FRIEDRICH-ALEXANDER
UNIVERSITÄT
ERLANGEN-NÜRNBERG
FACULTY OF SCIENCES

Science with DISCUS
Building complex and decorated nanoparticles with DISCUS
DIffuse **SC**attering **U**nd **S**tructure simulation

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Total scattering school 2023
Oak Ridge National Laboratory

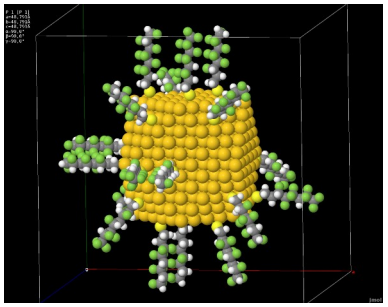
Small Box Modelling

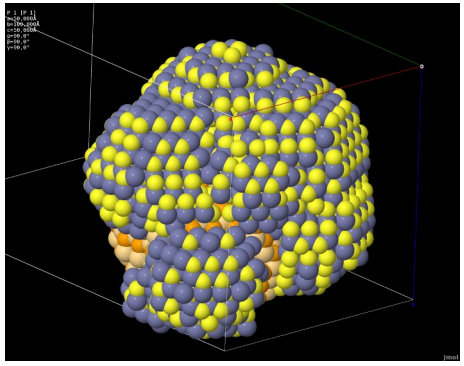
PDFgui

DISCUS
DiffPy

Large Box Modelling

Reverse Monte Carlo
RMCprofile
RMC_POT++
DISCUS



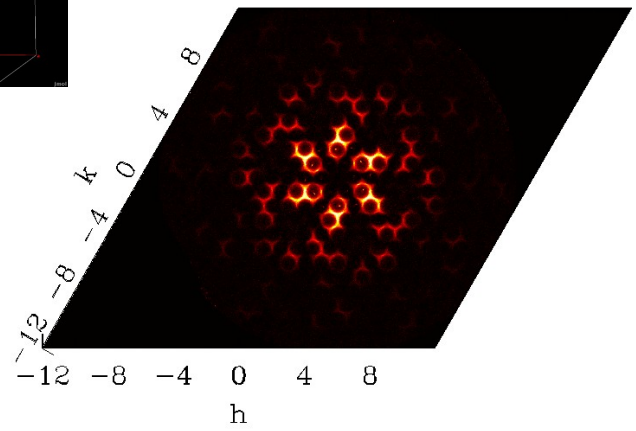


Multi level /
Complex Modelling

DISCUS
DiffPy

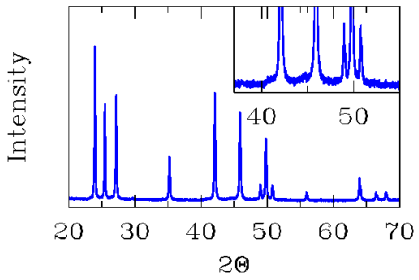
Single Crystal

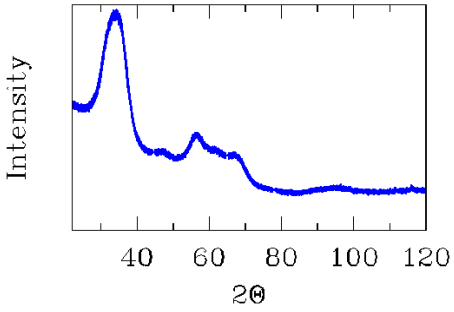
DISCUS



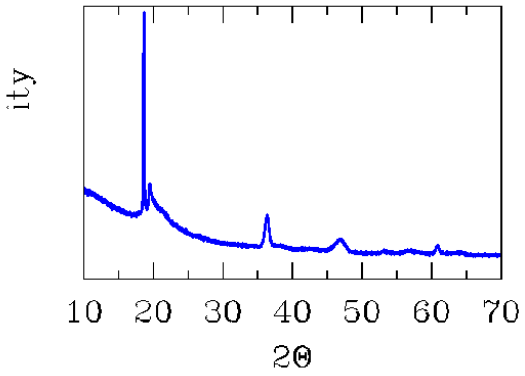
F. Zernike & J.A. Prins Z. Phys. (1927) 41, 184
Die Beugung von Röntgenstrahlen in Flüssigkeiten als Effekt der Molekülanordnung

