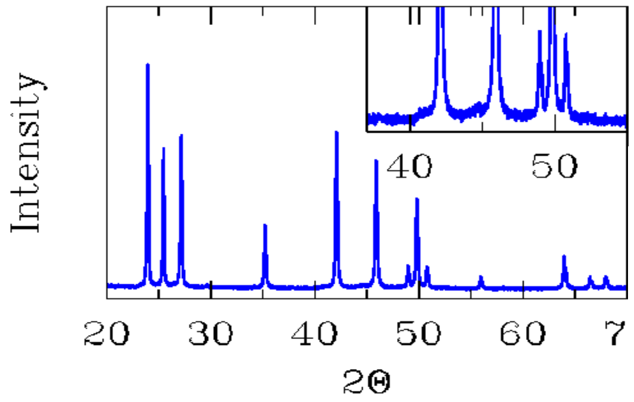
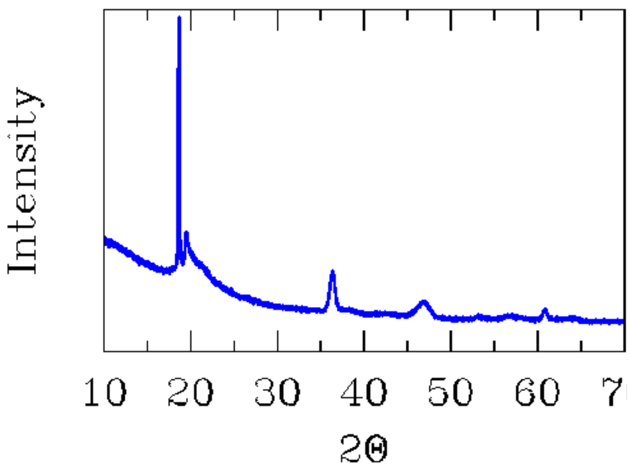
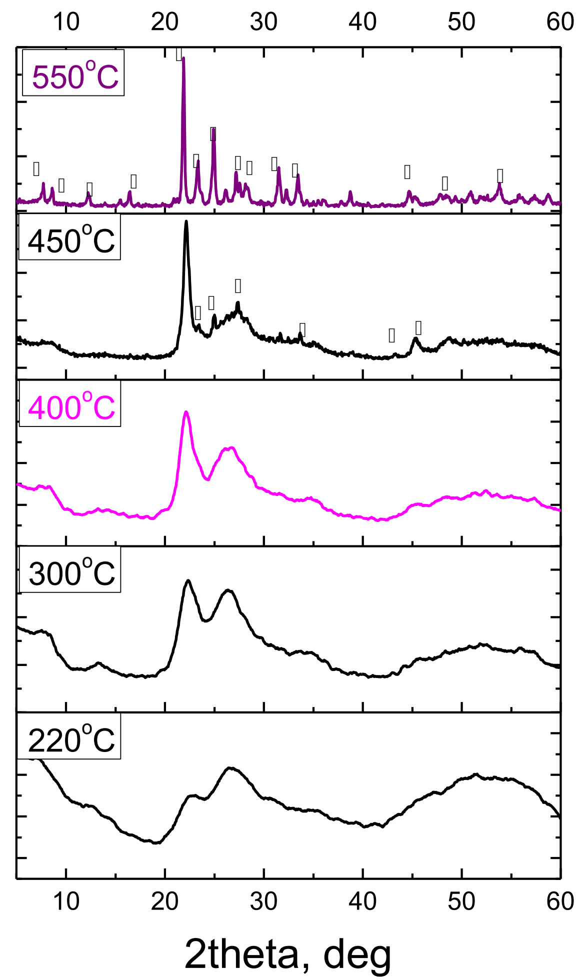
Powder Diffuse Scattering

CdSe crystalline material

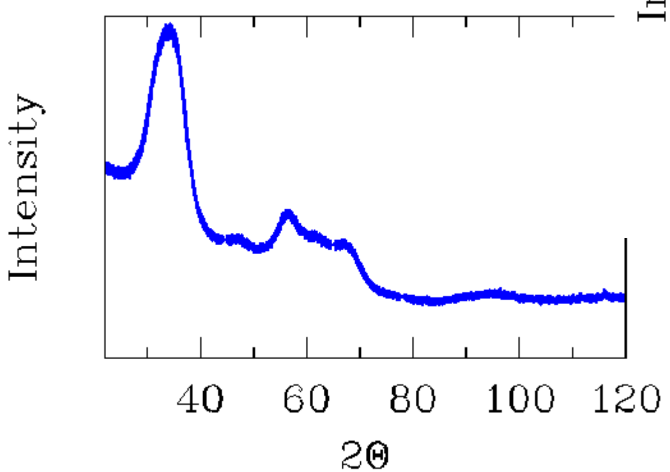




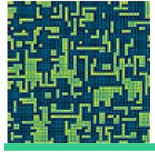
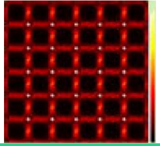
Layered H_2TiO_3



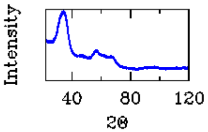
Mo-V-Nb oxides



Nano crystalline ZnO

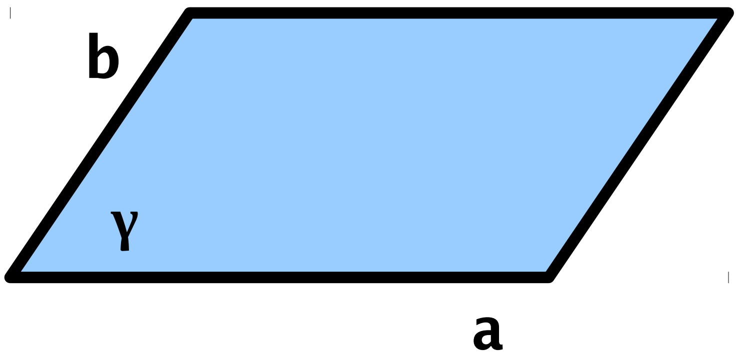
Rietveld refinement

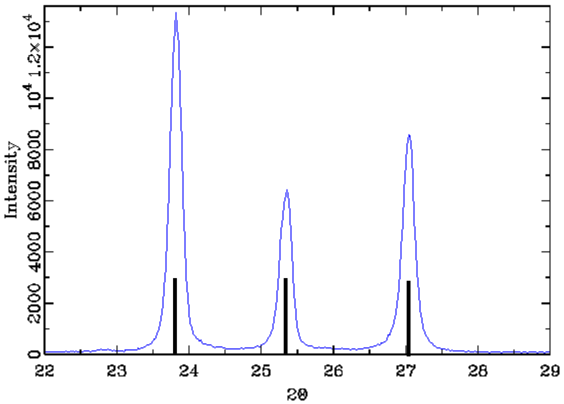


Basic assumption: perfect periodic crystal structure

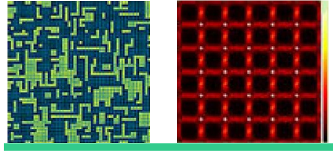
for all lattice planes: $$I(2\Theta) = S \sum_{hkl} M(\vec{h}) P(\vec{h}) \left(\left(\sum_{j=1}^{N} f_j Occ_j e^{2\pi i \vec{h} \vec{r}_j} \right) \circ Profile \right)$$

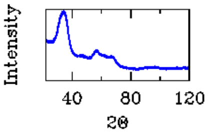
calulate d-values from unit cell (size and shape)





Scalefactor; **M**ultiplicity; **P**refered orientation





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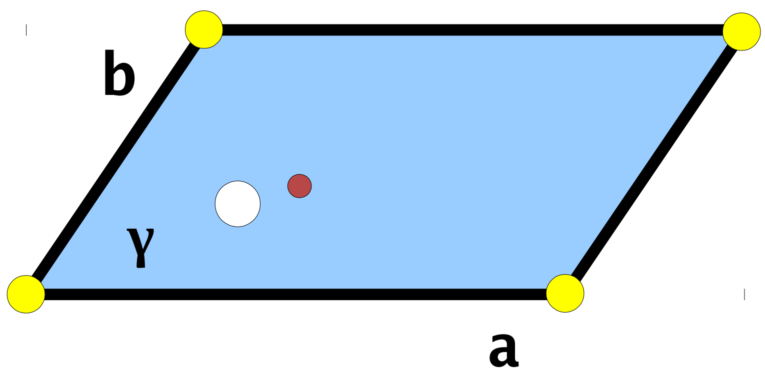
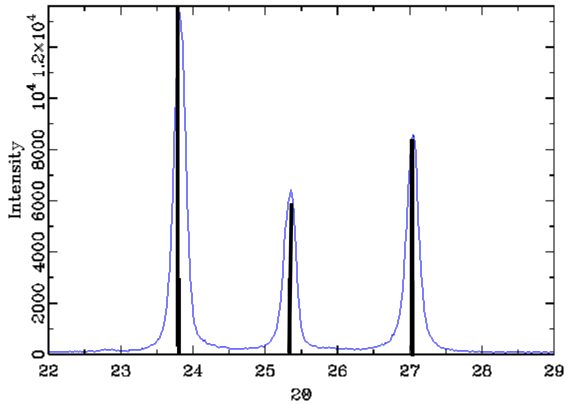
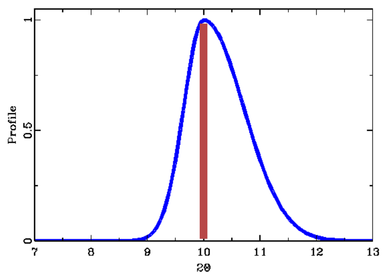
calulate d-values from unit cell (size and shape)





calculate intensity from **one** unit cell content: Position and type of atoms

create reflection shape via profil function



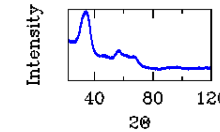
Instrumental parameters

resolution, wave length distribution, diffractometer

Structural parameters

strain, crystal size

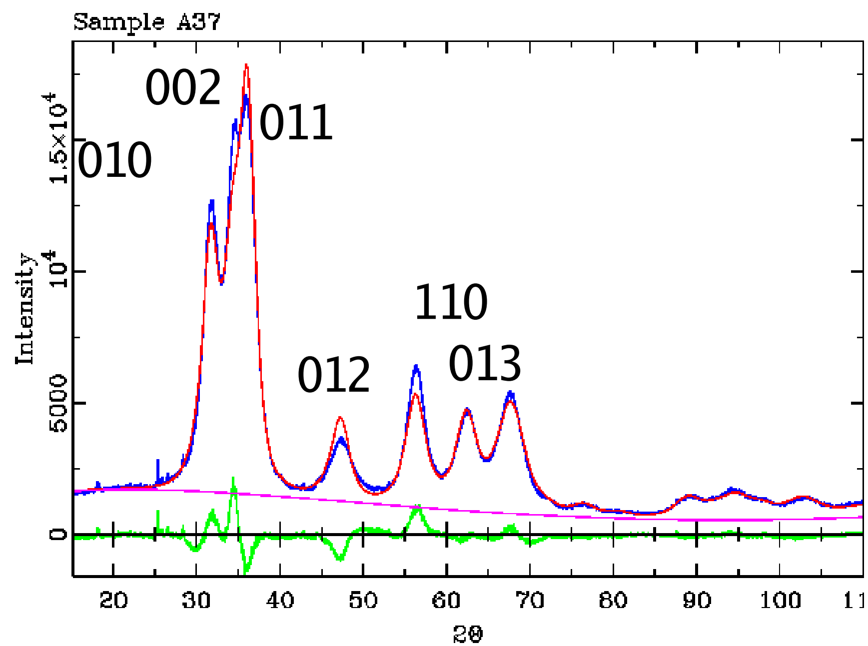
Scalefactor; **M**ultiplicity; **P**refered orientation



Example ZnO Nanoparticle
3,2nm diameter

Section of
Powder pattern

Laboratory data

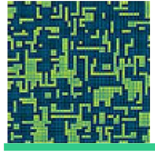
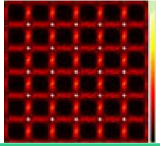


Line: exp. data

Line: calculated profile

Line: Difference: observed - calculated

Reflections hk0 are not matched
Reflection 012 broader than calculated
==> disorder
Not part of Rietveld refinement

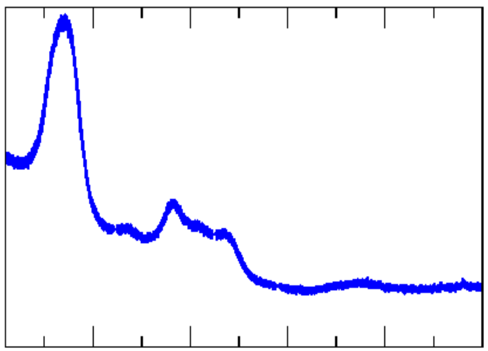
Debye Equation

calculates intensity from list of atom pairs! **ALL** atoms in the „*crystal*"

$$<|F(\boldsymbol{h})|^2> = \sum_j f_j^2 + \sum_i \sum_{j,\, j\neq i} f_i f_j \sin(2\pi \boldsymbol{h}\boldsymbol{r}_{ij})/(2\pi \boldsymbol{h}\boldsymbol{r}_{ij})$$

atom pairs

each individual atom



f_i atomic form factor scattered intensity by individual atom, depends on atom type, radiation

r_{ij} distance from atom i to atom j

Sum over all atom pairs

→ no restrictions on sample structure

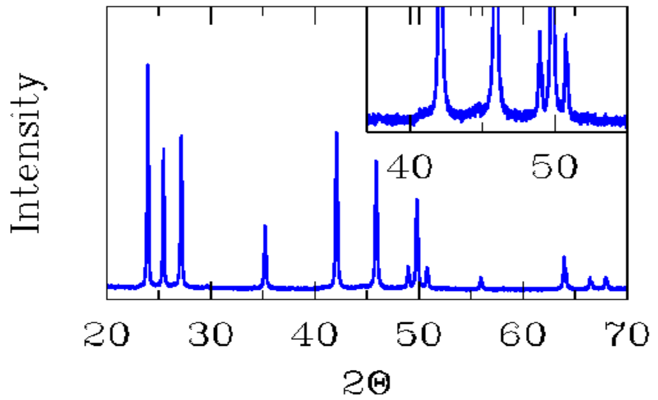
open to finite particle with any shape

defects, like stacking faults etc.

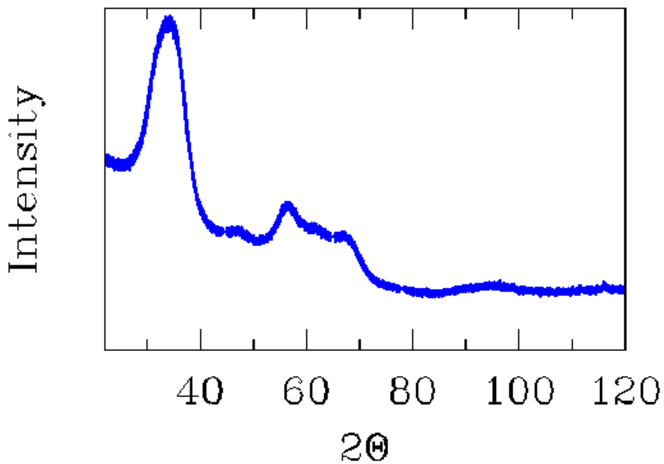
Post processing: convolute with instrumental resolution function

Powder Diffuse Scattering

CdSe crystalline material



Well separated reflections => structure solution



Nano crystalline ZnO

Structure ??

Just a small object with bulk structure ?

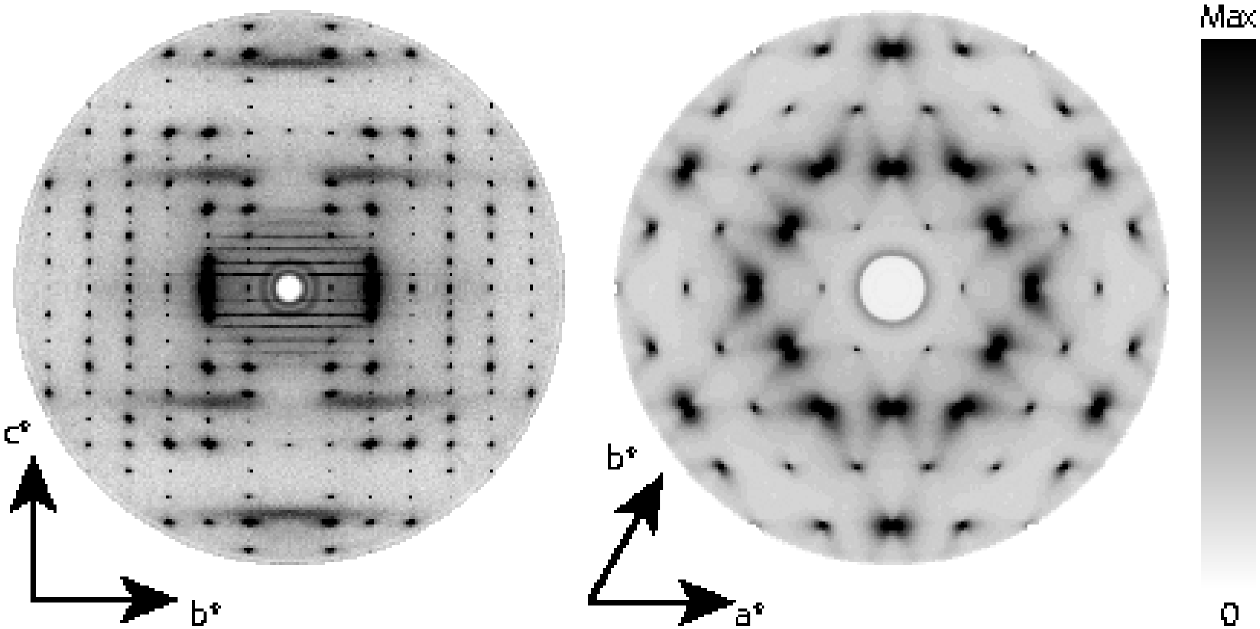
Unique *cluster* structure ?