CdSe crystalline material



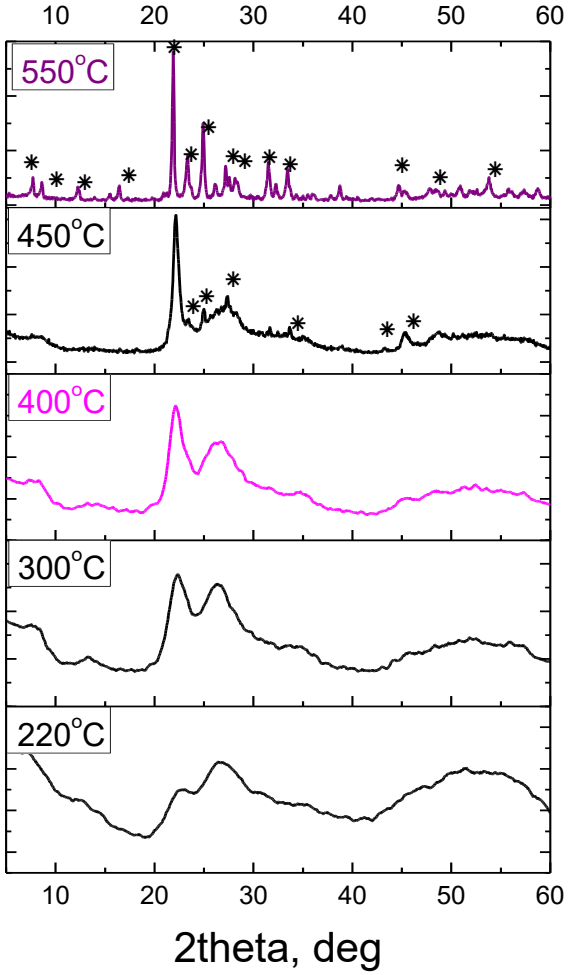


Nano crystalline ZnO



Massive stacking faults

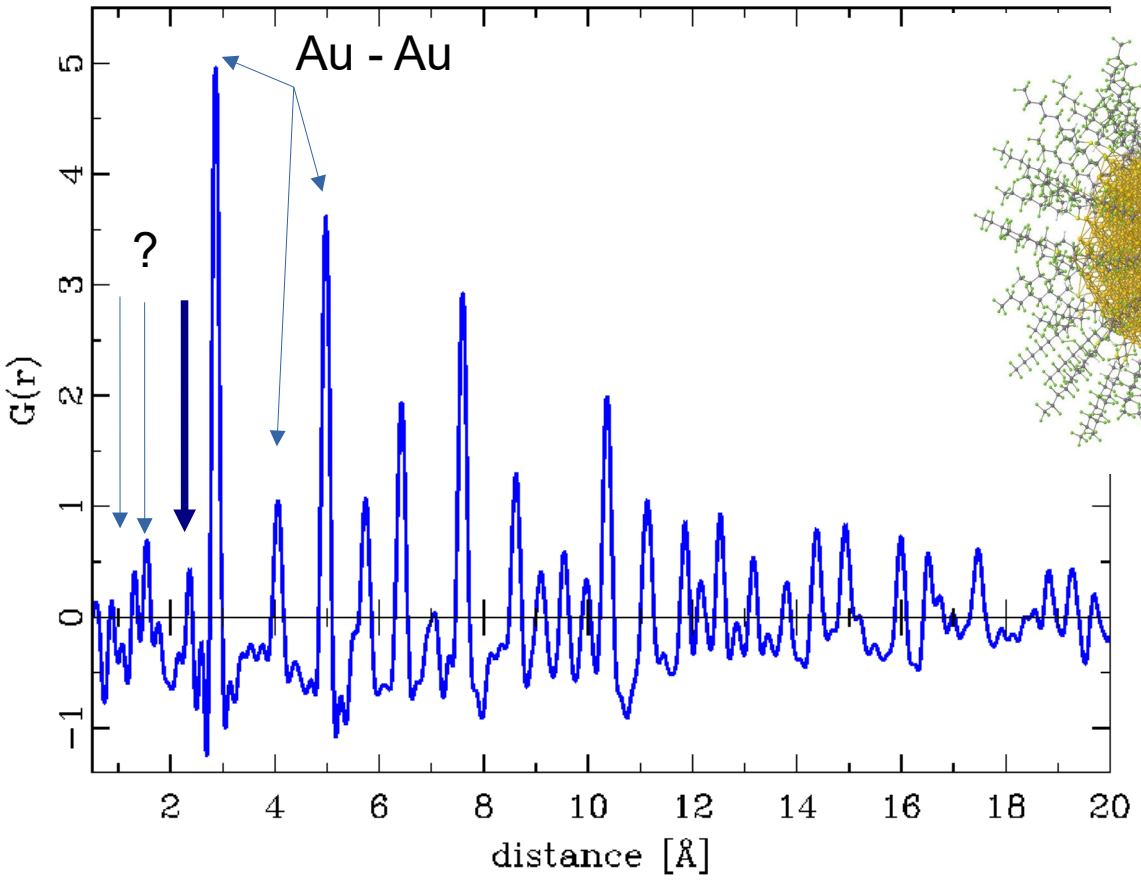
H_2TiO_3

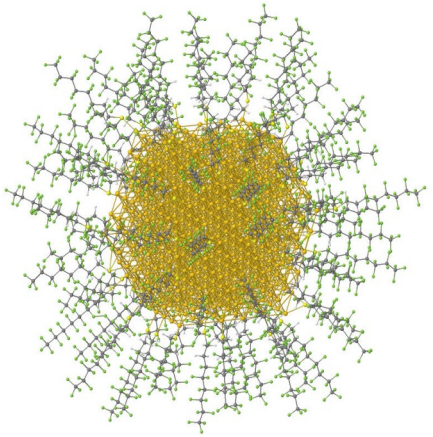


Mo-V-Nb oxides

Gold nanoparticles capped with fluorinated thio octane

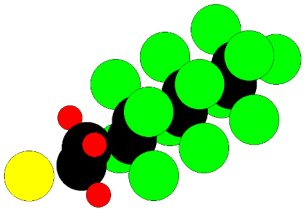
Gold -Ligand
Au – S 2.42 Å





Ligand -
Ligand
C-C 1.5Å
C-F 1.3Å

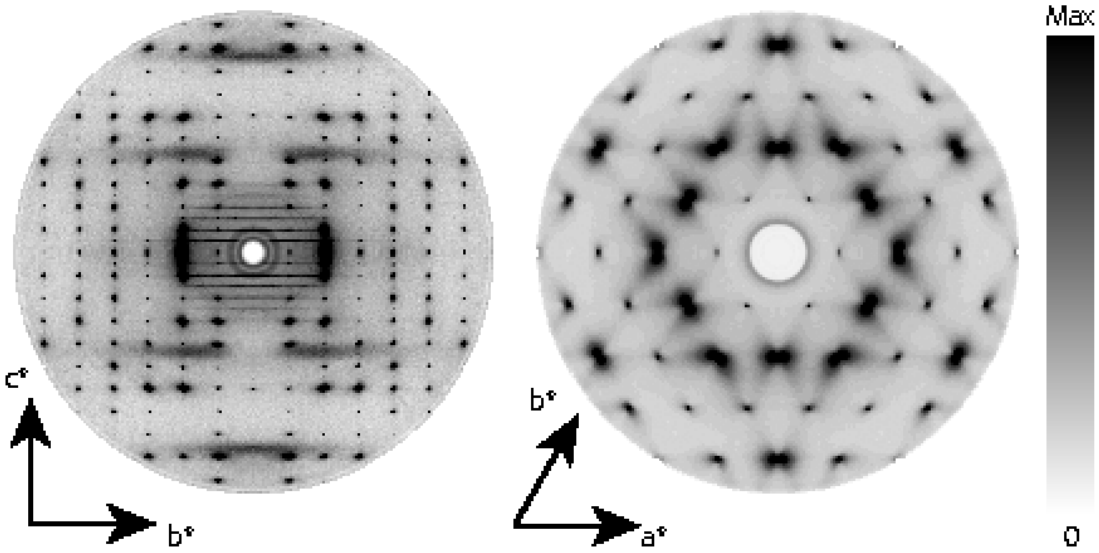
Number ?
Placement ?
Composition ?

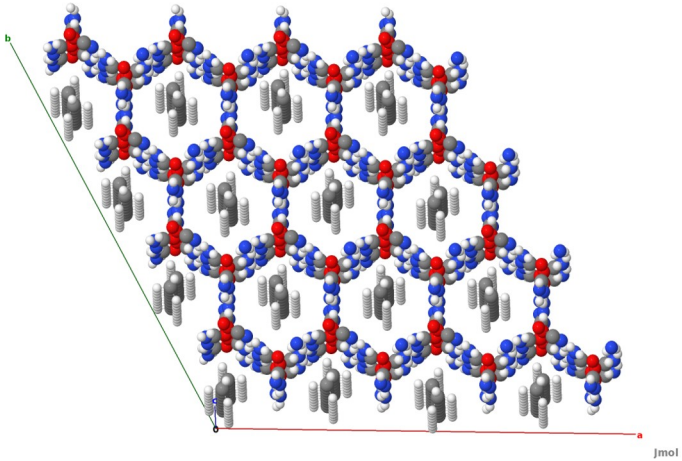


15 K
NPDF, Los Alamos
K. Page, Th. Proffen

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

Th Weber PhD München 1994





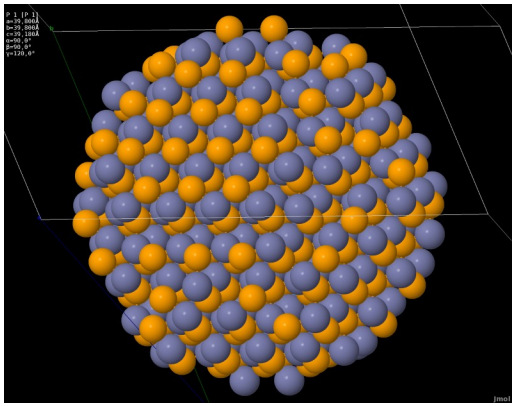
Alkane chains in Urea

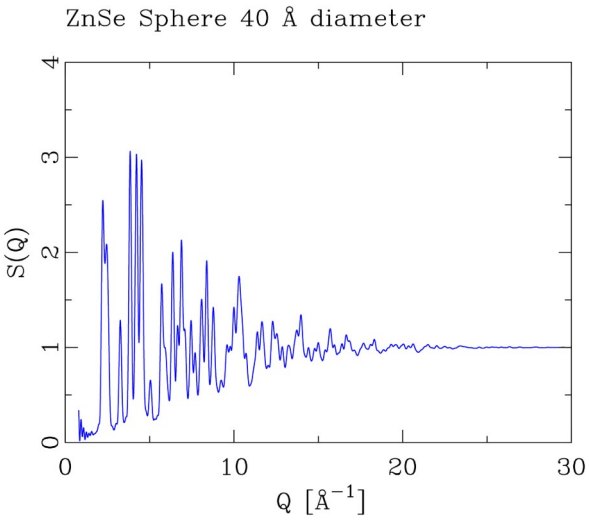
Diffuse scattering by 0.05 μm³ single crystal
Neder et al Clays & Clay Minerals 1999

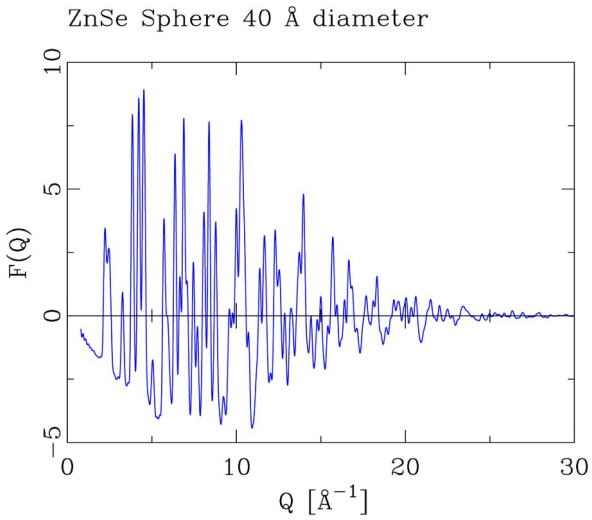
Welberry & Mayo J. Appl. Cryst 29, 1996

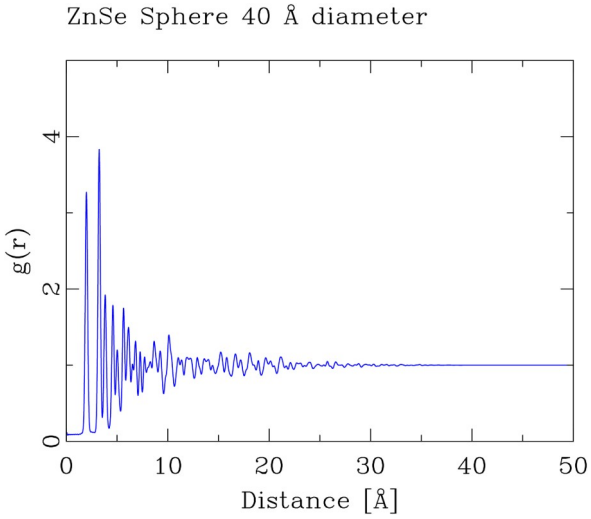
Simulate all sorts of nanoparticles

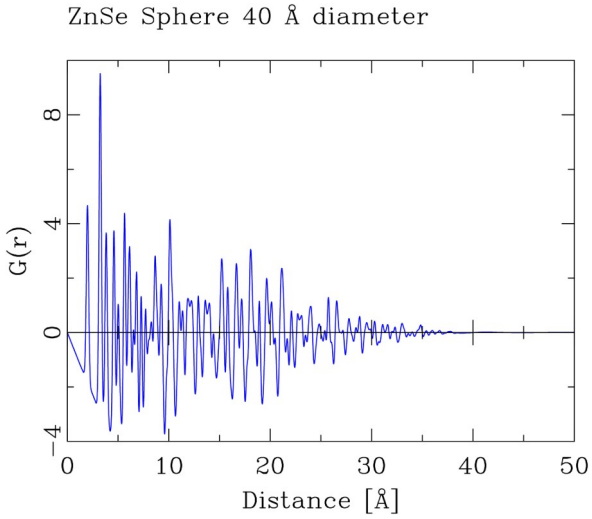
simple





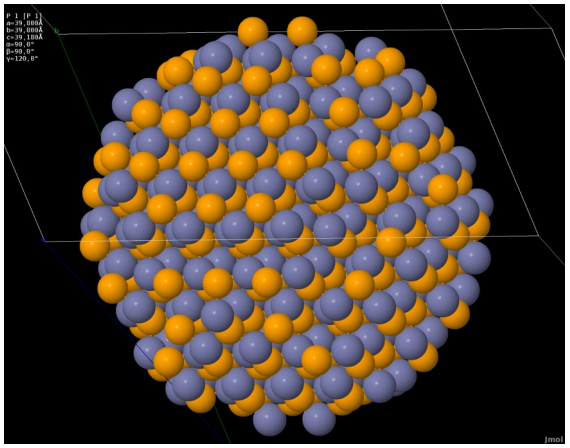




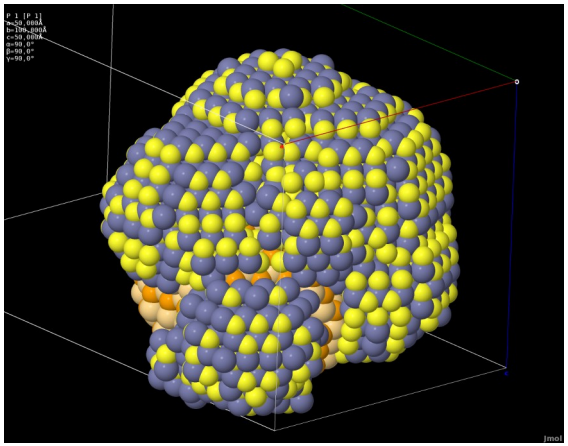


Simulate all sorts of nanoparticles

simple



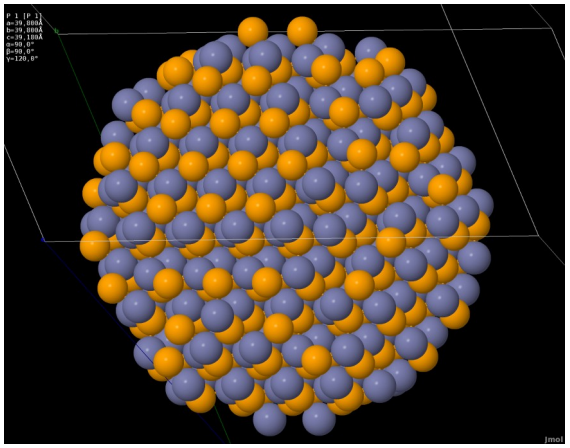
and complex



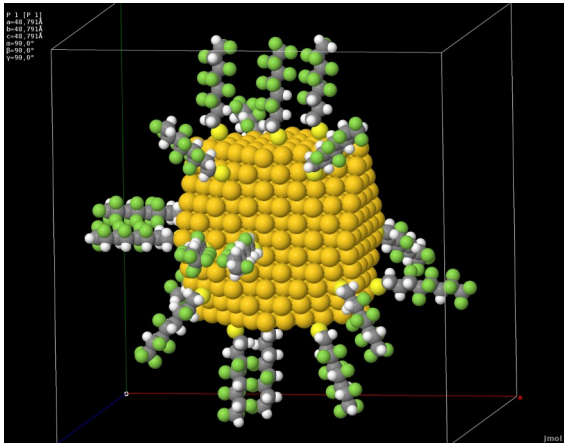
Build /shape individual objects
Assemble into larger