Not enough detail for standard structure determination techniques

Interatomic distances **can** be determined

→ Pair Distribution Function PDF

Single Crystal Diffuse Scattering



Alkane Chains in Urea

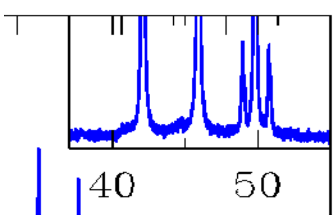
Diffuse scattering between Bragg reflections

Deviations from perfect structure

Unit cells (slightly) different

Additional order beyond translation of perfect unit cells
or
Disorder

Effect on powder pattern: weak modulated ***background***



CdSe crystalline material

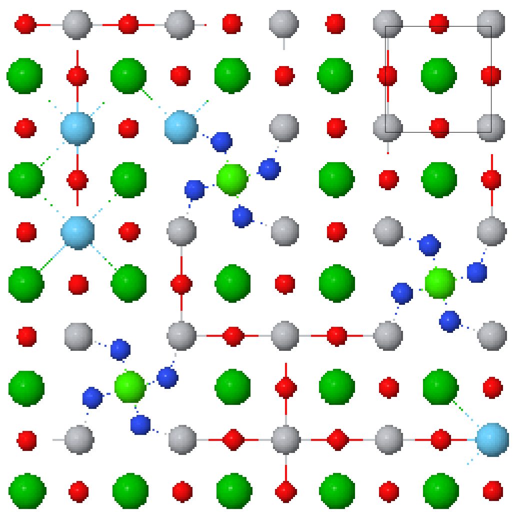
Not enough detail for single crystal disorder analysis

Interatomic distances **can** be determined

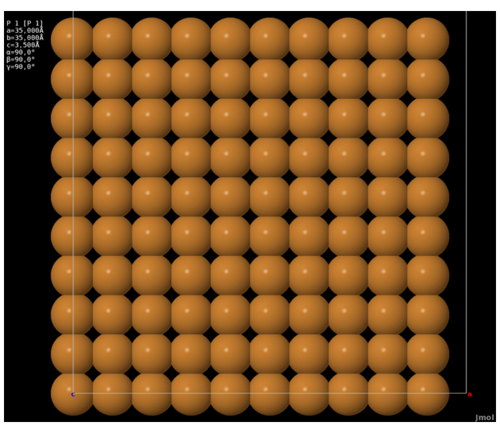
→ Pair Distribution Function PDF

Local structure

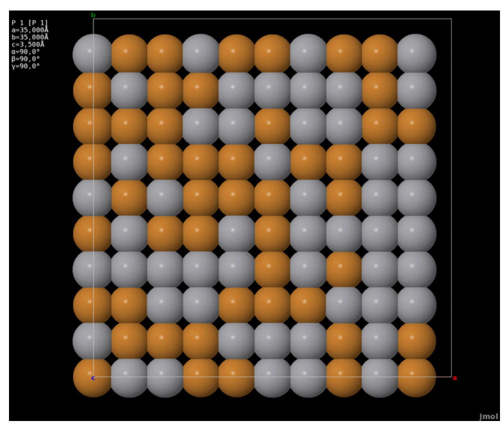
Any deviation from average crystal structure



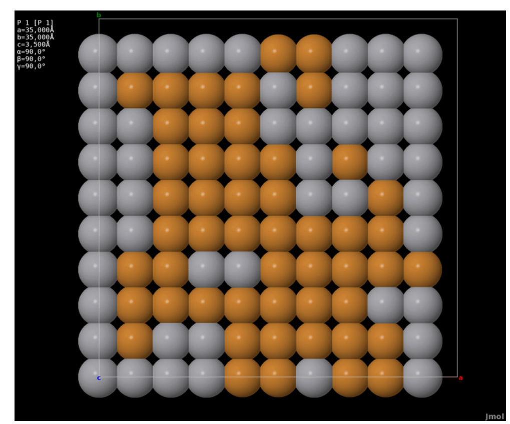
Defects may follow (many) different distribution models



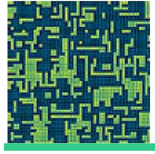
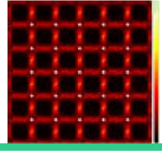
perfect



random distribution



or short range ordered

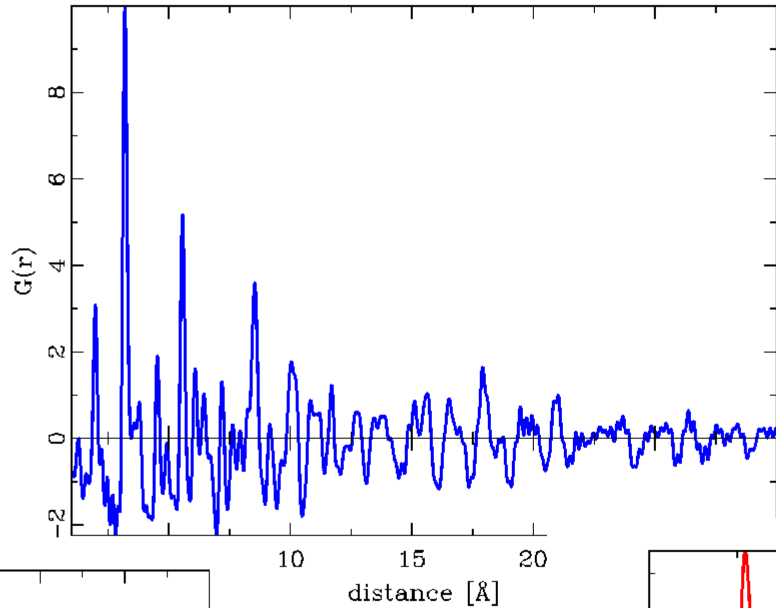
Pair Distribution Function

direct measure of

bond length

number of neighbors

bond length distribution

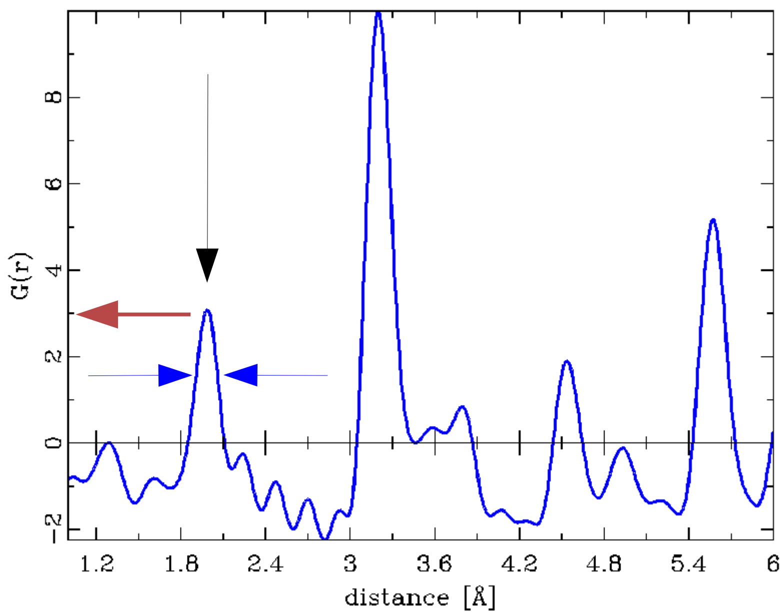


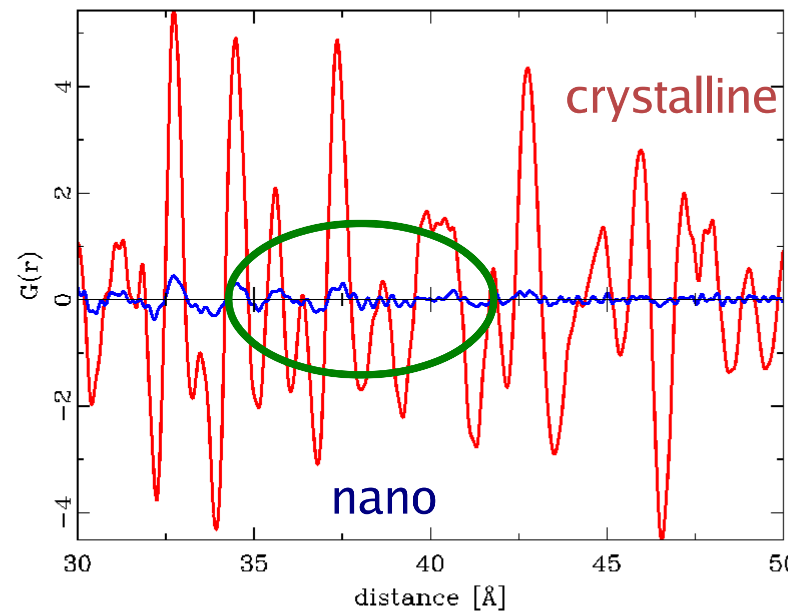
A pattern in direct space,

essentially a histogram of interatomic distances,

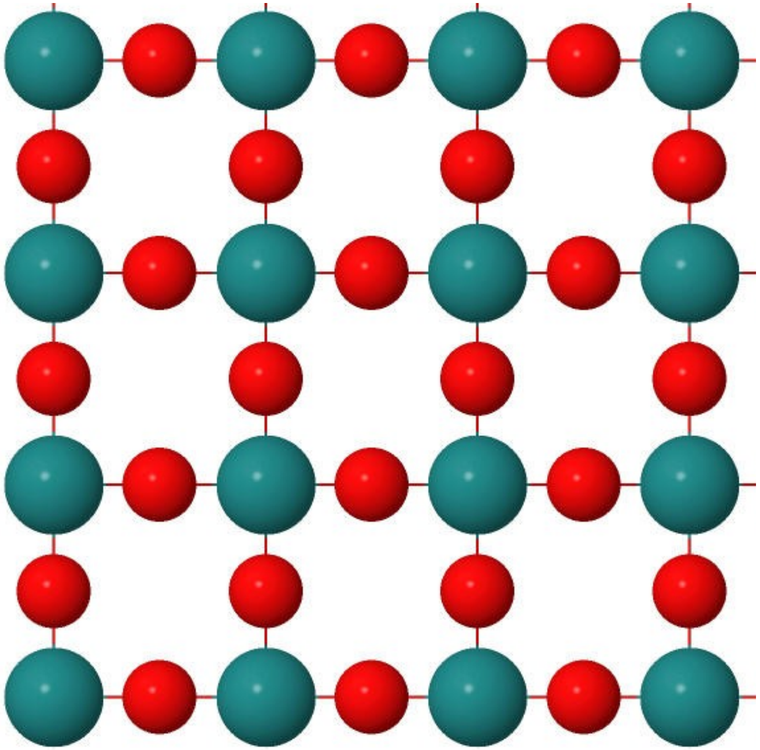
directly converted from powder diffraction pattern

particle diameter
defects



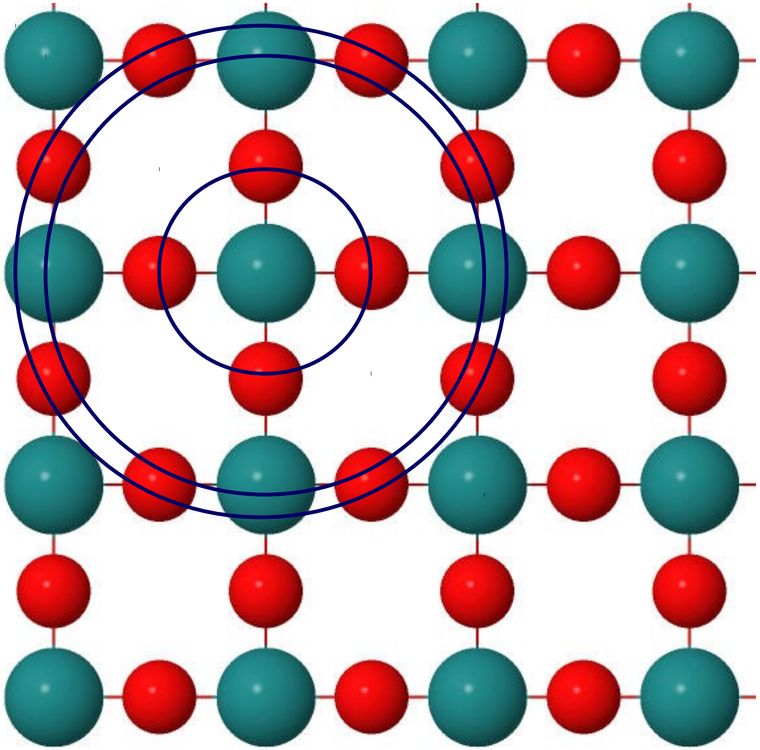


Relationship to crystal structure



Section of crystal structure

Determination from crystal structure

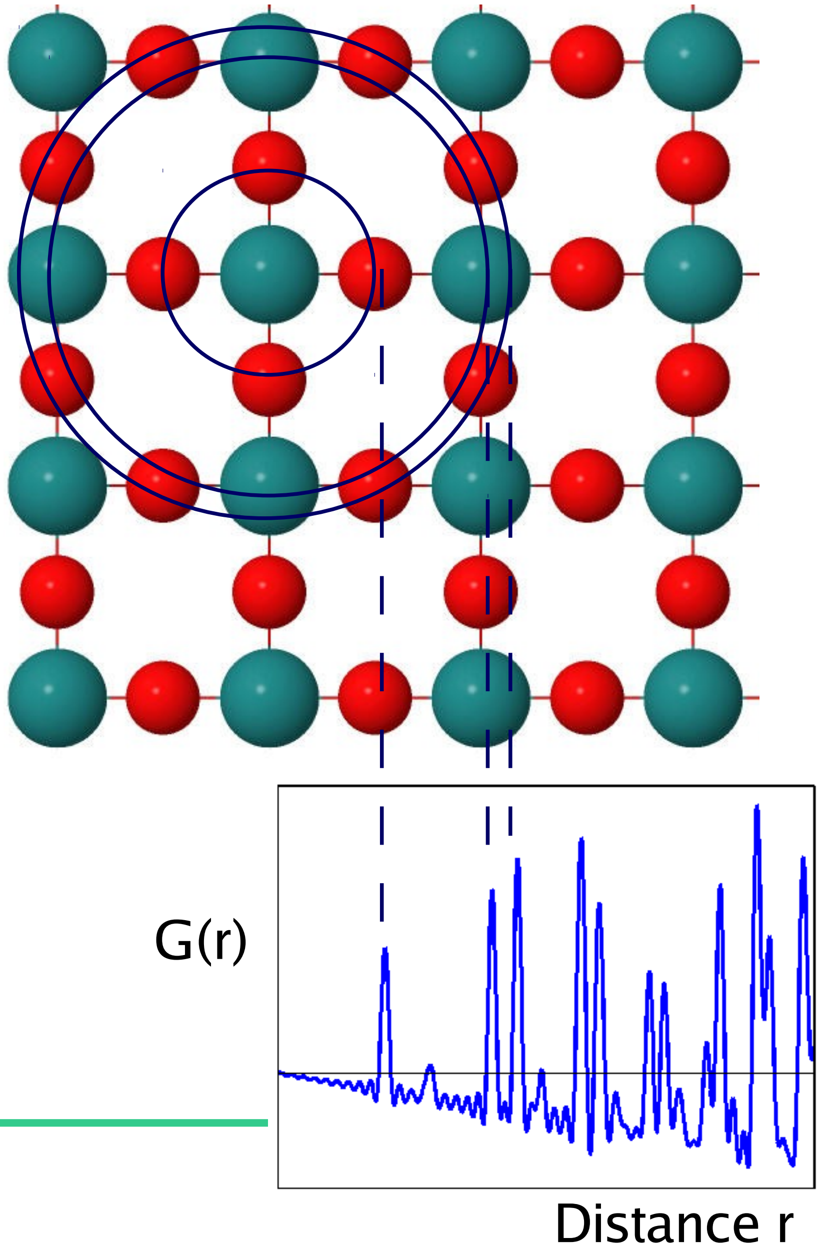


Section of crystal structure

measure all interatomic distances

Determination of the Pair Distribution Function

Determination from crystal structure



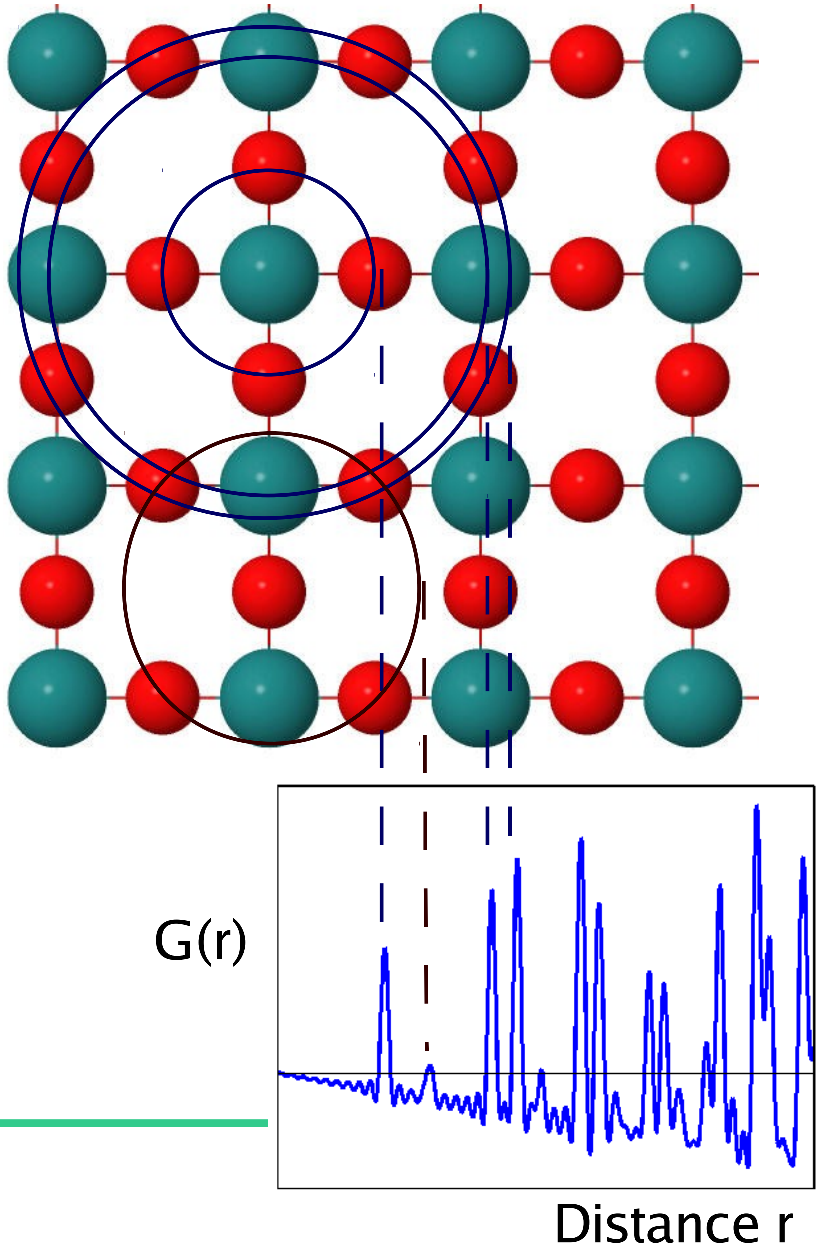
Section of crystal structure

measure all interatomic distances

Project distances into 1-D diagram

Determination of the Pair Distribution Function

Determination from crystal structure



Section of crystal structure

measure all interatomic distances

Project distances into 1-D diagram

$G(r) = 0$
Number of neighbors at r is identical to that in a random structure.

$G(r) > 0$
More neighbors than in a random structure.

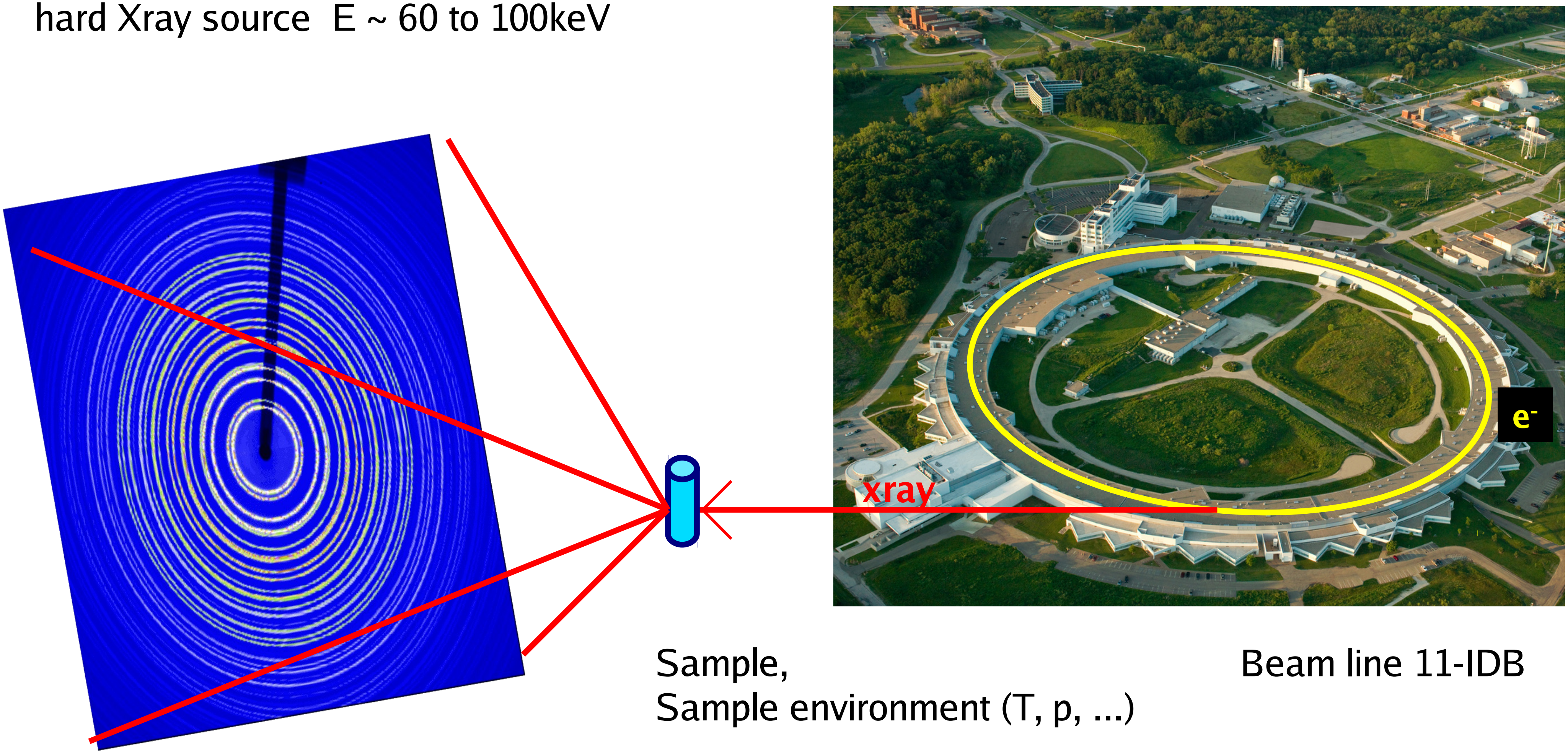
$G(r) < 0$
Less neighbors than in a random structure.