Simulate all sorts of nanoparticles

simple

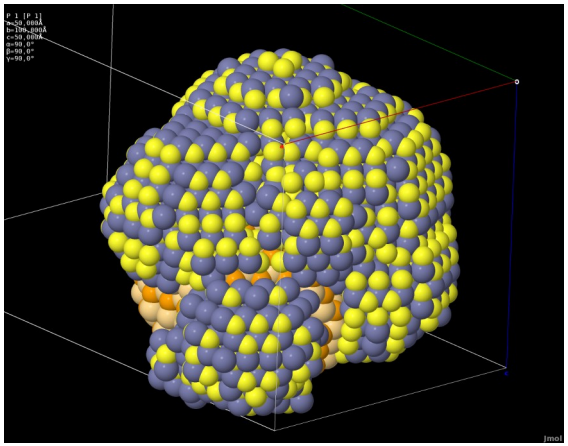


or decorated



Shape core
Decorate

and complex

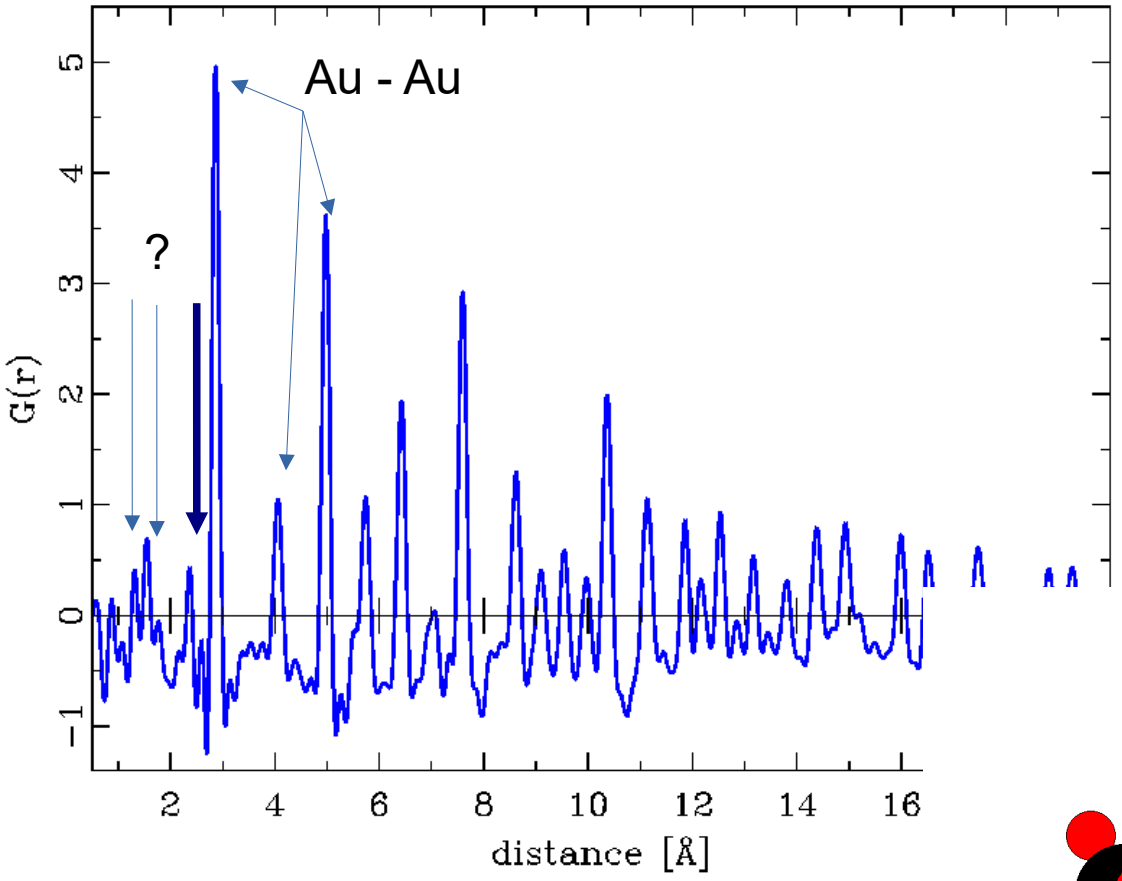


Build /shape
individual objects
Assemble into larger

Nanoparticle + Ligand + Neutron Scattering

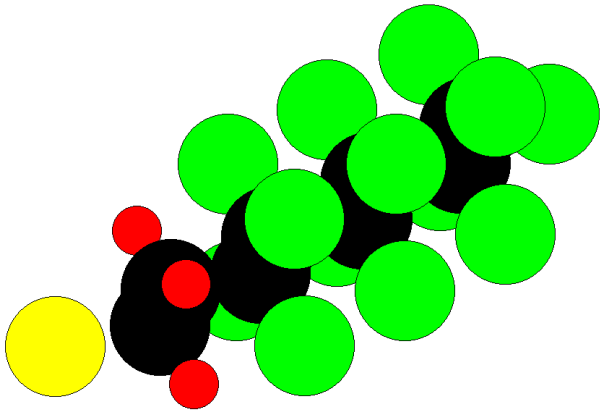
Gold -Ligand
Au – S 2.42Å

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

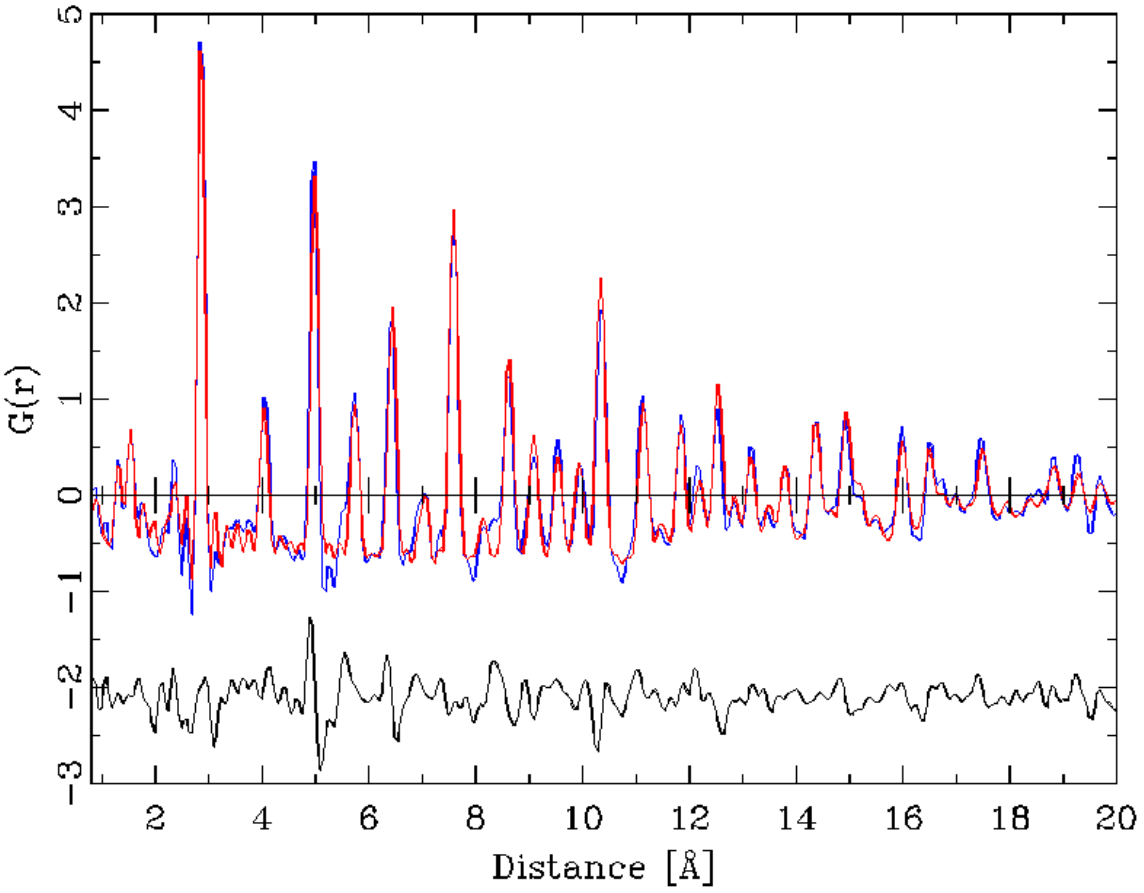
Au + S-CH2-CH2-(CF2)5-CF3

$S\ C_8\ H_4\ F_{13}$

Ligand internal distances
from DFT calculations

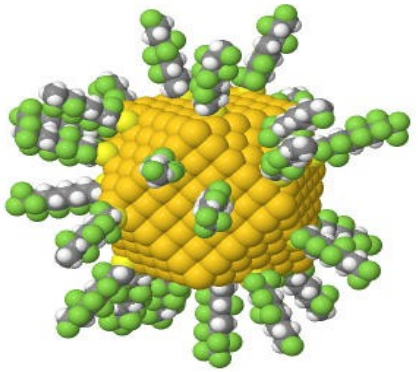
Page, *et al.*, *Chem. Phys. Lett.* **393** (2004) 385-388.

Nanoparticle + Ligand + Neutron Scattering



15 K
NPDF, Los Alamos

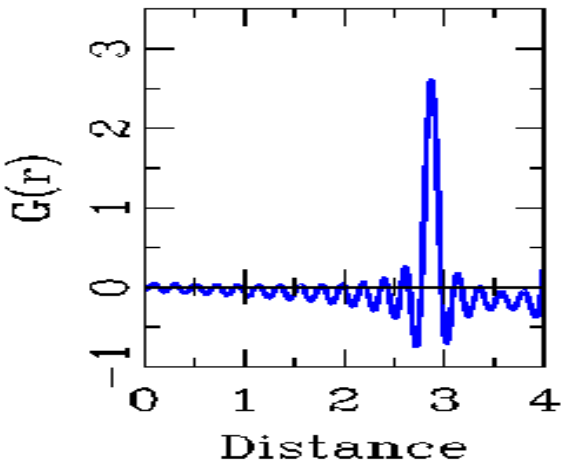
a(Au)	4.0658Å	(1)
Au – Au	2.8750Å	(1)
B(Au)	0.32Å^2	(4)
B(Ligand)	0.45Å^2	(10)
Diameter	20Å	(2)
N(ligand)	20	(6)
P(Fluorine)	0.65	(15)
Au – S	2.42Å	fixed!



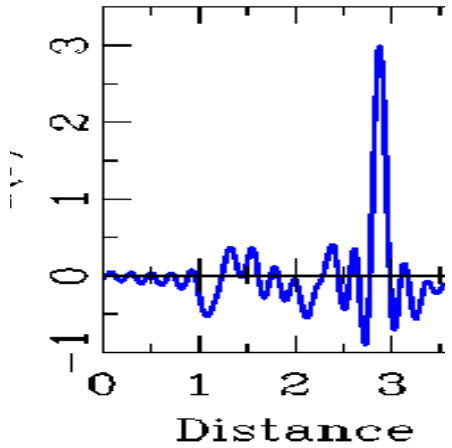
K. Page et al. J. Appl. Cryst. (2011)

Direct or not direct

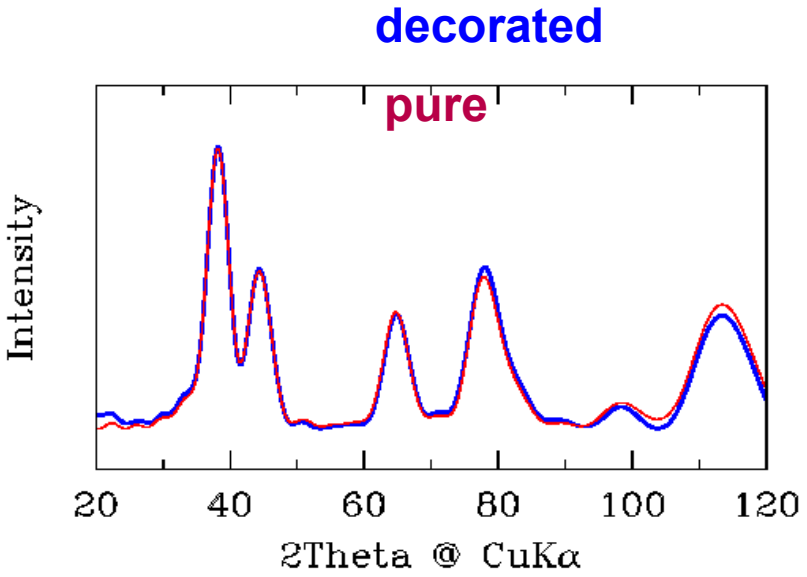
PDF

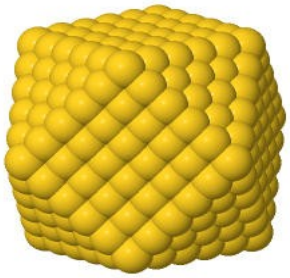


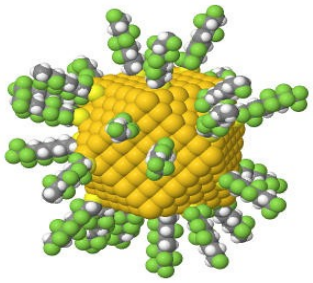
PDF



Calculated Debye-Scattering-Equation



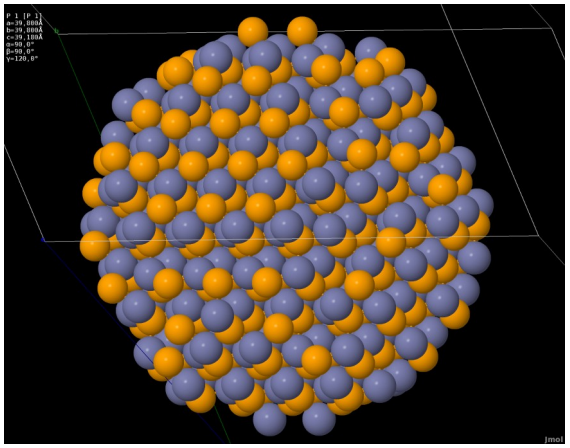




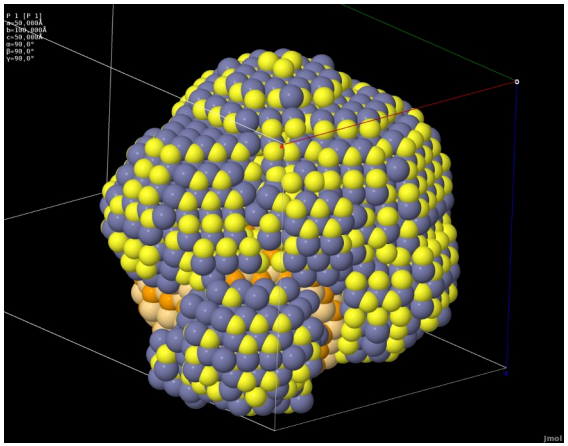
Essentially no *modulated* difference in NEUTRON powder diffraction pattern

Simulate all sorts of nanoparticles

simple

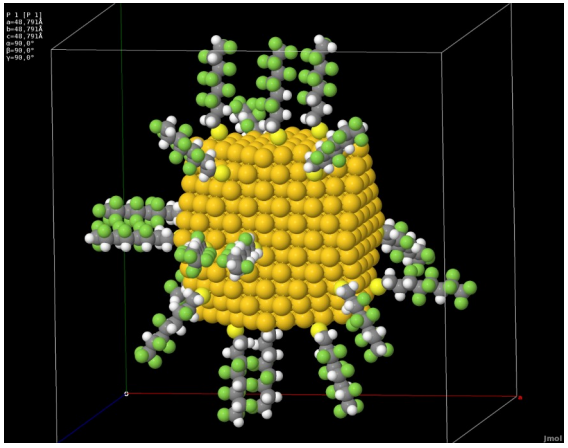


and complex



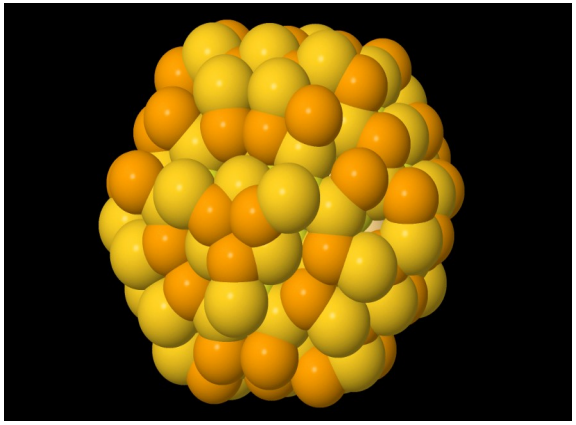
Build /shape
individual objects
Assemble into larger

or decorated



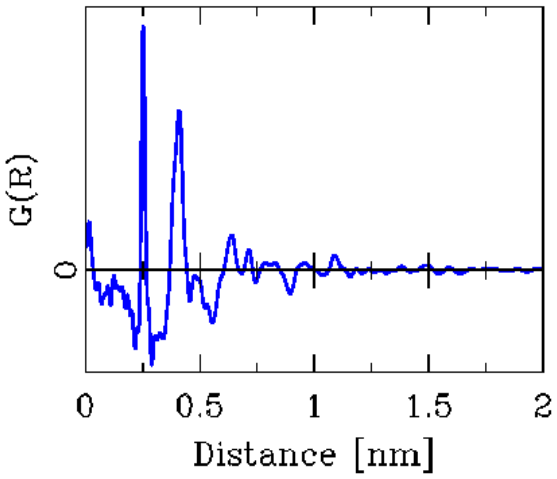
Shape core
Decorate

or distorted



Shape core
Distort
surface / core

CdS nanoparticles



CdS / Glutathione

Composition: $Cd_1\ S_{0.5}\ Glutathione_{0.5}$

Raman: No H-S vibration

All organic sulfur bound to CdS surface

Half surface S

Half core S

1.5 to 2 nm diameter

Korsounksi et al. J. Appl. Cryst. (2003), **36**, 1389

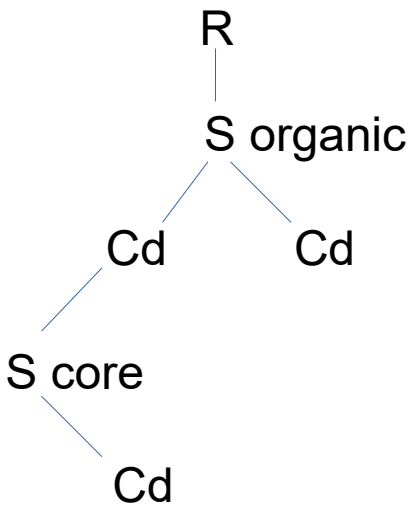
Strain determined by Ligand molecule

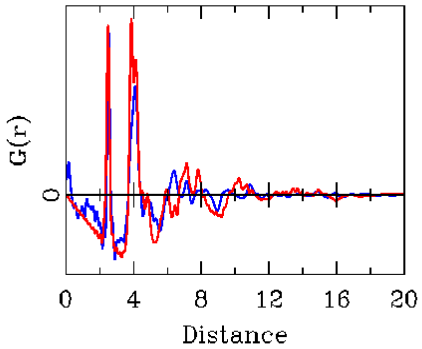
Different bond angles (distances) at surface / core

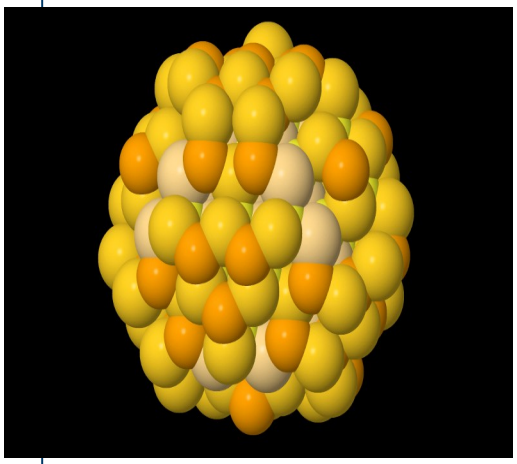
Inhomogeneous strain field accross particle