PDF definitions: Keen, J.Appl. Cryst (2001) **14**, 172

Experimental Determination of the PDF

Synchrotron Radiation from
hard Xray source E ~ 60 to 100keV

Advanced Photon Source, USA



Sample,
Sample environment (T, p, ...)

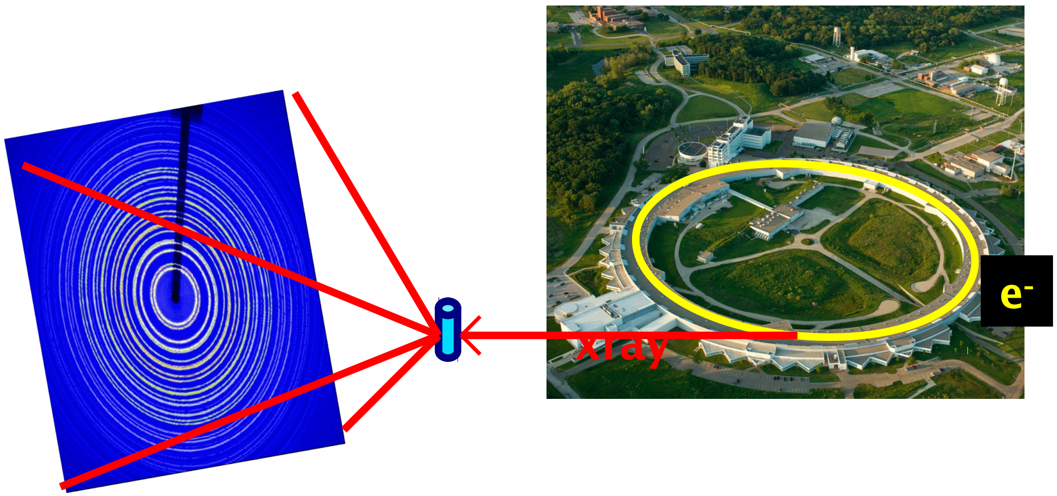
Beam line 11-IDB

Fast area detector

Chupas et al., J. Appl. Cryst (2003) **36**, 1342

Experimental Determination of the PDF

Synchrotron Radiation from
hard Xray source E ~ 60 to 100keV



Dedicated beam lines

11-ID-B APS, Argonne, USA
P. Chupas, K. Chapman

ID15, ESRF, France
S. Kimber
ID31, ESRF, France
T. Buslaps

P21 PETRA III, DESY, Hamburg
DIAMOND, ISIS, England

High resolution beam lines

ID22, ESRF, France
A. Fitch
MS X04SA Materials Science Beamline, SLS
A. Cervellino

P03, PETRA III, DESY; Hamburg

Chupas et al., J. Appl. Cryst (2003) **36**, 1342

Experimental Determination of the PDF

Synchrotron Radiation from
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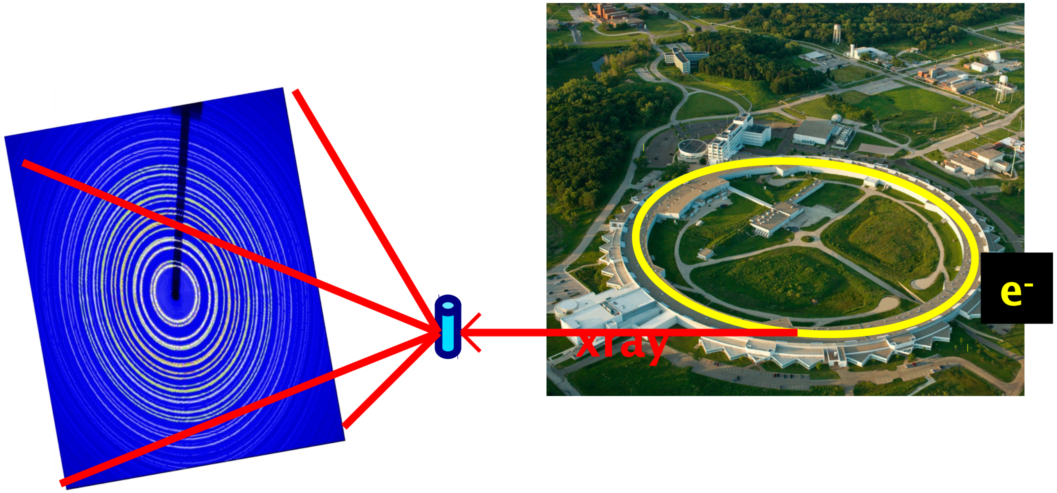
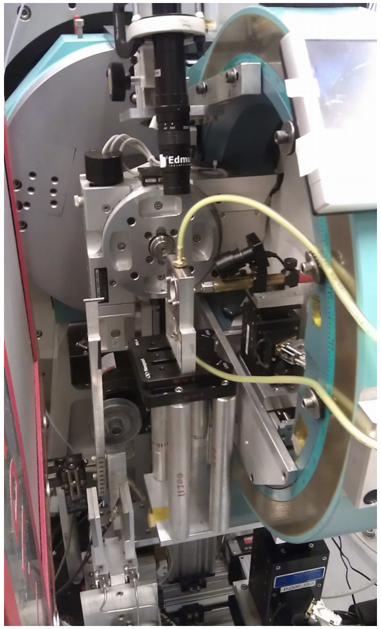
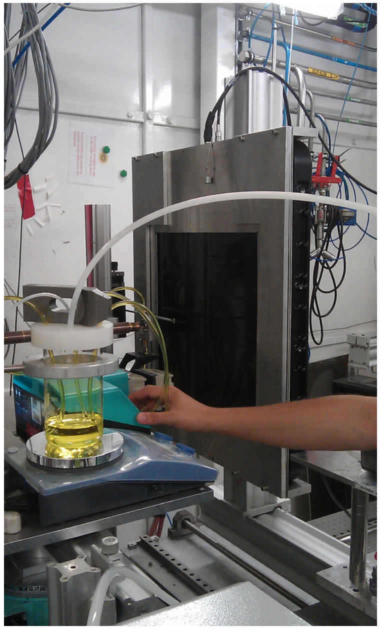


Sample,
Sample environment (T, p, ...)

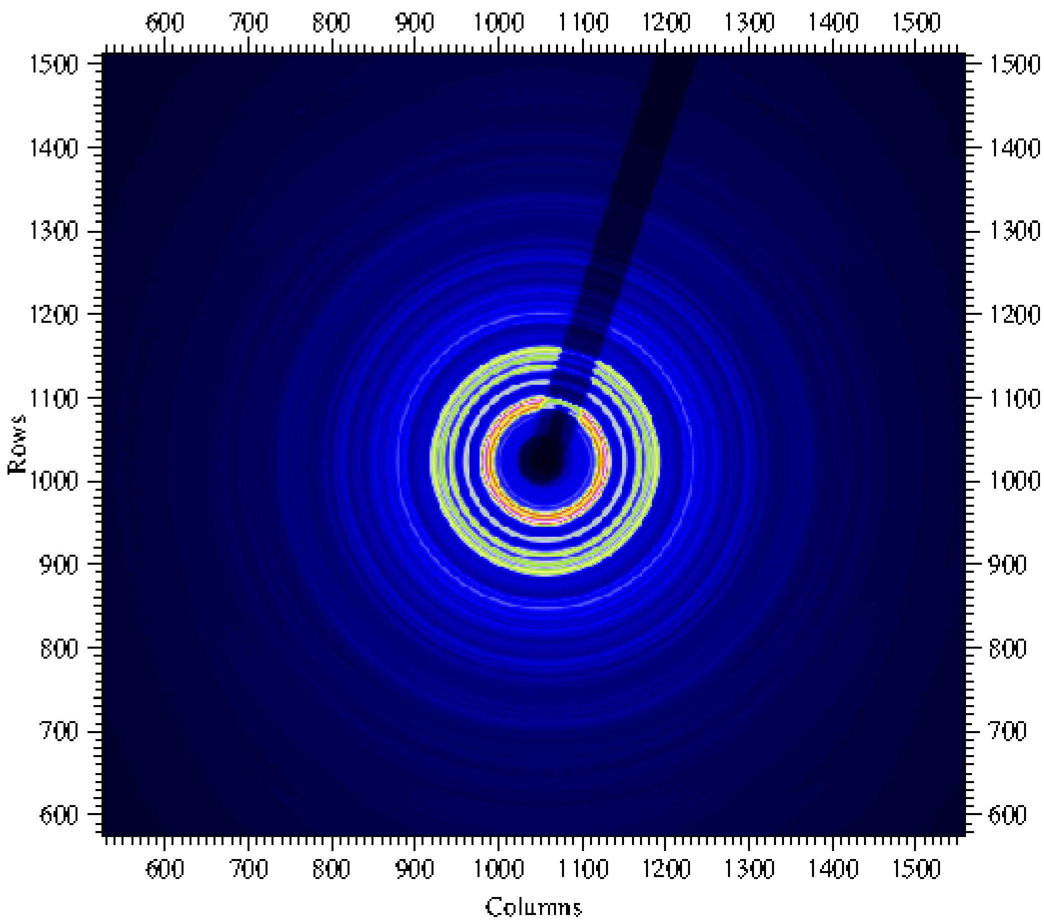




Counting time 1/16 s   to 30 sec !!!

Experimental Determination of the PDF

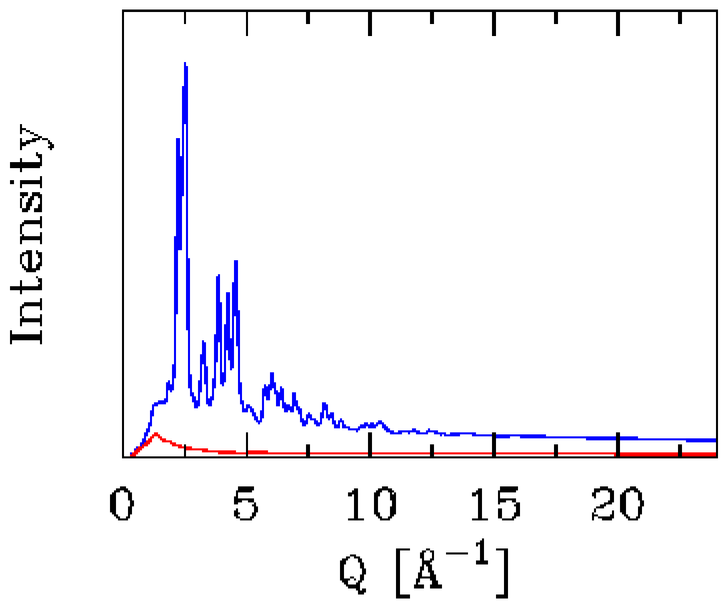
Rapid-aquisition PDF



appr. 1/9 of detector area

Counting time 1/16 s   to 30 sec !!!

1st step radial integration   FIT2D

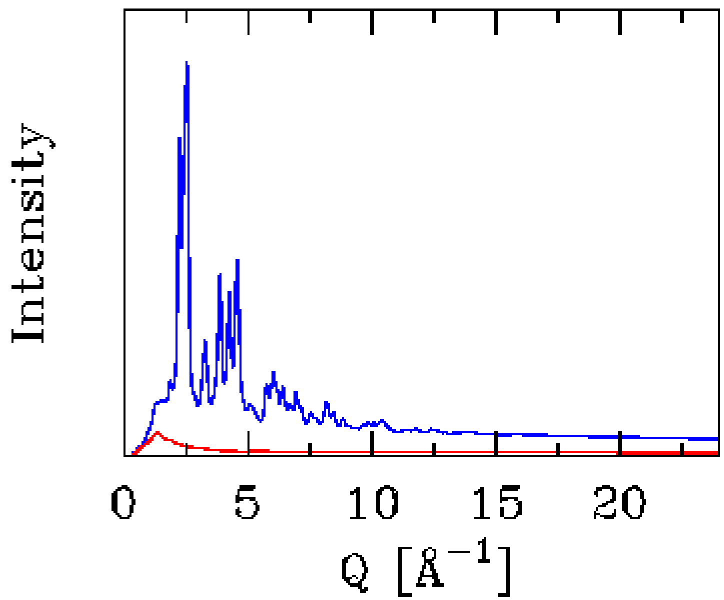


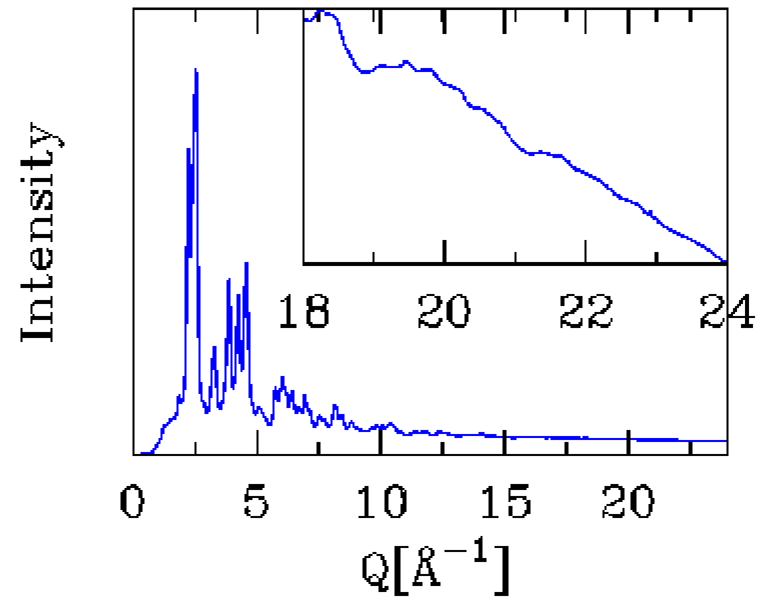
Measure **data** and
background = empty capillary
with good counting statistics
σ(I) <<<< I !!!!!

Issues: very accurate detector mask

Rapid-aquisition PDF

2nd step background subtraction PDFgetx3





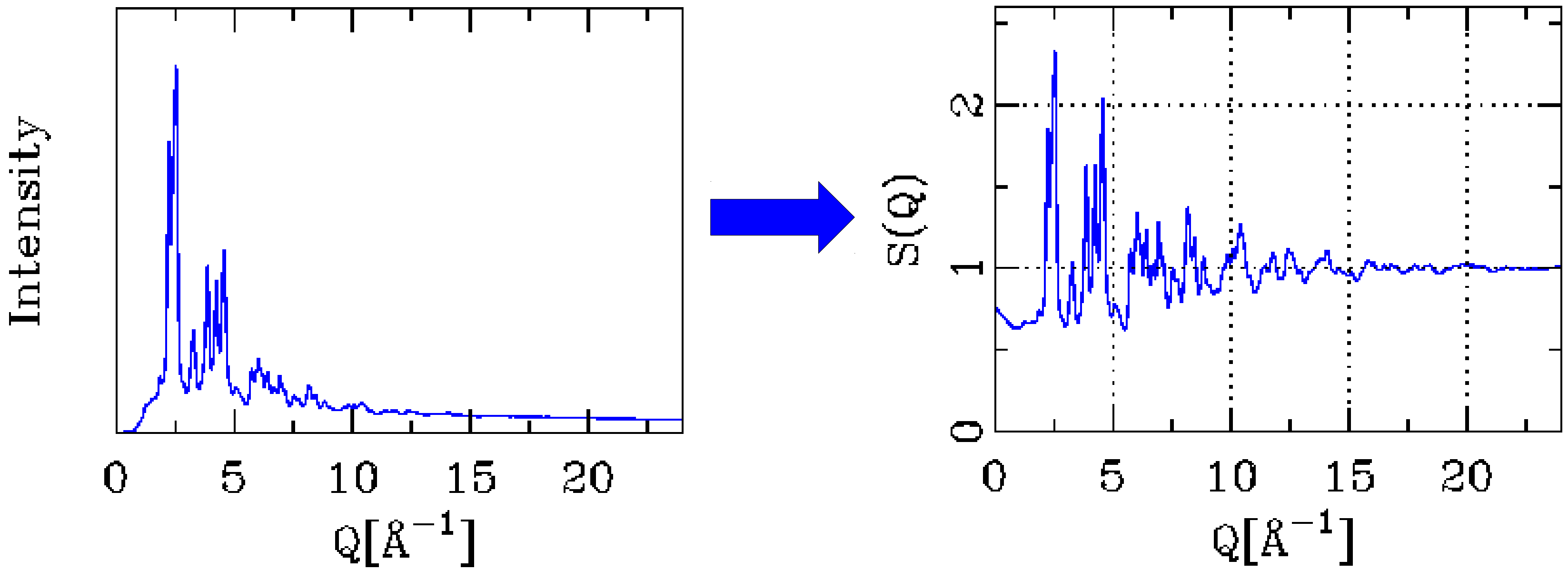
Measure **data** and
background = empty capillary
with good counting statistics

Issues: background scale; I >= zero !

Experimental Determination of the PDF

Rapid-aquisition PDF

3rd step *corrections* PDFgetx3

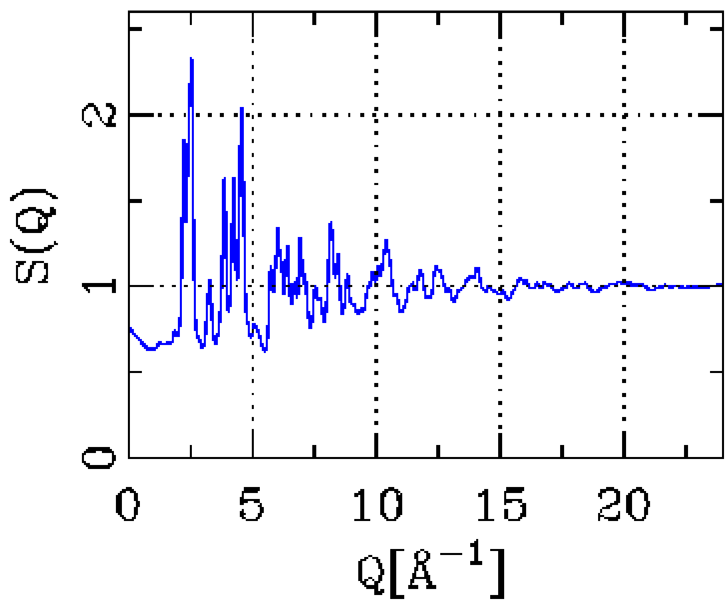


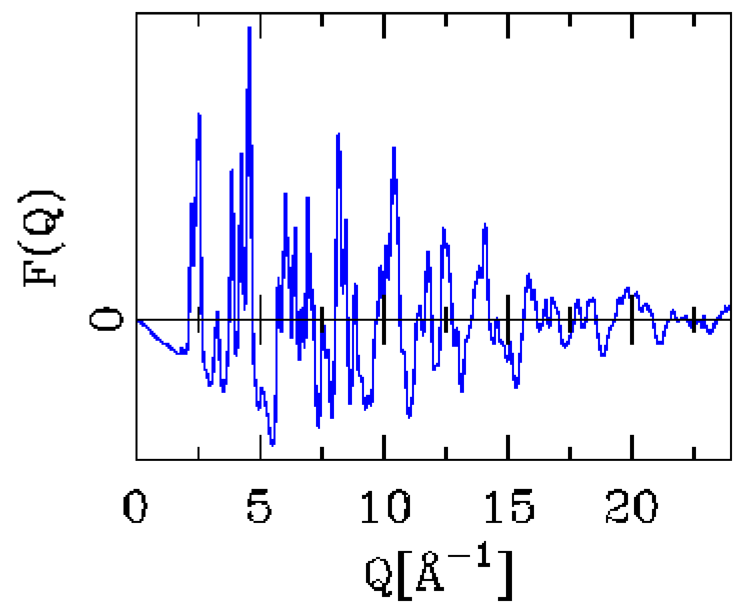
Normalize such that S(∞) = 1.0
(Compton scattering, etc.)
Numerical alchemy

Issues: Is S(q) on average = one
Any odd modulations?
Chemical composition correct?
High absorption ?

Rapid-aquisition PDF

4th step calc F(Q) PDFgetx3





$$F(Q) = Q[S(Q)-1]$$

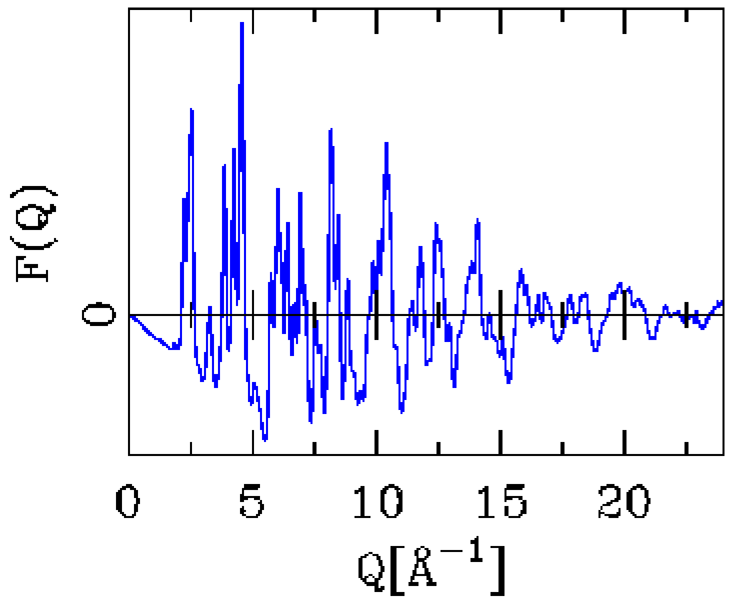
Choose Qmax such that F(Qmax) = 1.0
Qmin usually less critical

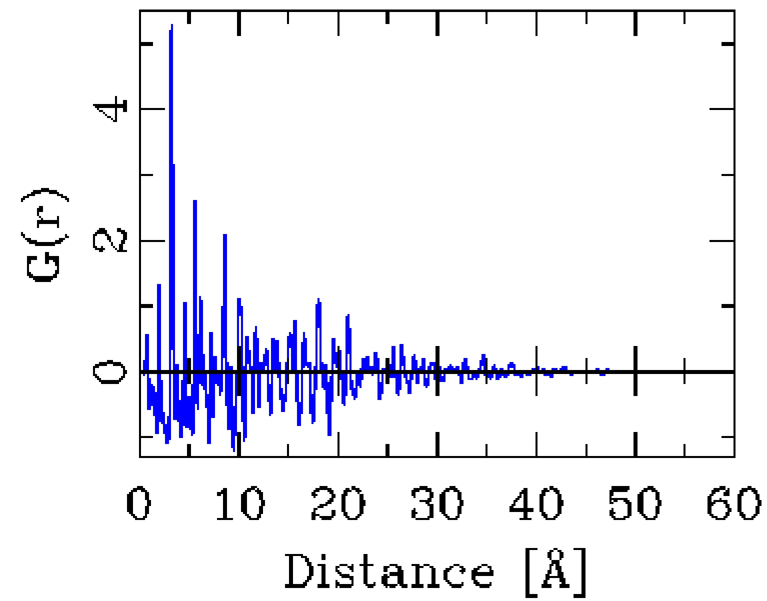
Issues: Is F(q) on average = zero
Any odd modulations?

Experimental Determination of the PDF

Rapid-aquisition PDF

5th step calc G(r) PDFgetx3





$$G(r) = \frac{2}{\pi}\int_0^{\infty} Q[S(Q)-1]\sin(Qr)\,dQ$$

Choose step width ~ 0.01 Å
Rmax a matter of *choice*

Issues: Is G(r) on average = zero
Any odd modulations?
Odd spikes at low R region?
Region below r=*rpoly* is meaningless

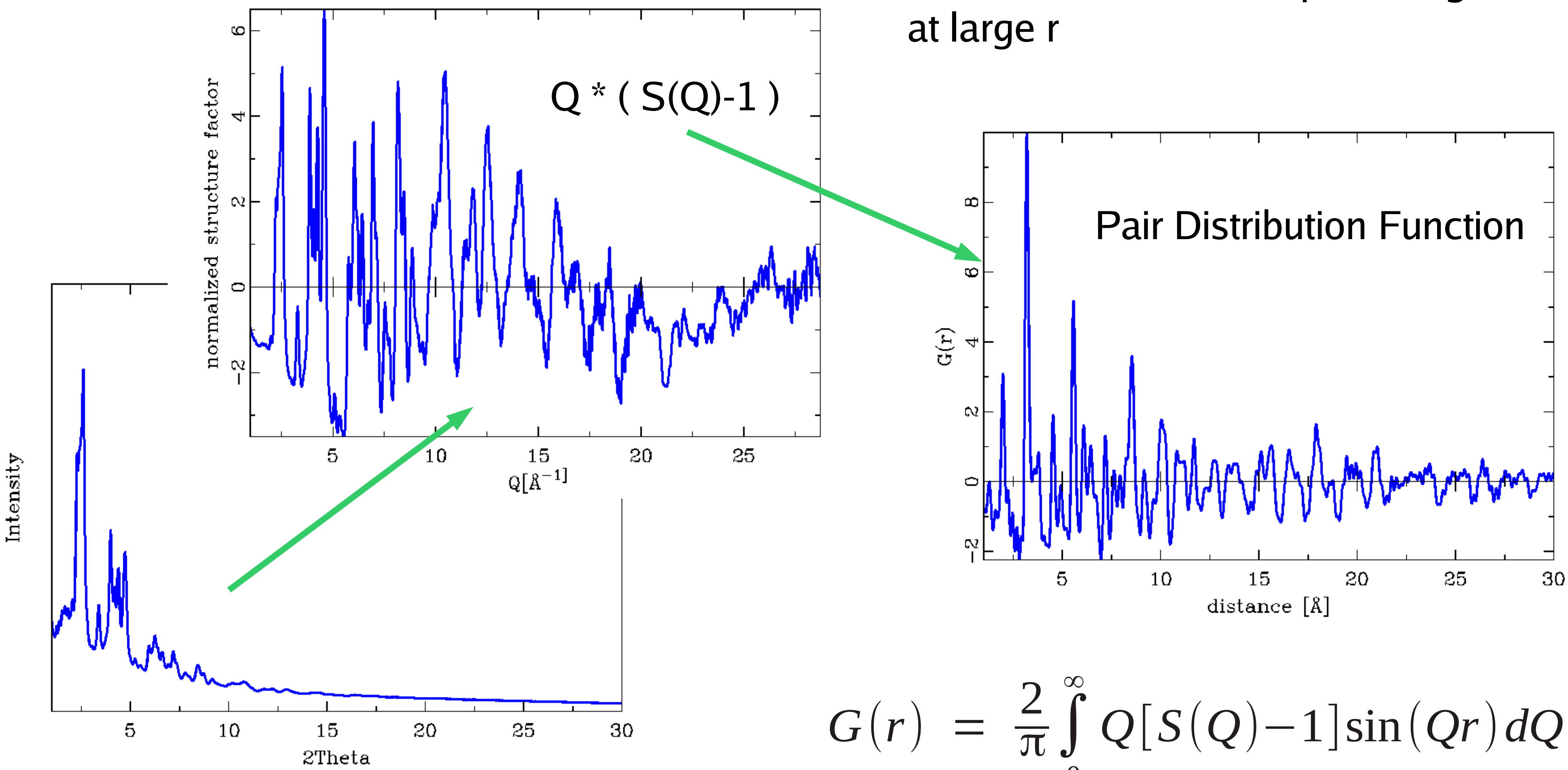
Juhas et al., J. Appl. Cryst (2013) 46, 560

http://www.diffpy.org

Experimental Determination of the PDF

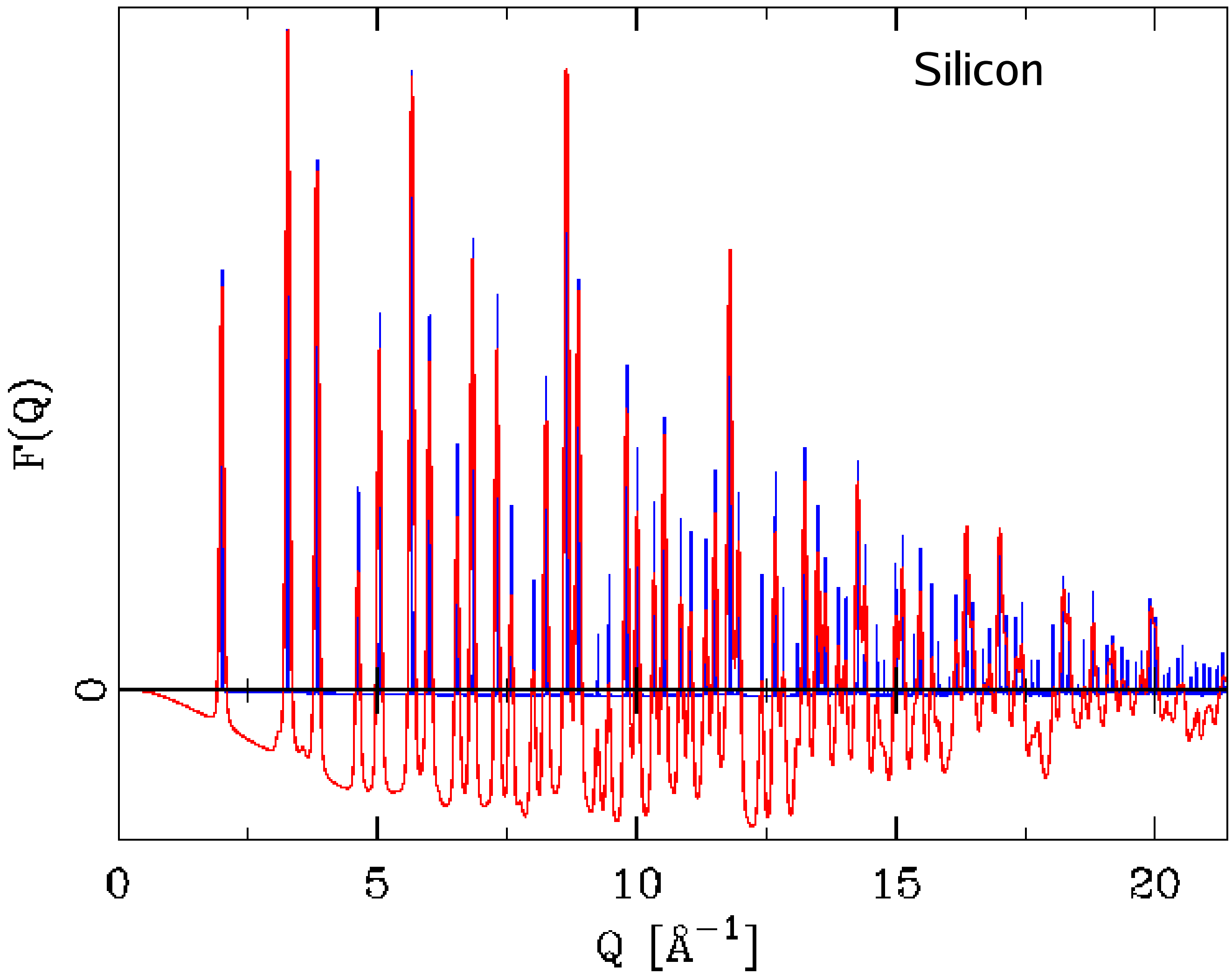
Q_{max} determines width of PDF peaks

Resolution determines peak height at large r



$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin(Qr)\,dQ$$

Experimental Determination of the PDF, Intsrumental resolution

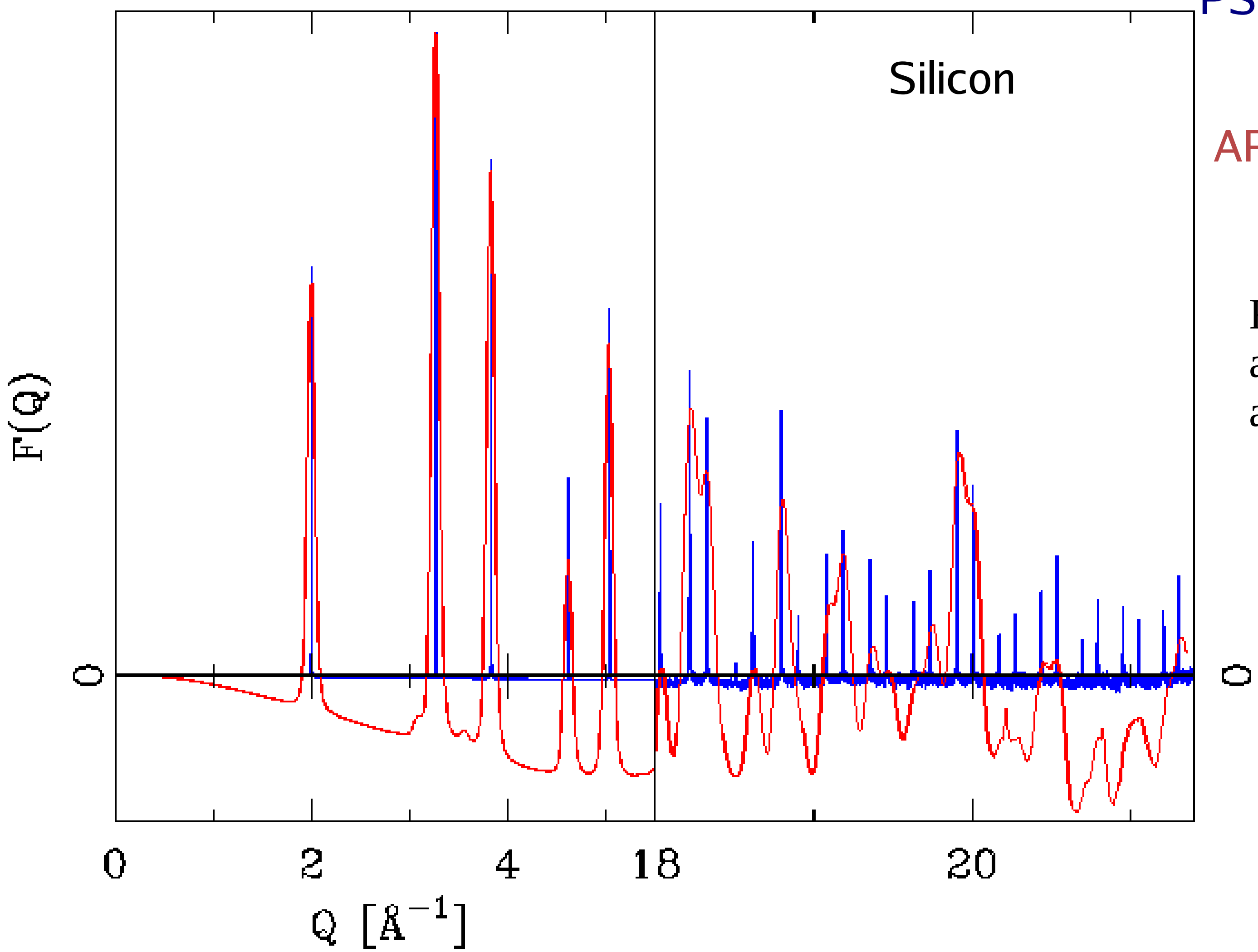


PSI high resolution data
~ 30 min

APS low resolution data
~ 1 min

Reflections well resolved at PSI up to and beyond 21.4 Å^{-1}

Experimental Determination of the PDF



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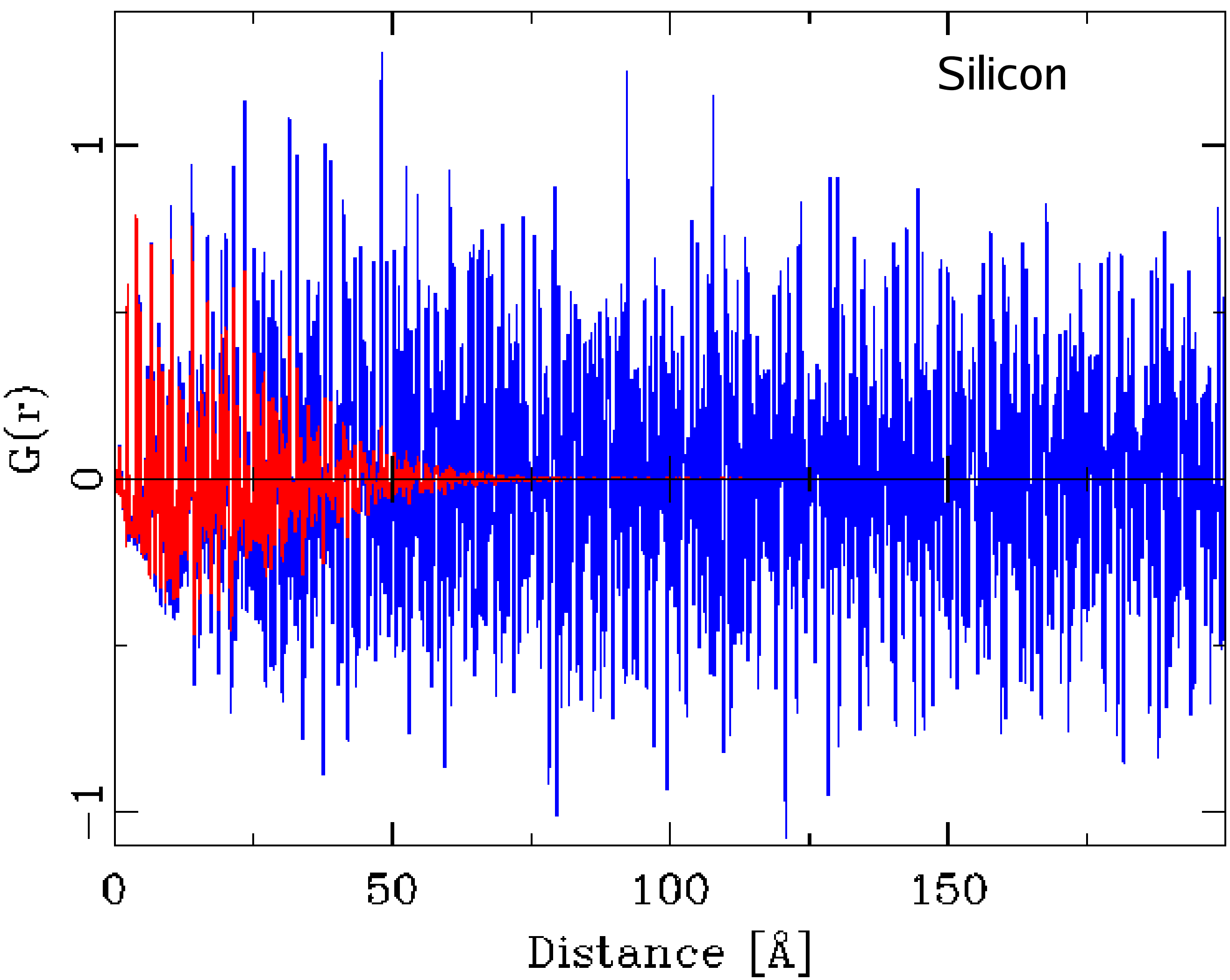