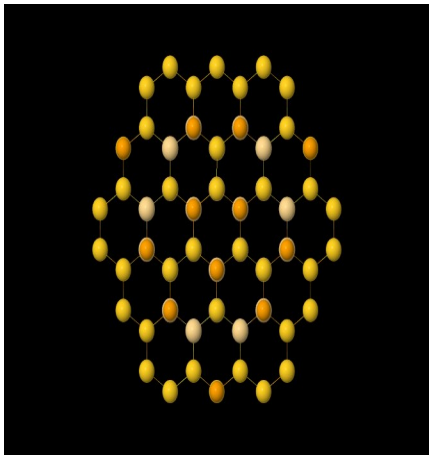
Relax particle to minimize energy

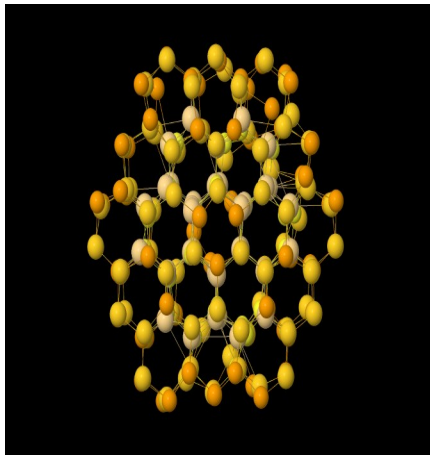
Potential: Cd – S (organic) – Cd angle
Cd – S (inorganic) – Cd angle
Cd – S first neighbor distance

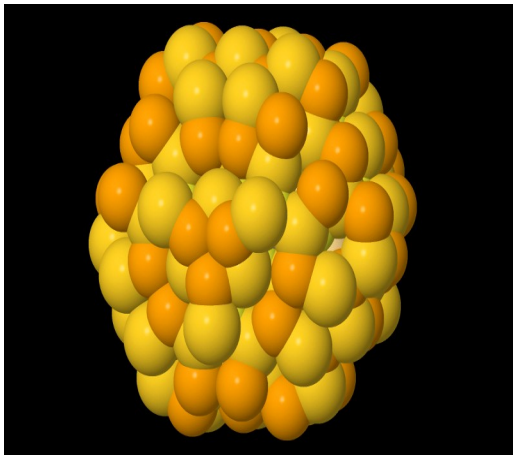








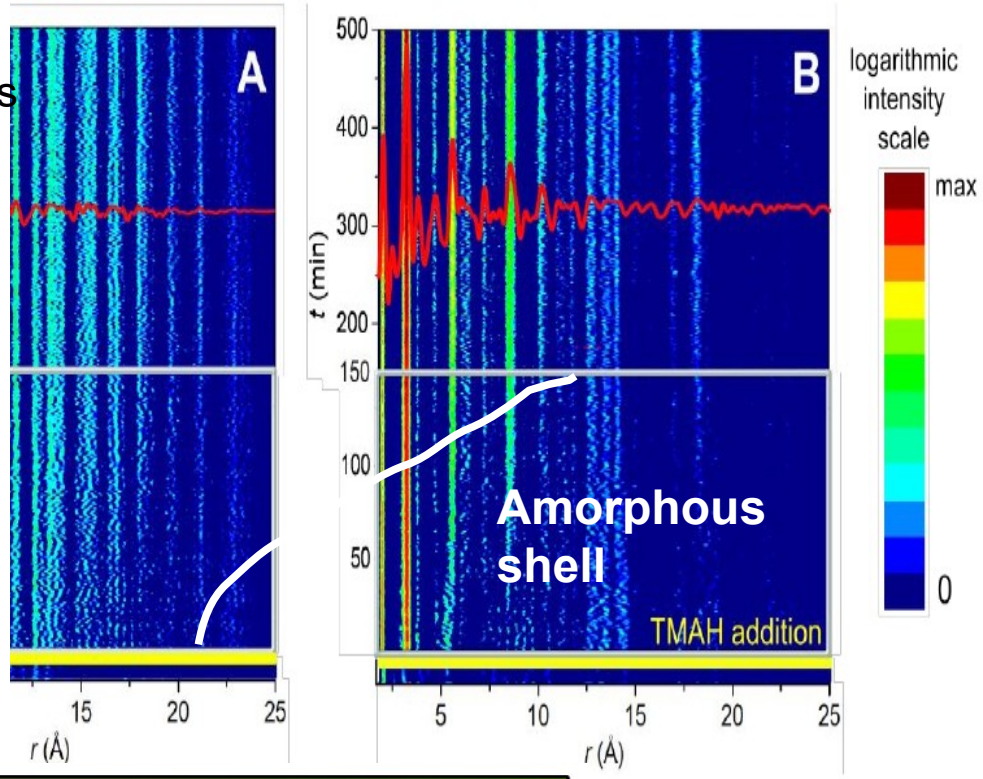


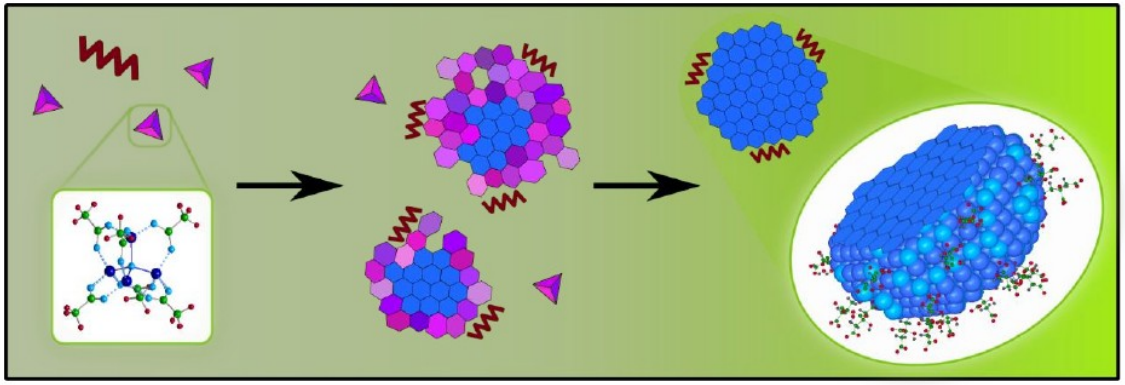


Not amorphous !