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~ 30 min

APS low resolution data
~ 1 min

Reflections well resolved at PSI up to and beyond 21.4 $Å^{-1}$

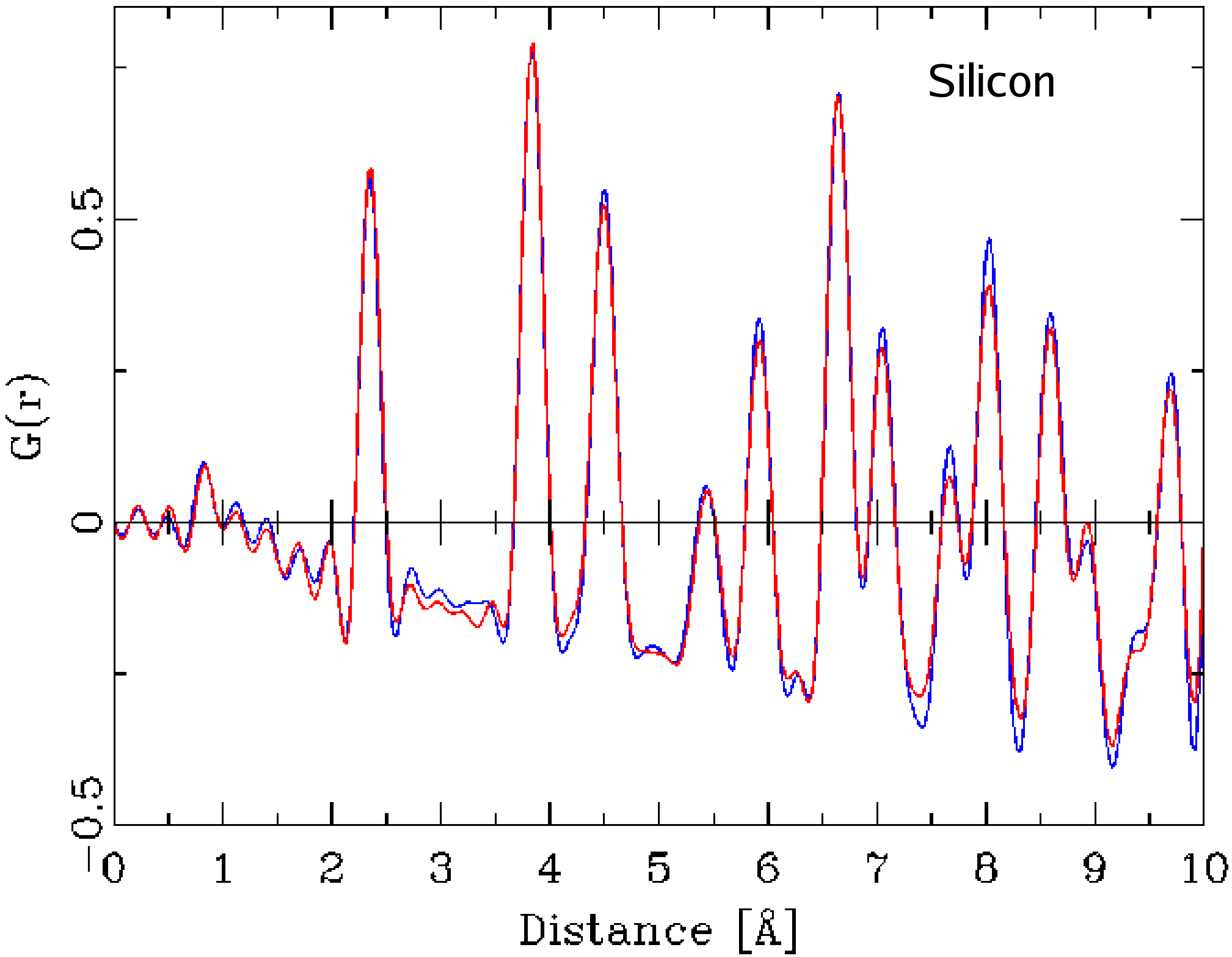
G(r) @ PSI extents well beyond 200 Å !

G(r) @ APS almost ZERO beyond 70 Å !

PDF peak height influences determination of nanoparticle diameter

High resolution NOT needed for small (<5nm) objects; only good if sample has narrow Bragg

Experimental Determination of the PDF



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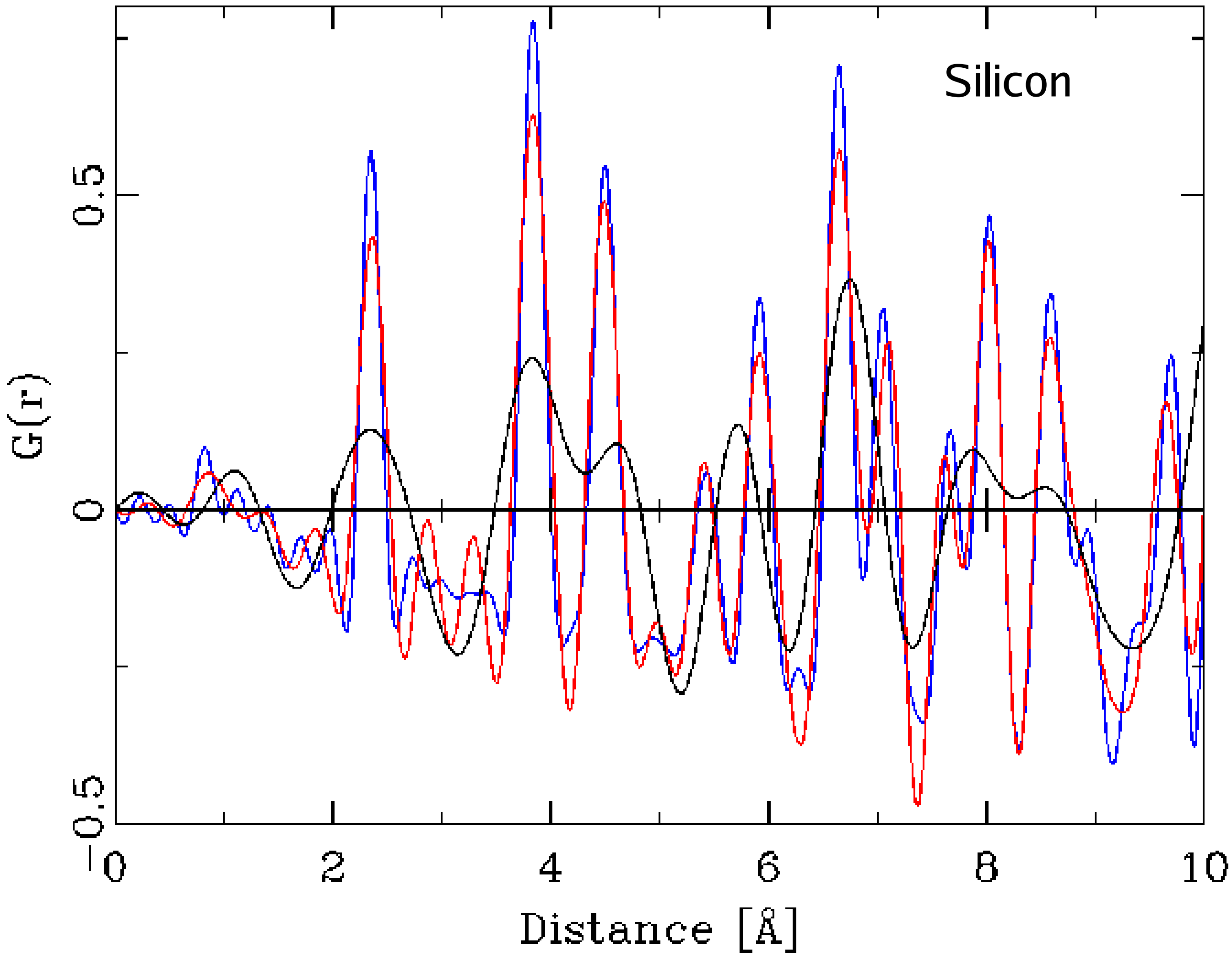
Reflections well resolved at PSI up to and beyond 21.4 $Å^{-1}$

G(r) @ PSI extents well beyond 200 Å !

G(r) @ APS almost ZERO beyond 70 Å !

Width of PDF maxima is identical
(at least for low r-region)

Experimental Determination of the PDF, Effect of Q_{max}



PSI high resolution data
Silicon

Q_{max} = 21. Å^{-1}
Synchrotron

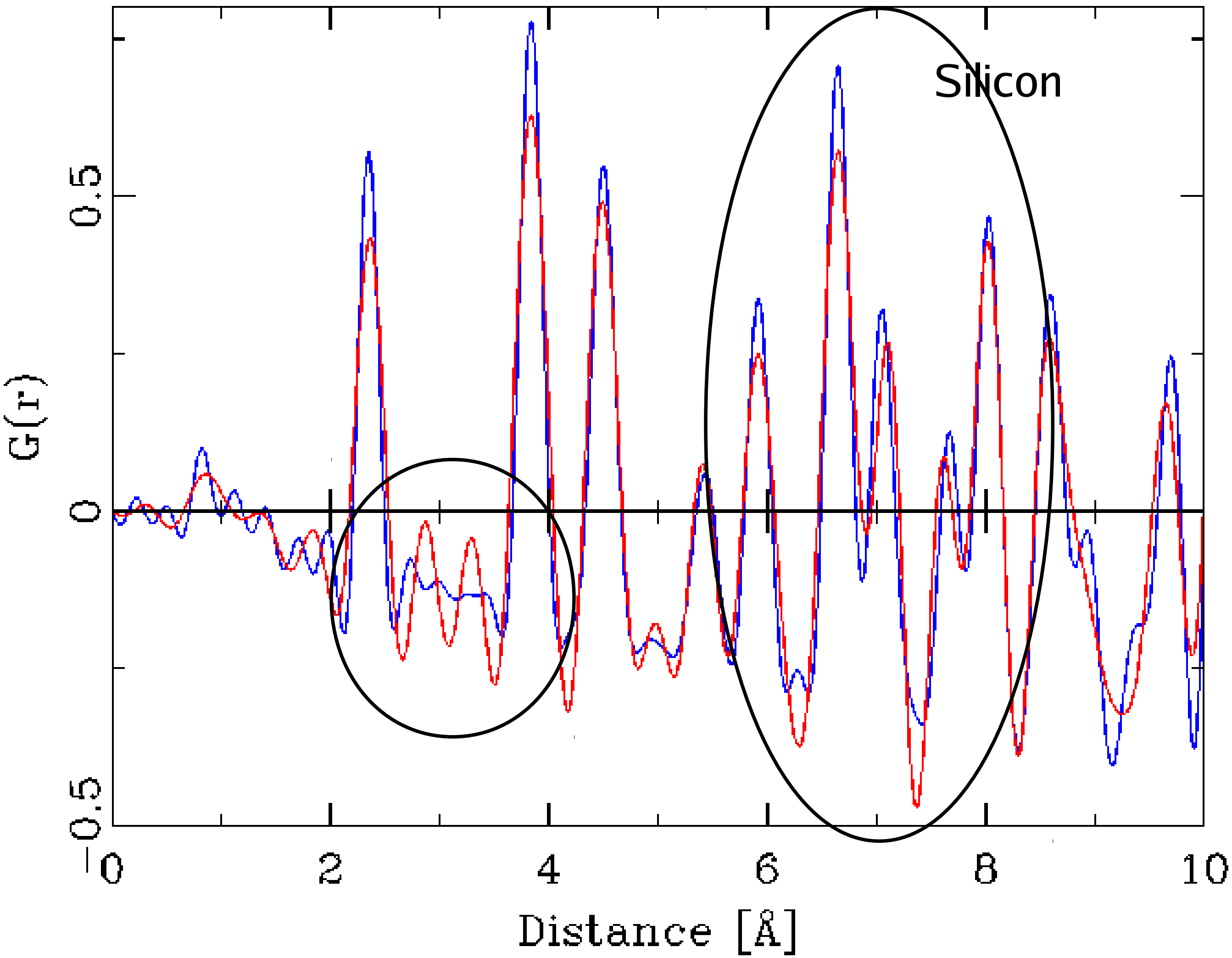
Q_{max} = 15. Å^{-1}
Mo-Kα

Q_{max} = 7. Å^{-1}
Cu-Kα

Width of PDF maxima decreases with increasing Q_{max}

Reasonable for Q_{max} > 20 Å^{-1}

Experimental Determination of the PDF, Effect of Q_{max}



PSI high resolution data
Silicon

Q_{max} = 21. Å^{-1}
Synchrotron

Q_{max} = 15. Å^{-1}
Mo-Kα

Apparent shift of smaller PDF maxima !?!

decreases with increasing Q_{max}

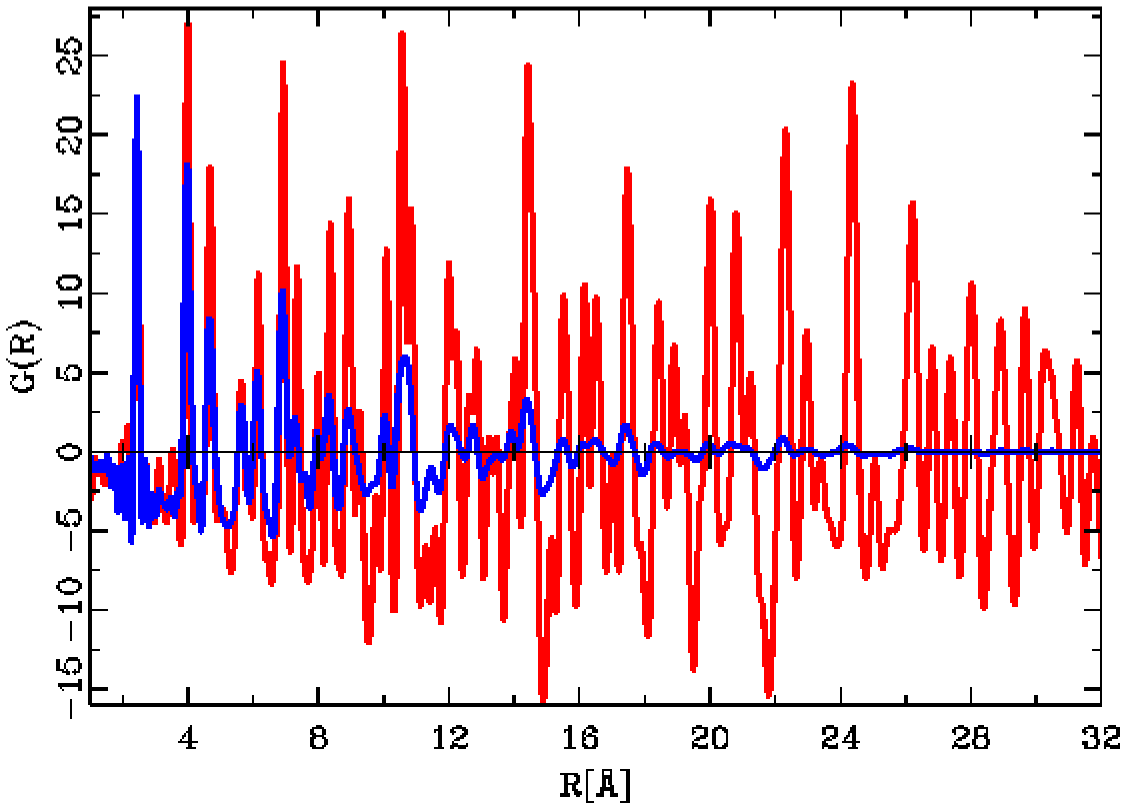
Be careful with direct interpretation of peak positions!

Local disorder in Si !?!

Anything that changes with Q_{max} is not real

Always calculate PDF for several different values of Q_{max}

Interpretation of the PDF; ZnSe nanoparticles

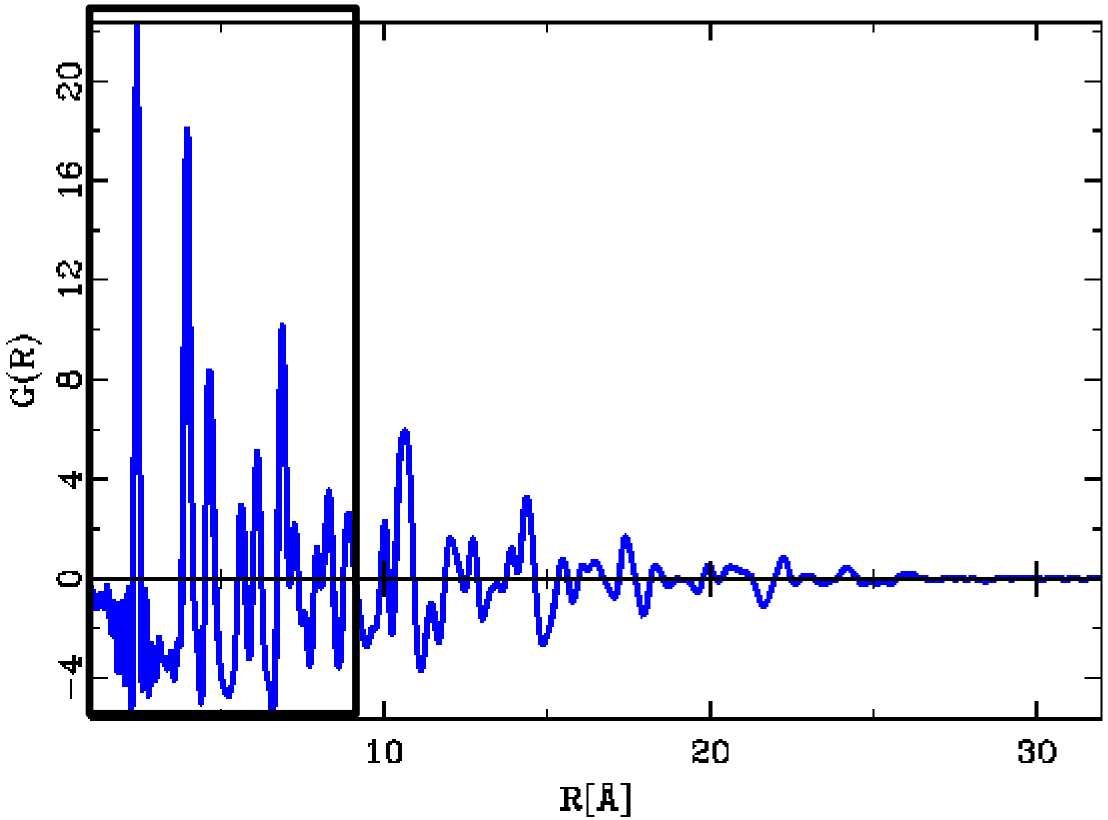


crystalline ZnSe

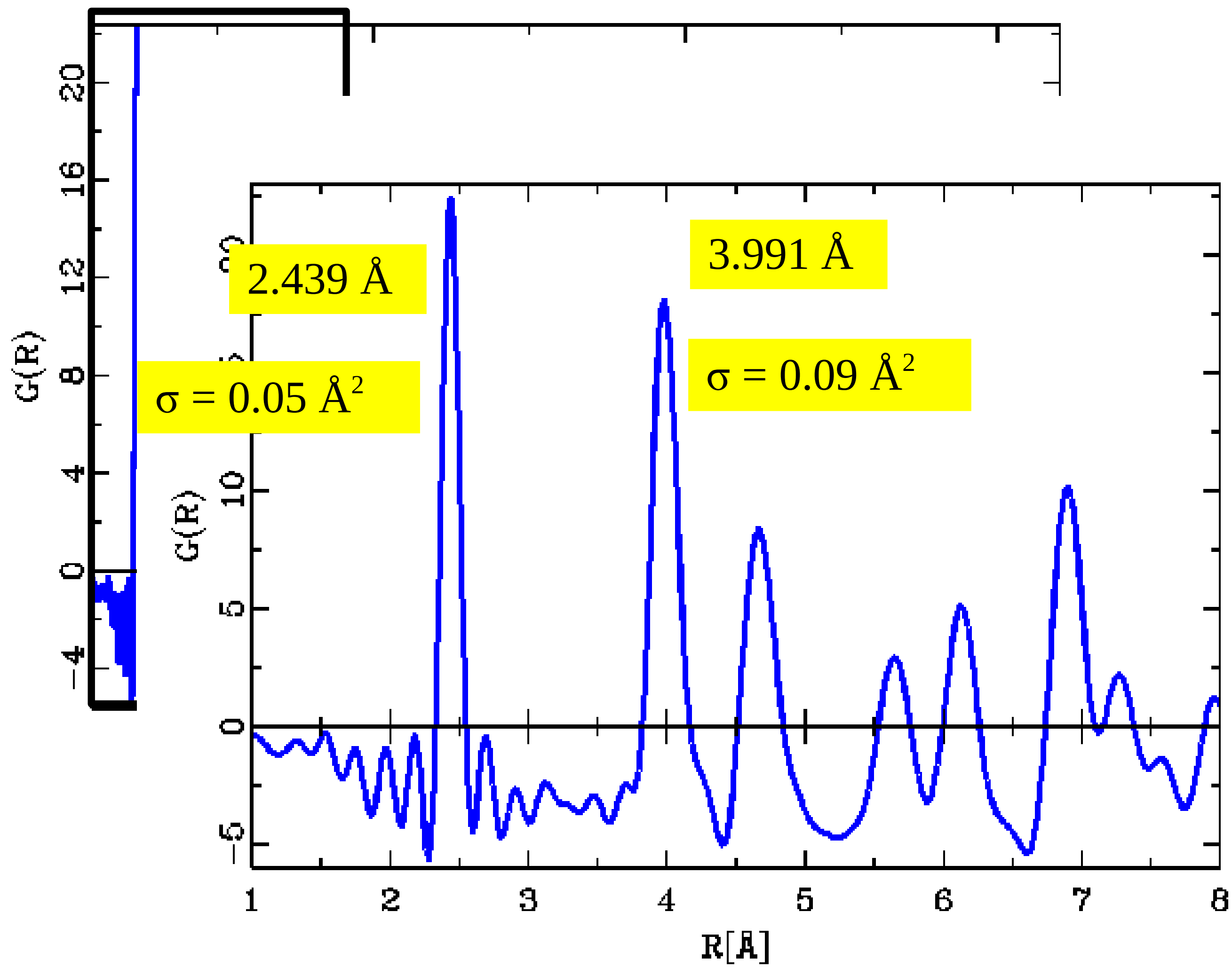
nanocrystaline ZnSe

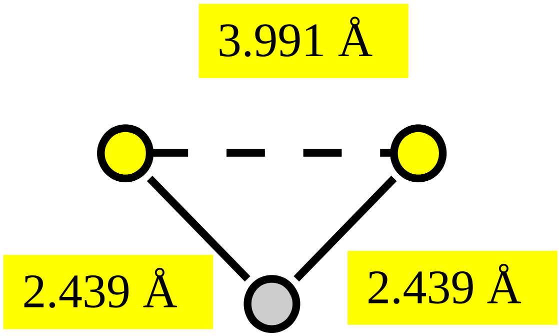
data collected under identical conditions

ZnSe nanoparticles



ZnSe nanoparticles

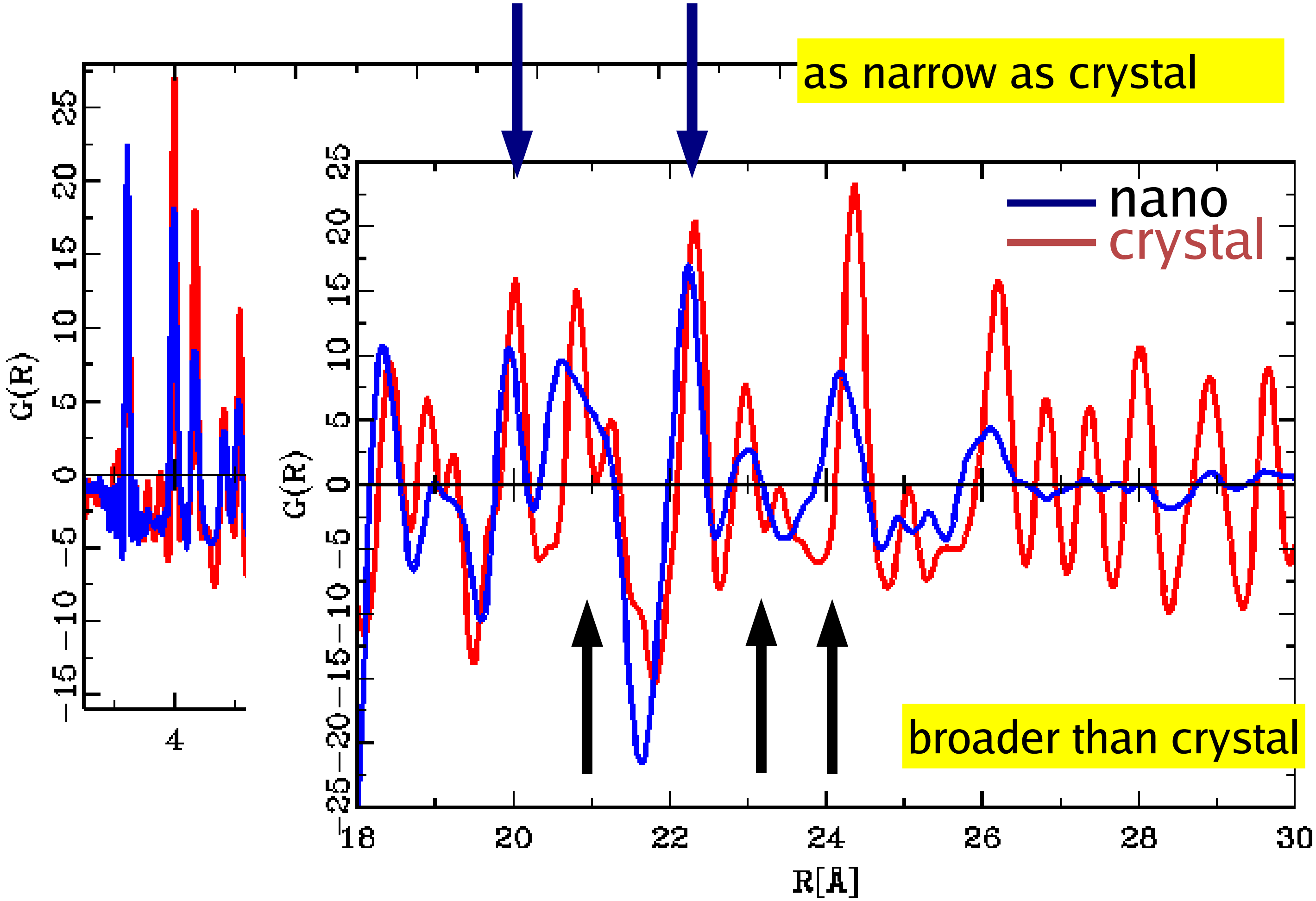


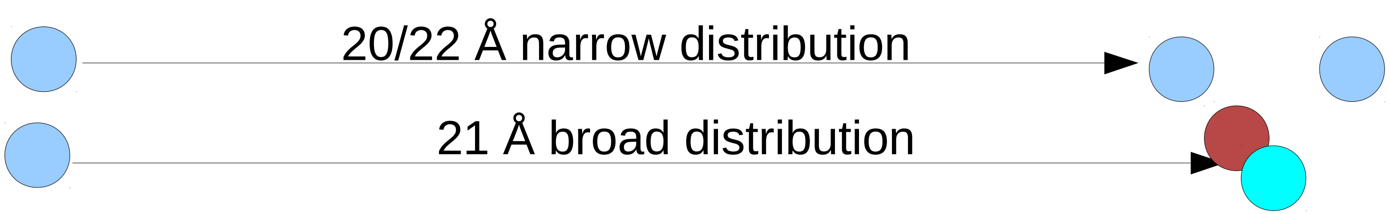


tetrahedral structure

bond angle 109.8

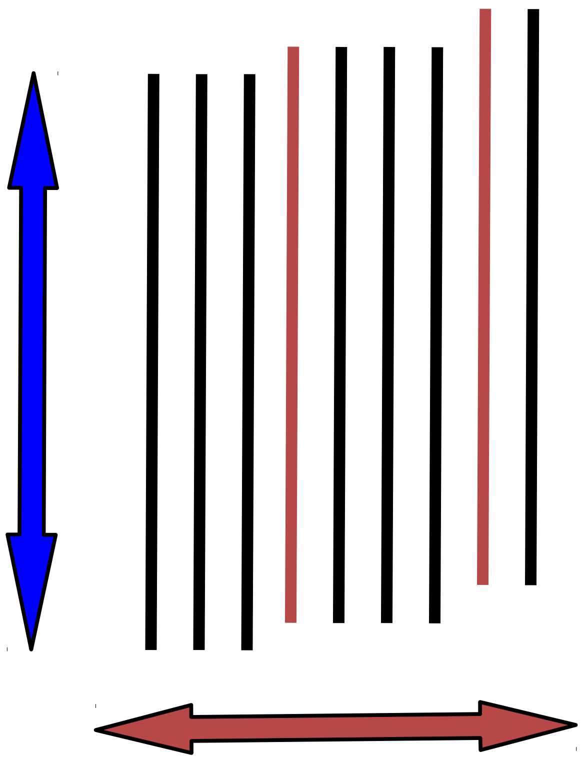
ZnSe nanoparticle: Indication of stacking faults





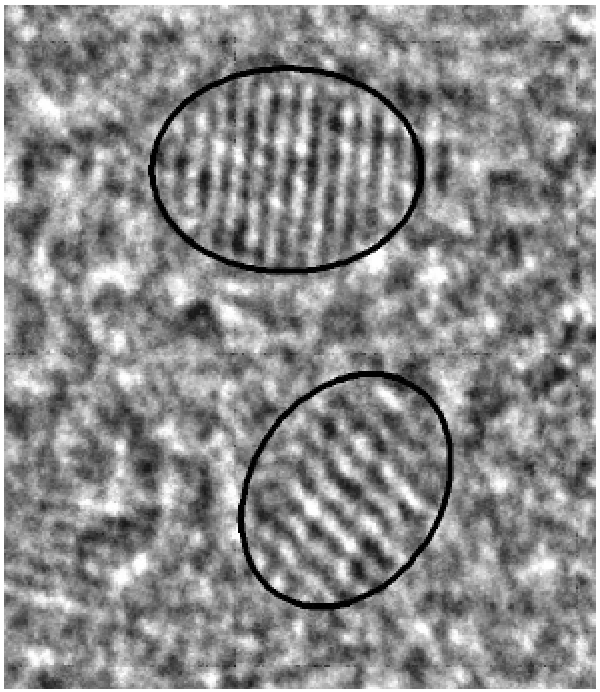
ZnSe nanoparticle: indication of stacking faults

structural coherence

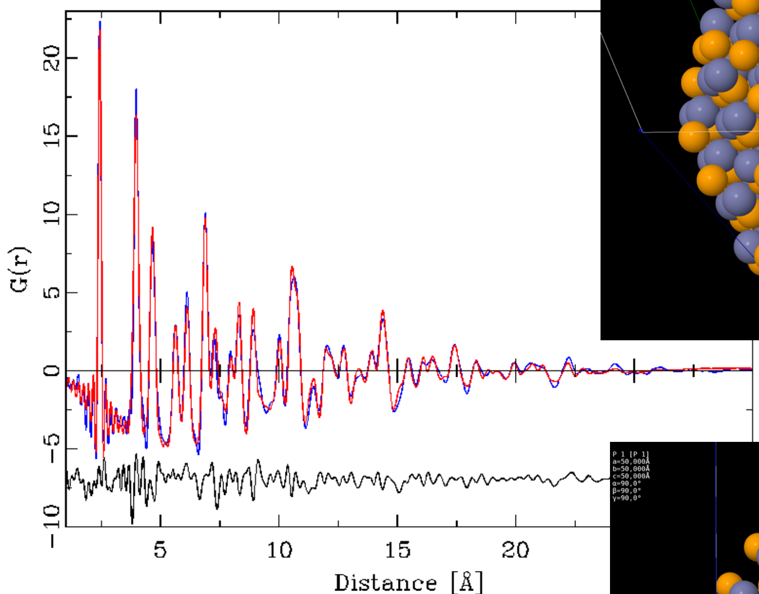


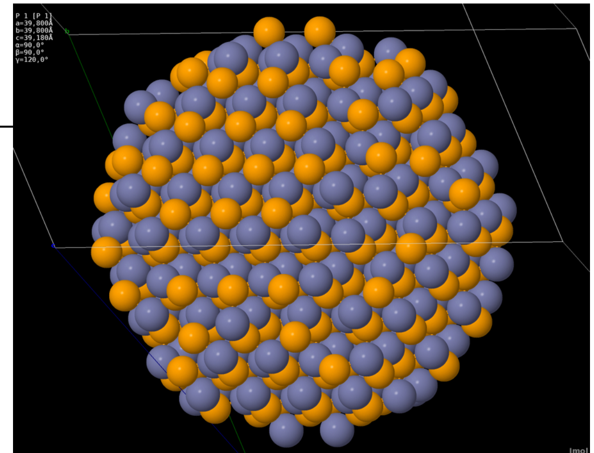
loss of coherence due
to stacking faults

~8 to 10 monolayers
= 4 to 5 unit cells along c
= 24 to 30 Å

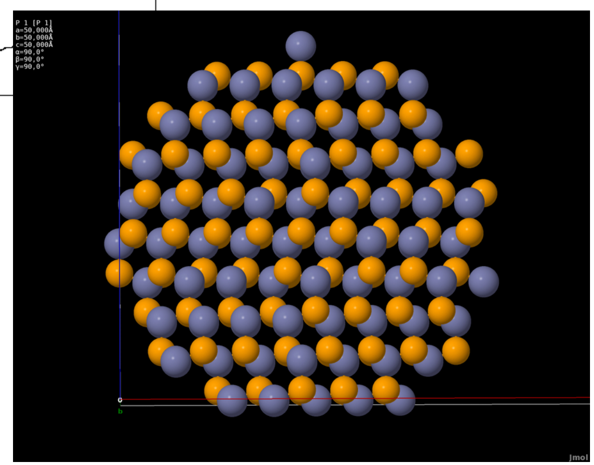


Calculate **all** atom positions





Presence of **defects**



3 nm sphere **600 atoms**
1800 coordinates !
600 ADP's !

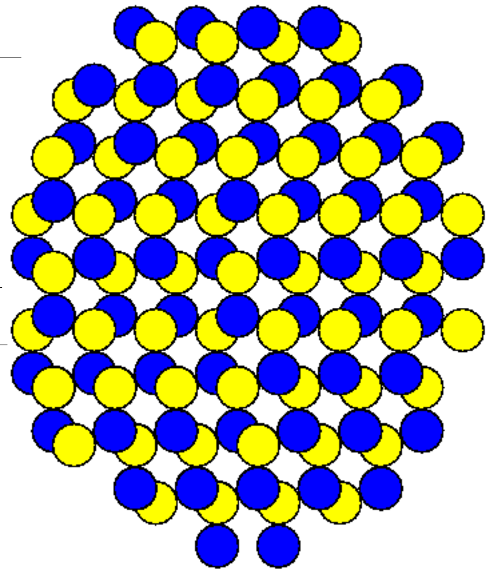
Parameterize description
coordinates in asymmetric unit
symmetry
diameter
2 lattice parameters
1 coordinate
1 ADP
1 radius

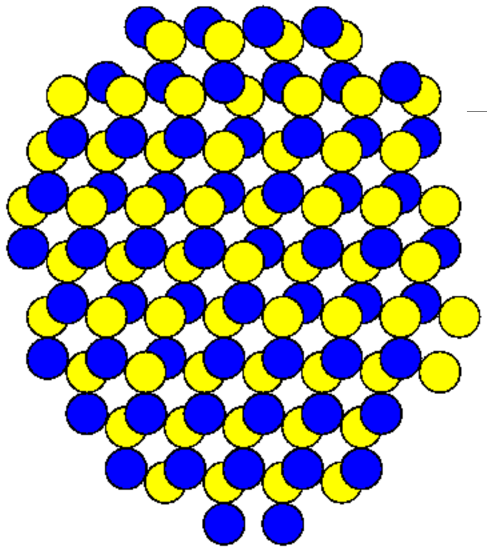
Parameterize description
probability of faults
strain field
chemical short range order
etc....
1 probability

limited only by imagination

BUT

Aspects of PDF calculation for small nanoparticles

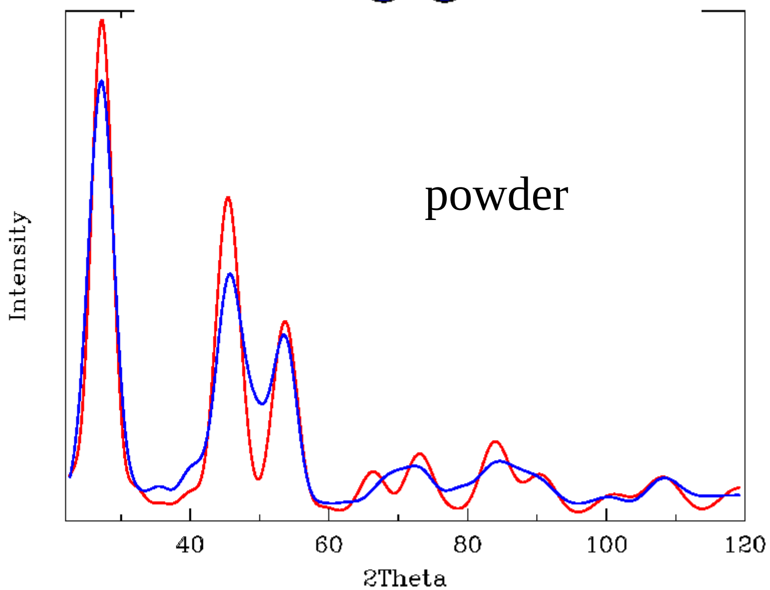


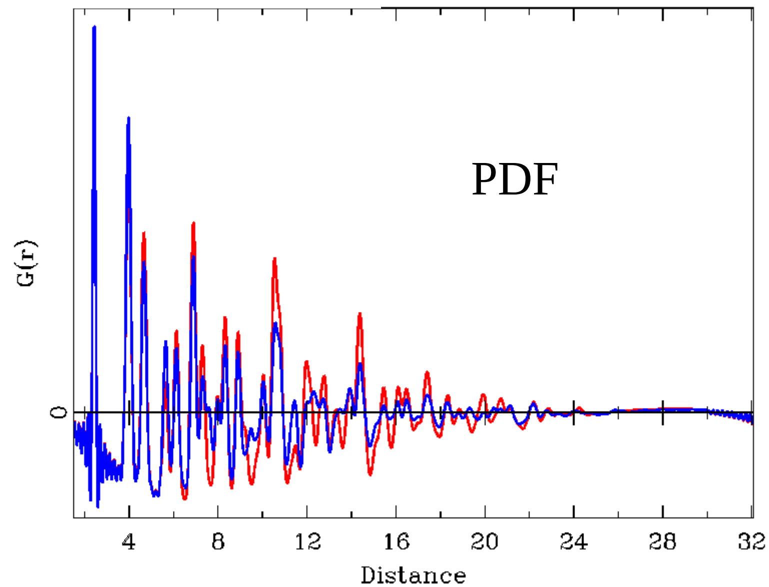


10 layers
simulated with
identical parameters

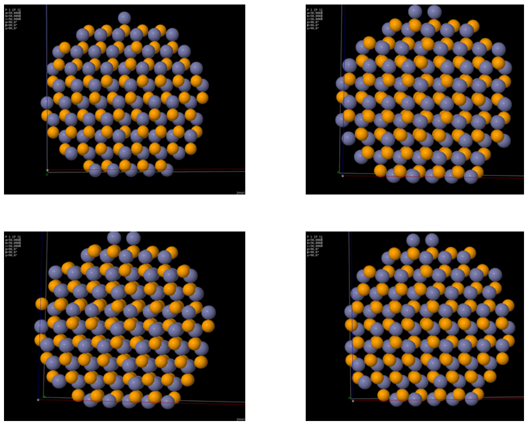
individual location
of stacking faults

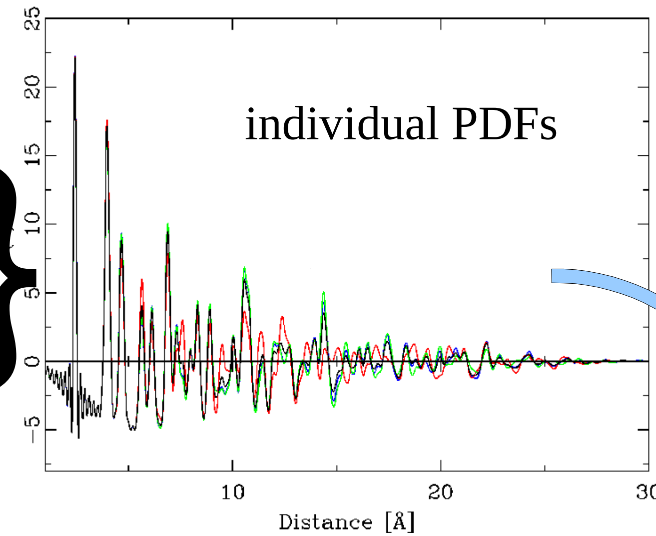
each particle is not
representative
==> need to average