Nanoparticle interaction with Solvents

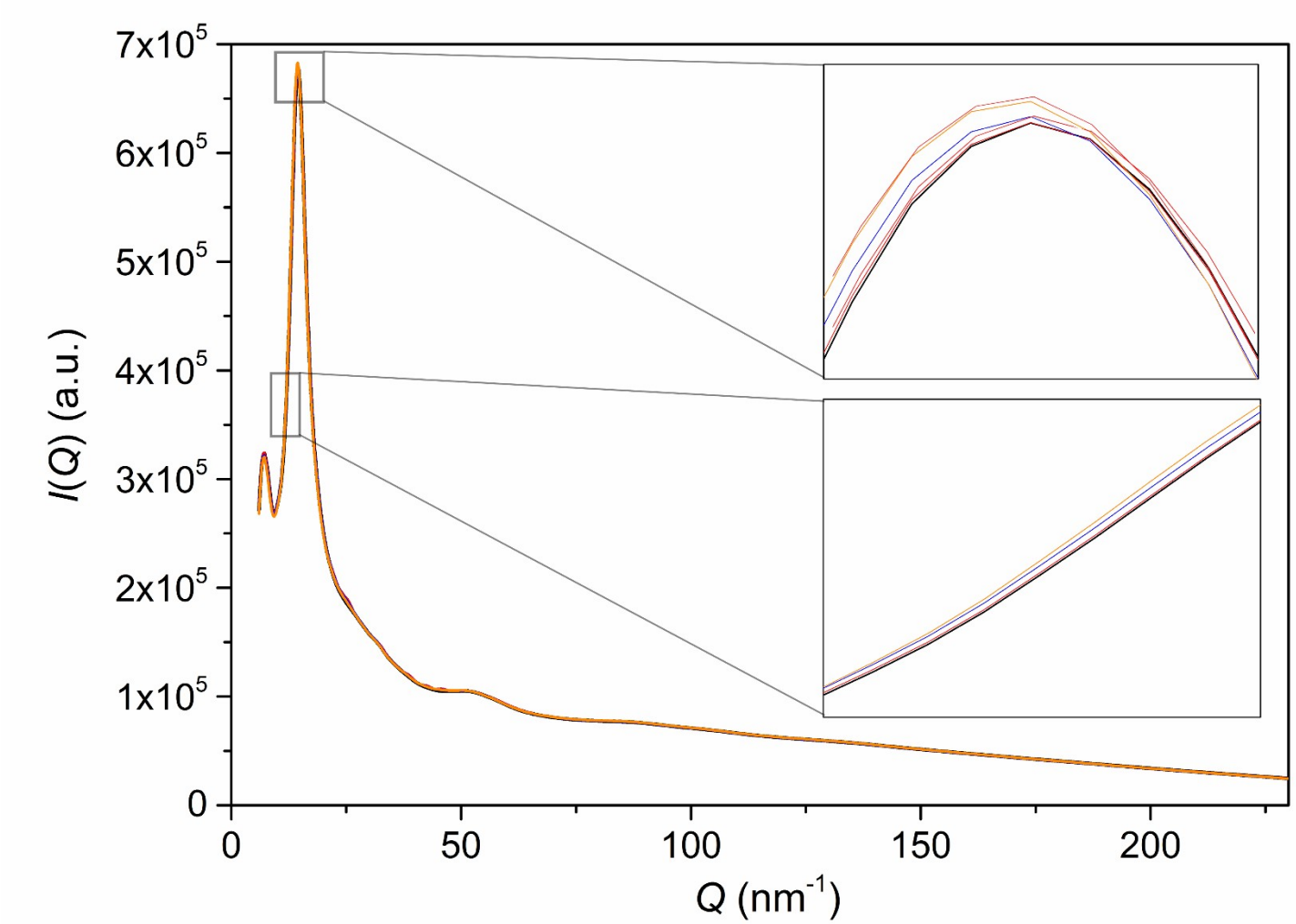
Initial formation of Zn-O precursor clusters
Rapid formation of disordered particles
Slow internal ordering of core structure





M. Zobel, A. Windmüller, …, R.B. Neder, (2016) Cryst.Eng.Comm, **18**, 2163

Nanoparticle interaction with Solvents

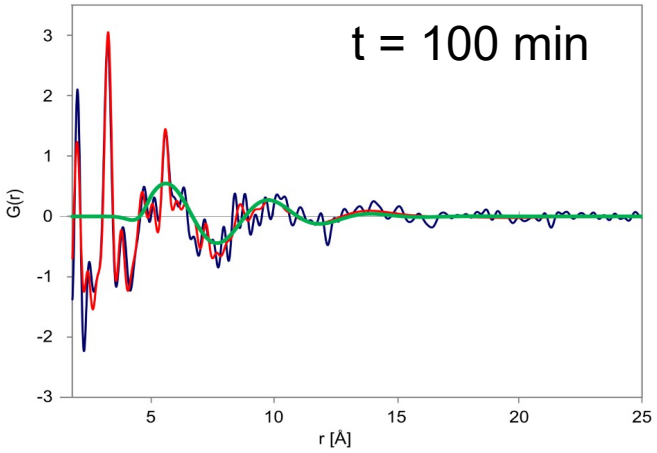


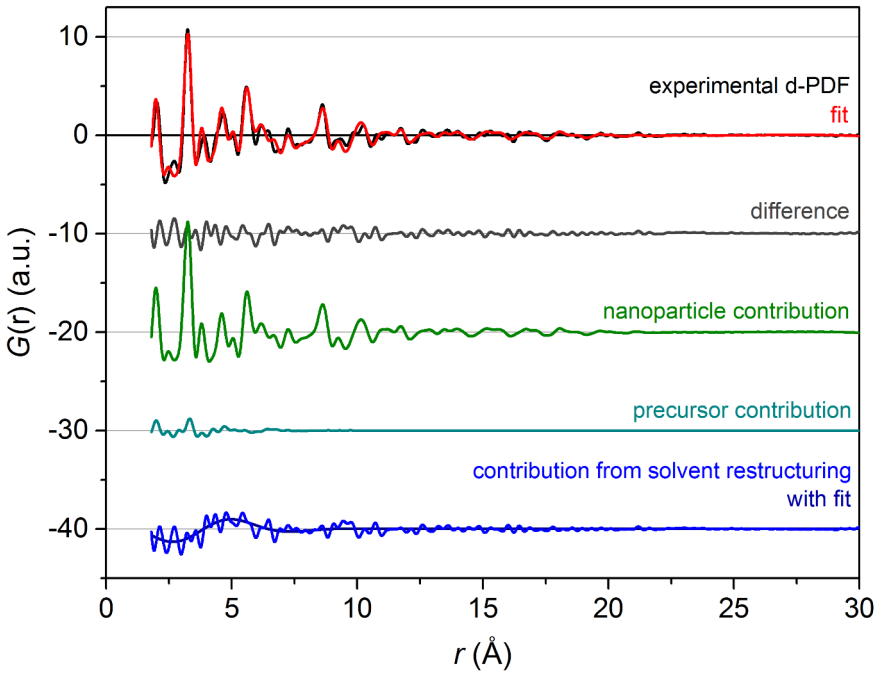
Hexane as solvent

Different Nanoparticles within solvent

Diffraction pattern of solvent changes!