Ensemble modelling





Calculate (many) individual nanos

Average PDF / powder pattern

coordinates in asymmetric unit

symmetry

diameter

defects

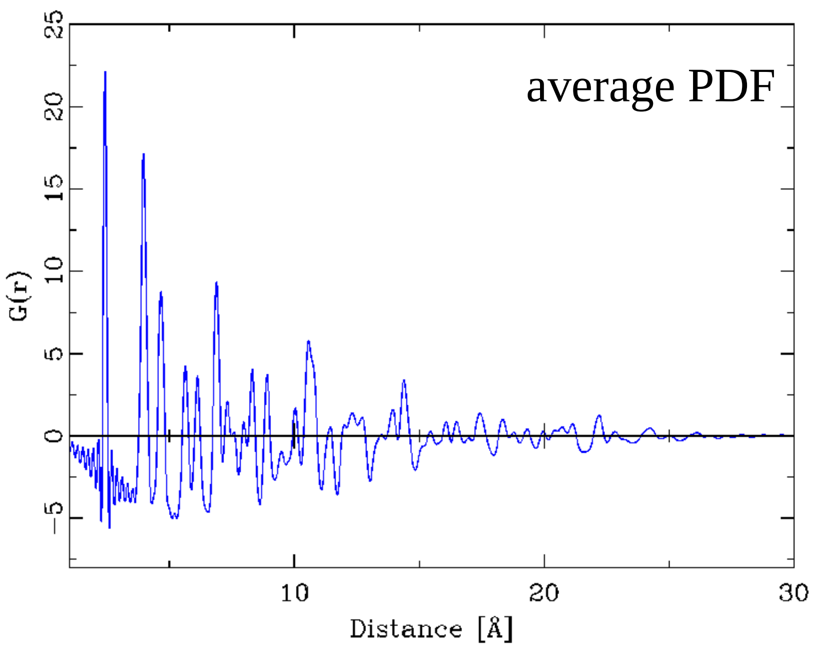
2 lattice parameters

1 coordinate

1 ADP

2 radii

1 probability



BUT

incoherent average of PDFs

requires evolutionary refinement

no Least-Squares

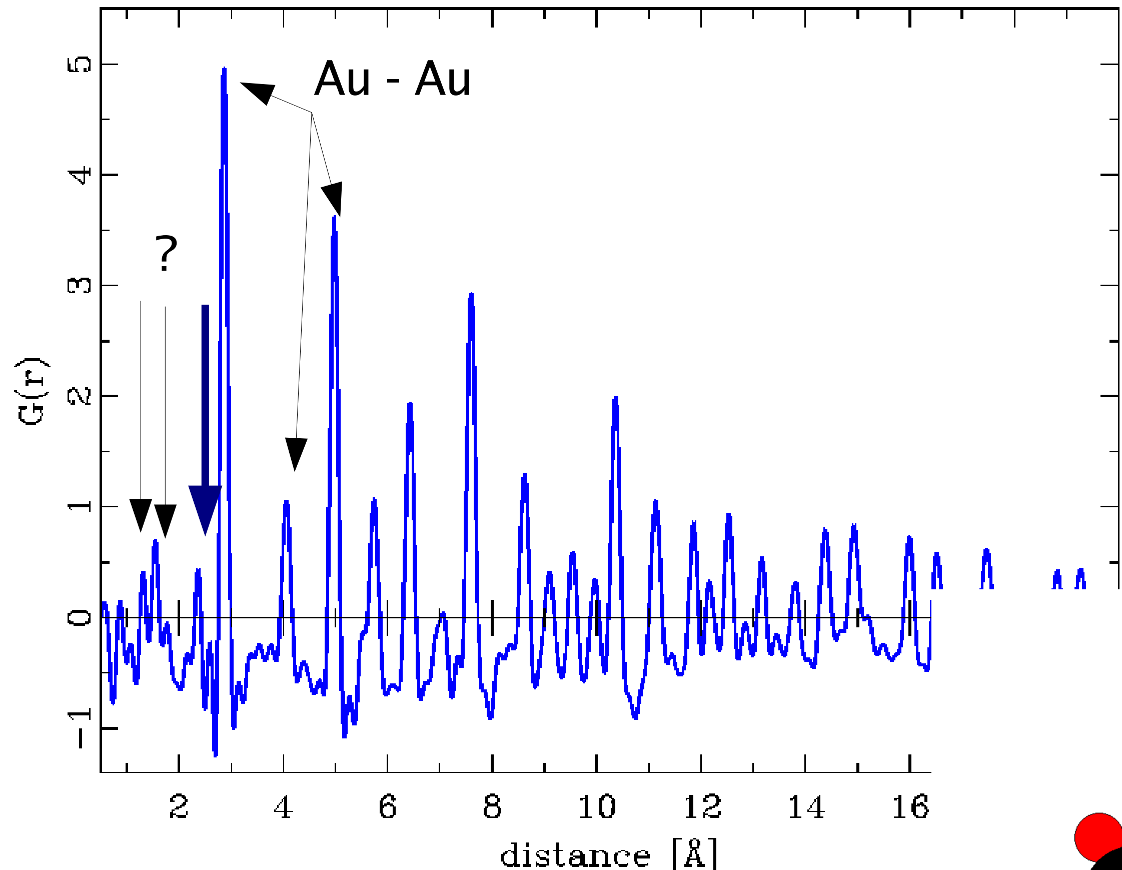
expensive

Niederdraenk et al. Phys.stat.sol c (2007);
Niederdraenk et al. PCCP (2011)

Nanoparticle + Ligand + Neutron Scattering

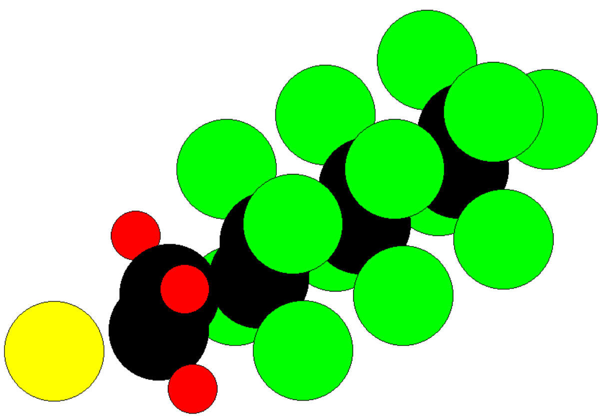
Gold -Ligand
Au – S 2.42Å

Ligand - Ligand
C-C 1.5Å
C-F 1.3Å



Au
F m 3 m
a 4.064 Å
Au-Au 2.837Å

Number ?
Placement ?
Composition ?



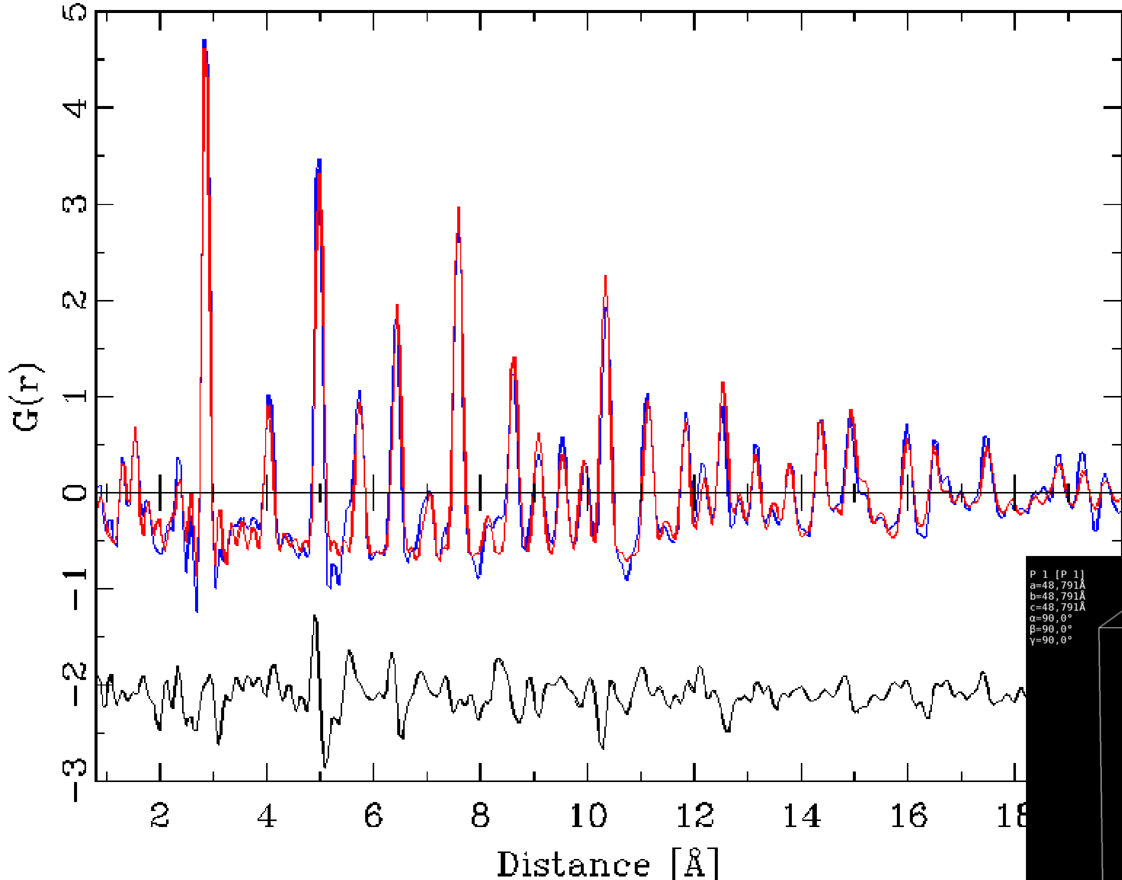
15 K
NPDF, Los Alamos
K. Page, Th. Proffen, T. Cheetham

Au + S-CH2-CH2-(CF2)5-CF3
$S\ C_8\ H_4\ F_{13}$

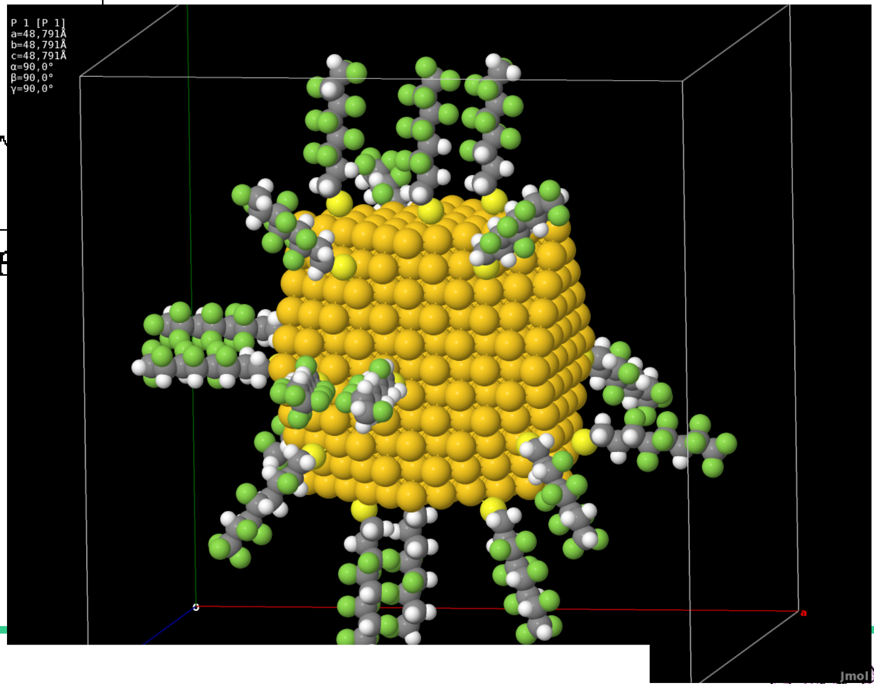
Ligand internal distances
from DFT calculations

Page, *et al.*, *Chem. Phys. Lett.* **393** (2004) 385-388.

Nanoparticle + Ligand



a(Au)	4.0658Å	(1)
Au – Au	2.8750Å	(1)
B(Au)	0.32Å^2	(4)
B(Ligand)	0.45Å^2	(10)
Diameter	20Å	(2)
N(ligand)	20	(6)
P(Fluorine)	0.65	(15)
Au – S	2.42Å	fixed!

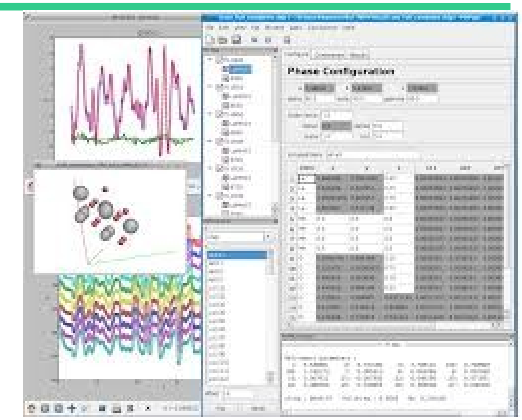


15 K
NPDF, Los Alamos

K. Page et al. J. Appl. Cryst. (2011)

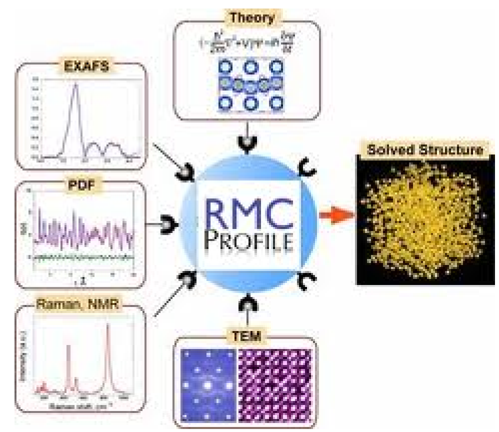
Small Box Modelling

PDFgui



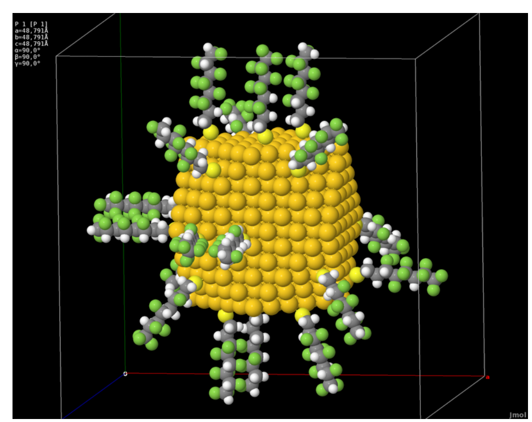
Large Box Modelling

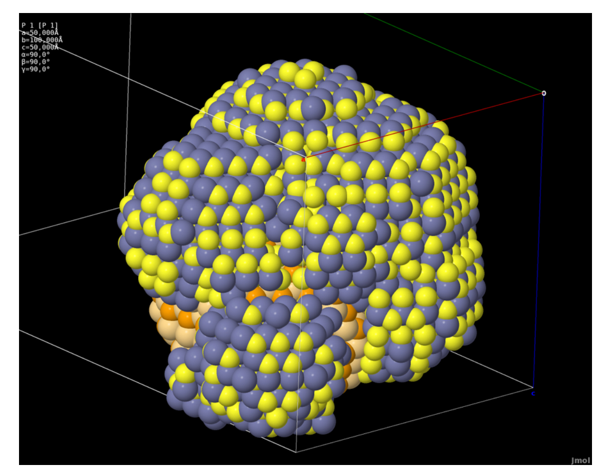
Reverse Monte Carlo
RMCprofile
RMC_POT++
DISCUS



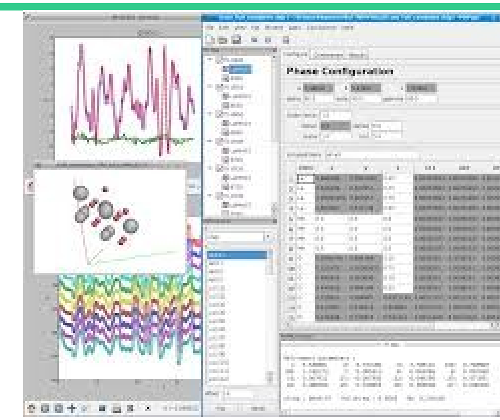
Bottom Up Modelling

DISCUS





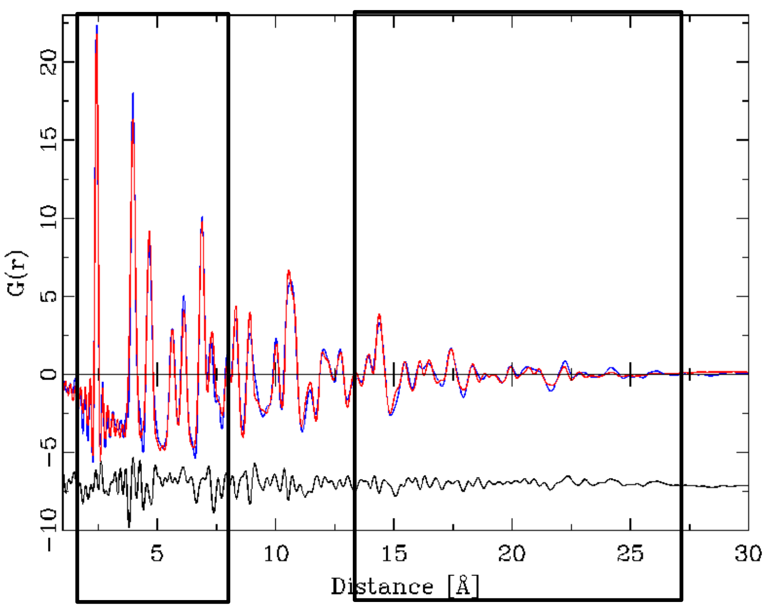
Small Box Modelling

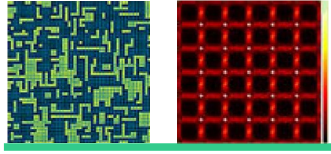


Rietveld type refinement

Calculate PDF from single unit cell or **small** block of cells

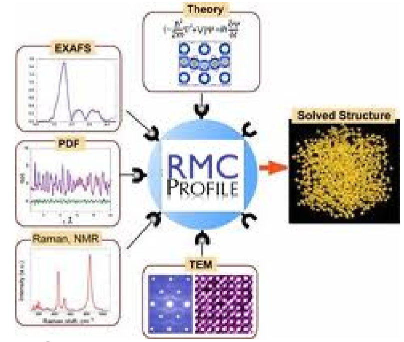
Determine changes in local versus moderate structure by
Separate refinement in restricted r-range



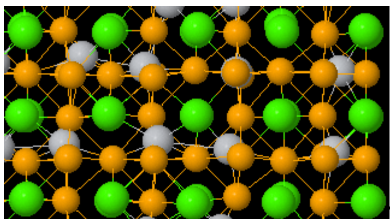


Large Box Modelling

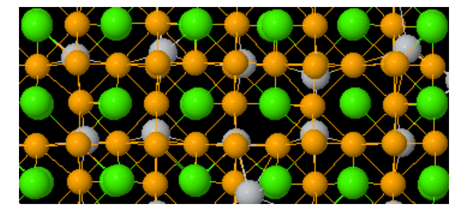
Reverse Monte Carlo
RMCprofile
RMC_POT++

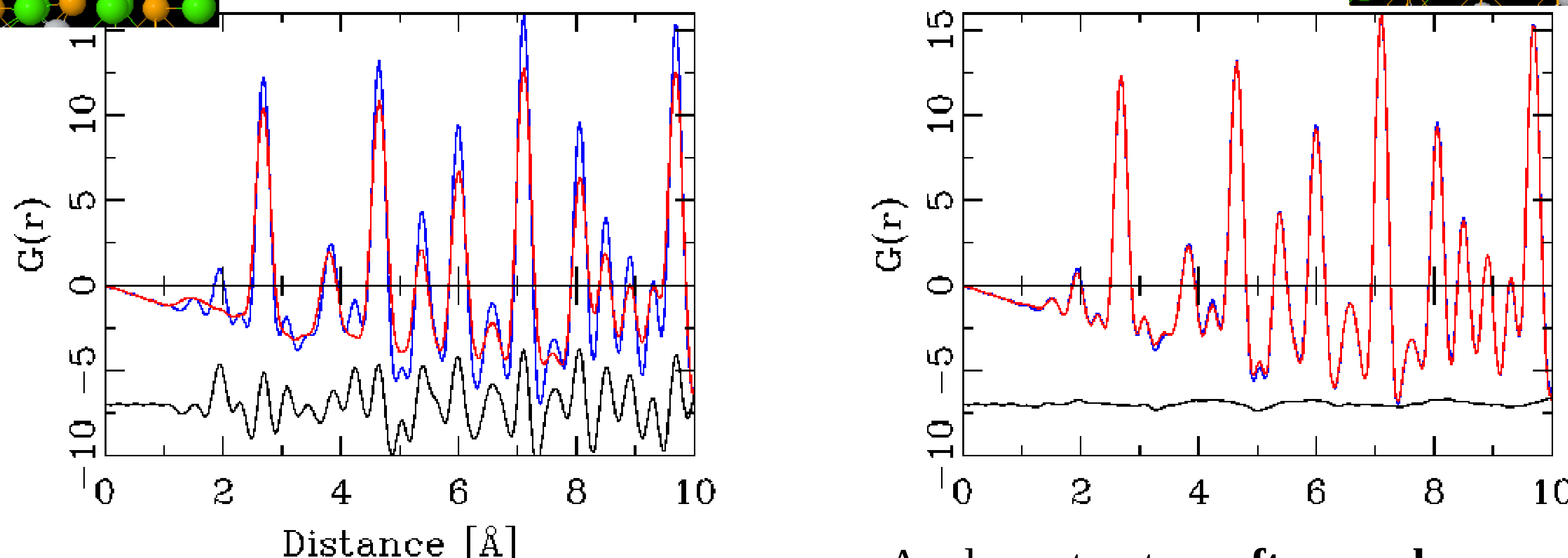


Model initial (random) **large** structure
Calculate PDF (+ powder + ...)



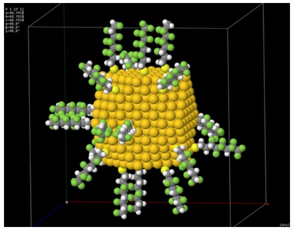
Modify structure (shift, exchange...)
while agreement improves
Usually requires constraints!

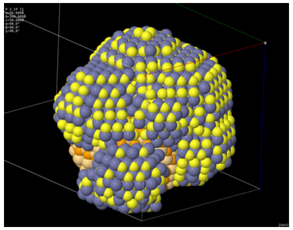




Analyze structure **afterwards**
Local coordination, shifts, etc.

Bottom Up Modelling DISCUS





Define disorder rules to simulate complete structure

Non-periodic boundary conditions

Extended defect toolboxes

Resources

Egami, T. & Billinge, S.J.L.	Underneath the Bragg Peaks, Elsevier
Dinnebier, R.E. & Billinge, S.J.L.	Powder Diffraction, RSC Publishing
Guagliardi, A. & Masciocchi, N.	Diffraction at the Nanoscale
Neder, R.B. in	Structure from Diffraction , Wiley
Nield, V. & Keen, D. A.	Diffuse Neutron Scattering from Crystalline Materials, Oxford
Welberry, R.	Diffuse X-ray Scattering and Models of Disorder, Oxford
Neder, R. & Proffen, T	Diffuse Scattering and Structure Simulation, Oxford

Beam lines
Synchrotron
11-ID-B APS
ID15-B, ESRF
P02, DESY
P21, DESY
Diamond

Beam lines
Neutron
GEM, ISIS
POLARIS, ISIS
NOMAD, SNS; Oak Ridge

Thank you for your attention

PDFGui, SrFit: www.diffpy.org

RMCProfile: www.rmcprofile.org

RMC_POT: www.szfki.hu/~nphys/rmc++/opening.html

DISCUS: discus.sourceforge.net

Advanced PDF experiments

R-dependent refinement

In-situ studies

Catalysts	K. Chapman, P. Chupas
Nanoparticle growth	R.B. Neder B. Iversson
Batteries	

Element specific anaomalous scattering V. Petkov

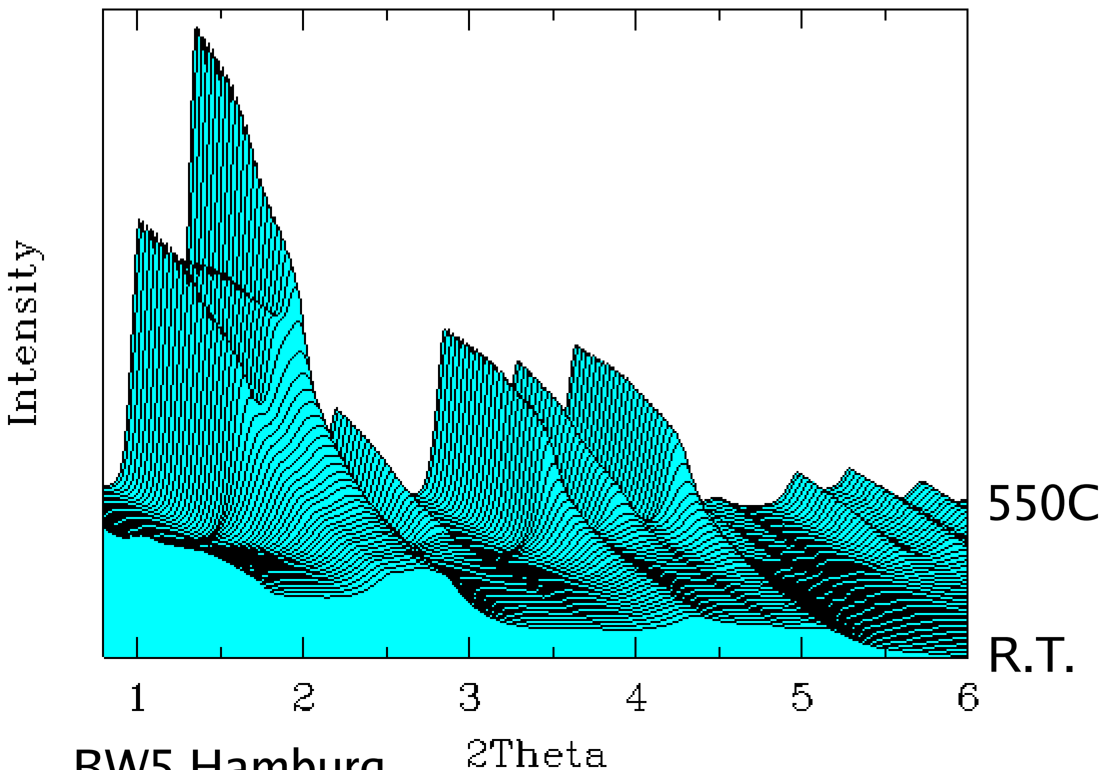
Several measurements close to an absorption edge

Neutron PDF

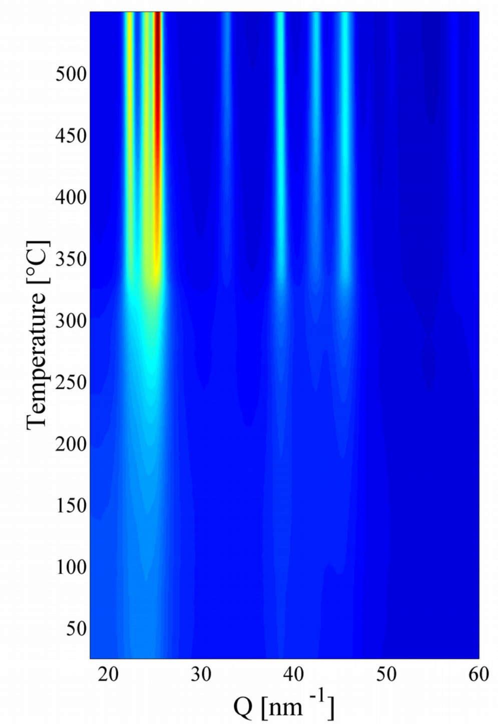
Electron PDF

Single crystal 3D PDF Th. Weber, ETH Zürich

ZnO in-situ obervation during heating run



BW5 Hamburg



4K / min

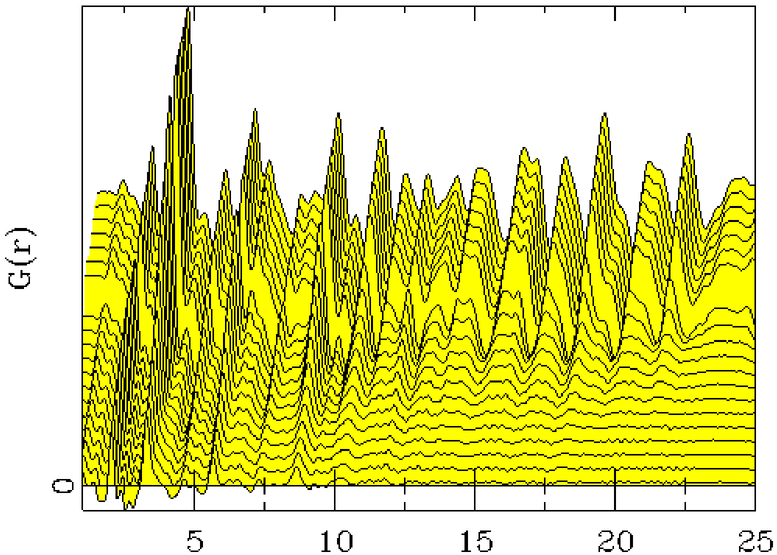
1s/frame ==> 30 per image

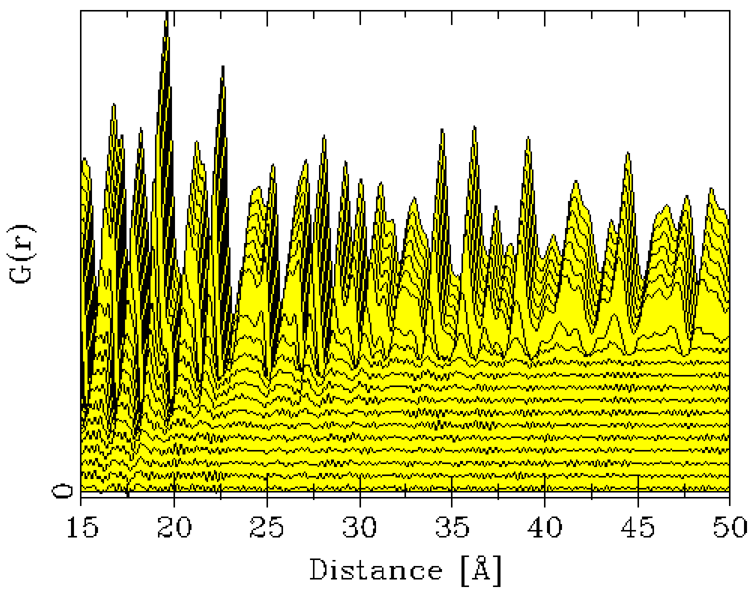
λ = 0.123 Å

Thermal annealing of ZnO nanoparticles at T ==> 550°C

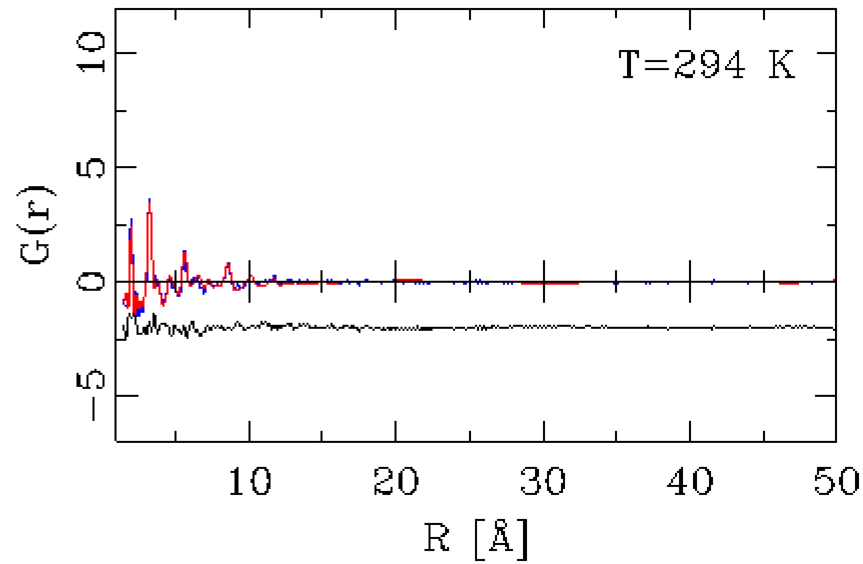
Solid state growth

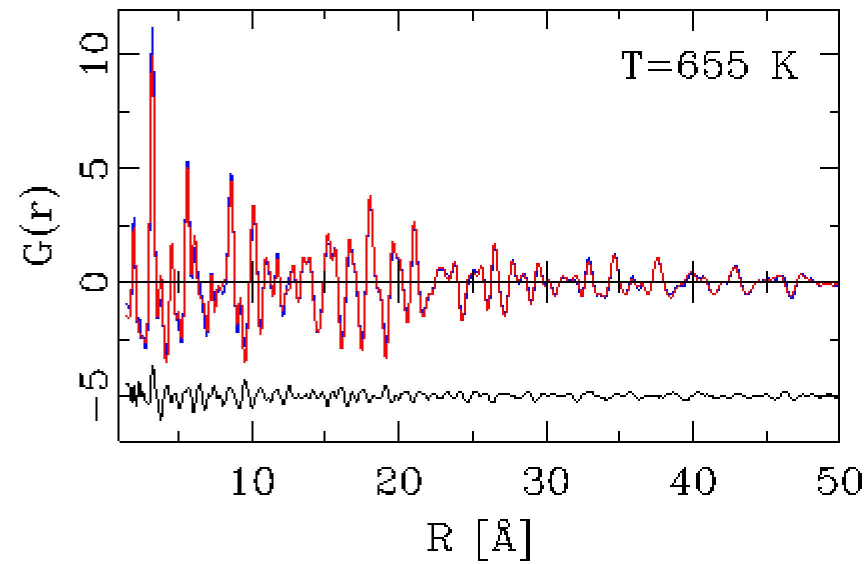
ZnO in-situ obervation during heating run



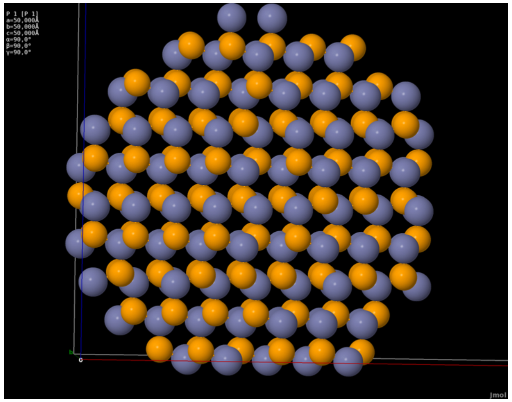


Explicit model
Triaxial ellipsoid
Wurtzite structure
Stacking faults

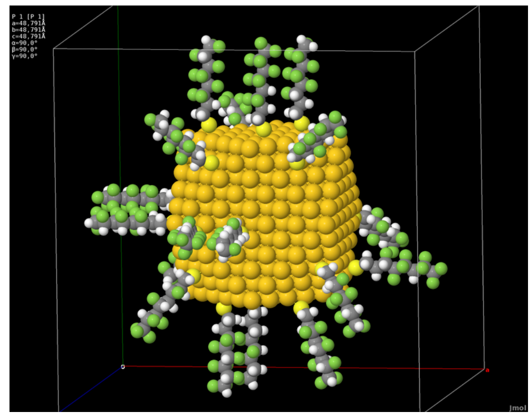




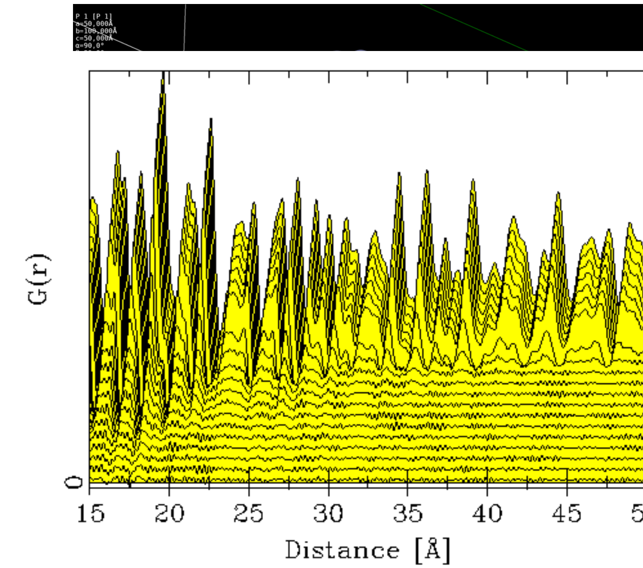
Very flexibel tool to analyze the local structure

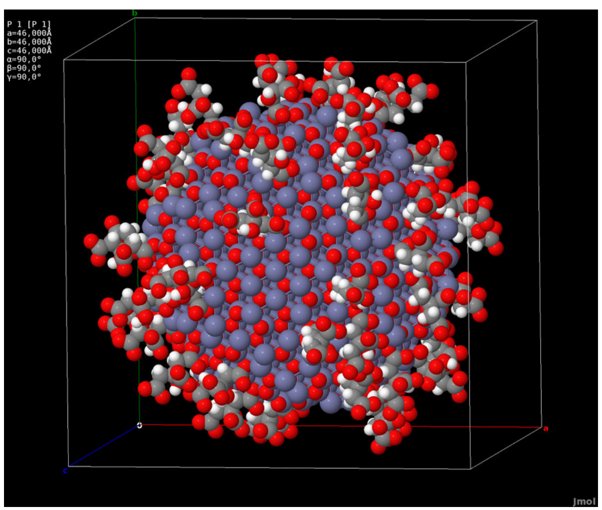


ZnSe Ellipsoid with
stacking faults

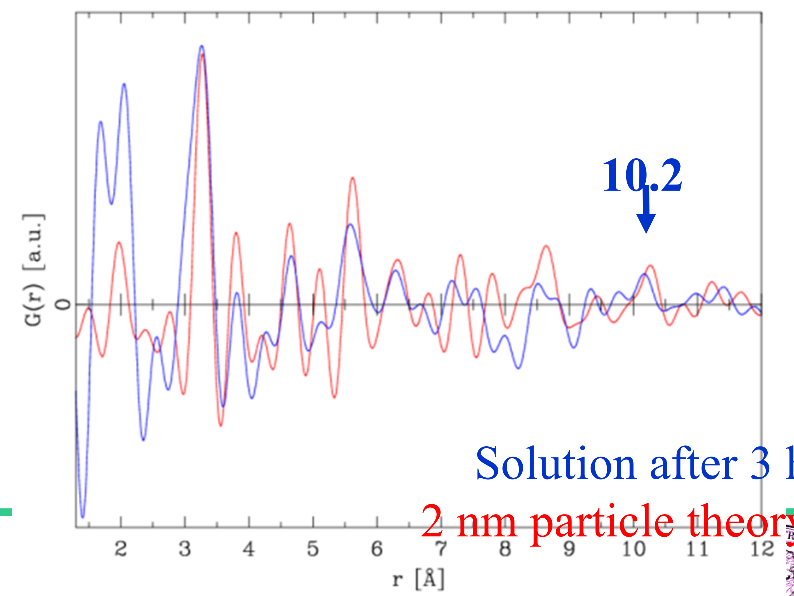


Gold cuboctahedron
with organic ligands





ZnO
with organic ligand



Resources

Total Scattering School
August 6 – 10, 2019   Oak Ridge national laboratory USA
https://conference.sns.gov/event/106/page/0

Workshop Analysis of Diffraction in Real Space ADD2019
March 18 – 22, 2019 ILL, Grenoble France
https://www.ill.eu/press-and-news/events/analysis-of-diffraction-data-in-real-space/

DISCUS Workshop ECM 2019 Vienna, Austria
August 18 – 23, 2019   Vienna, Austria
https://ecm2019.org/home/