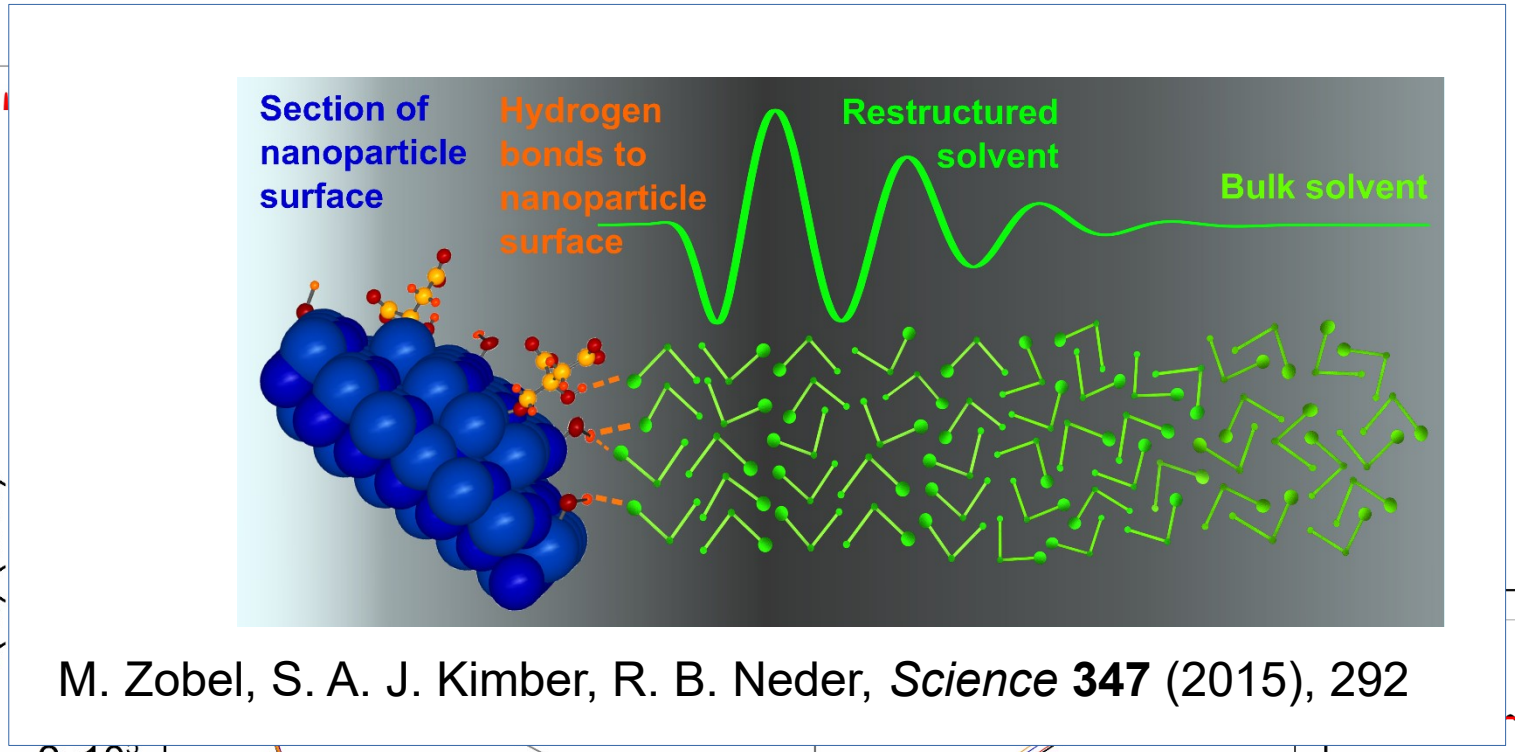
Nanoparticle interaction with Solvents





Additional dampened sinusoidal oscillation

Nanoparticle interaction with Solvents



M. Zobel, S. A. J. Kimber, R. B. Neder, *Science* **347** (2015), 292

Read asymmetric unit

Expand to full unit cell
Expand to a block sized crystal

Modify crystal

Introduce defects

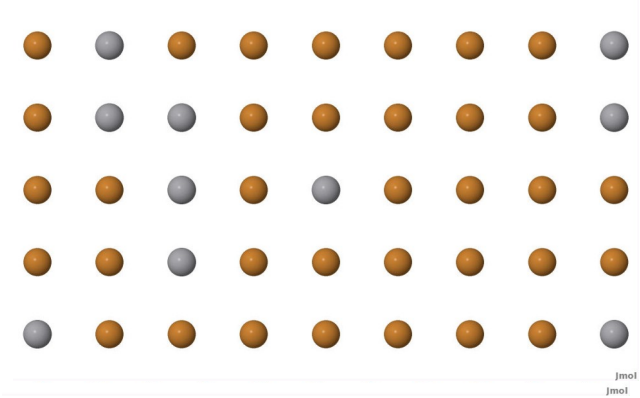
Extended tool box to introduce arbitrary defects

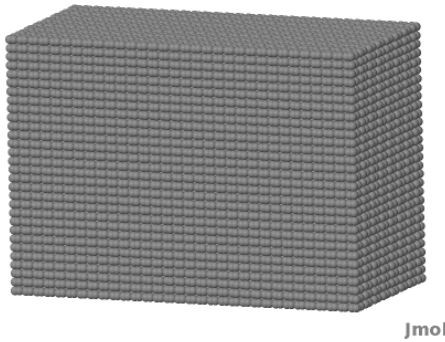
Modify crystal shape

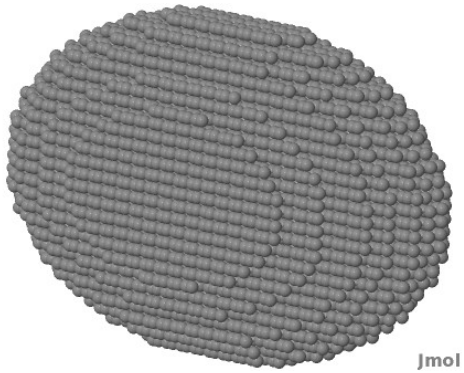
Calculate: **single crystal diffraction pattern**
powder diffraction pattern
Debye-Scattering-Equation
Complete integration
powder PDF
3D PDF

Xray, neutron, electron

Refine: structure and disorder
against experimental pattern

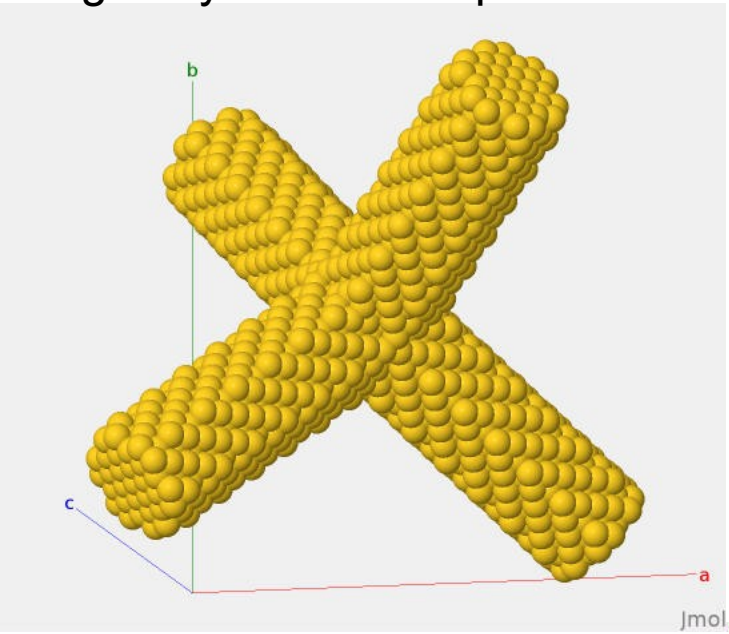


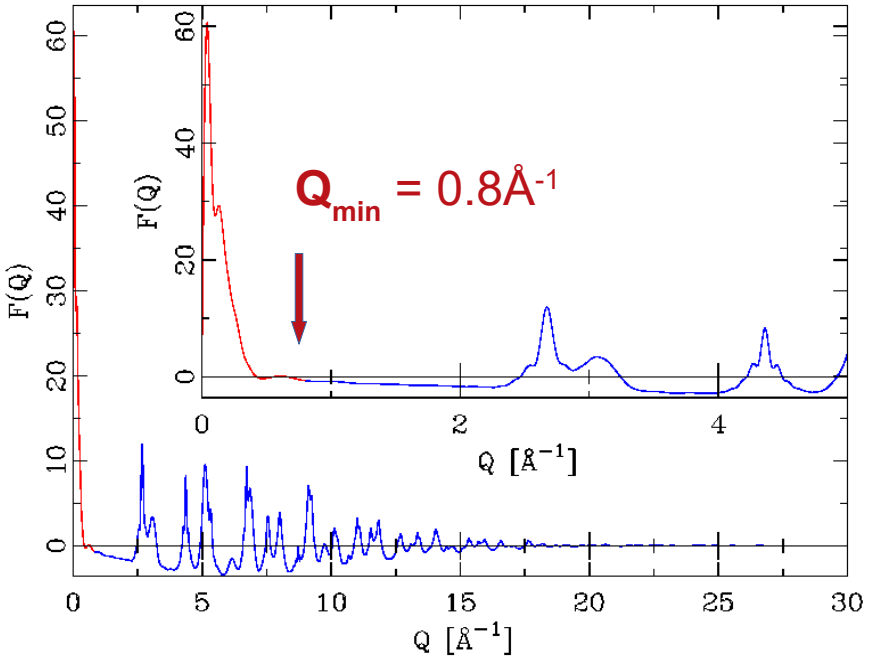




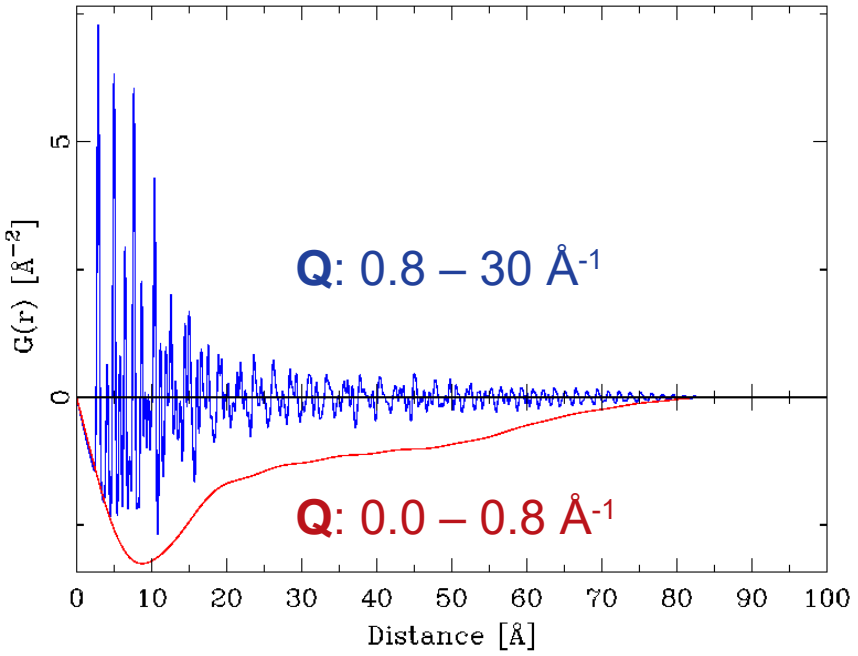
Complex Nanoparticle shape

Single crystal Au tetrapod





PDF as Fourier of diffraction pattern

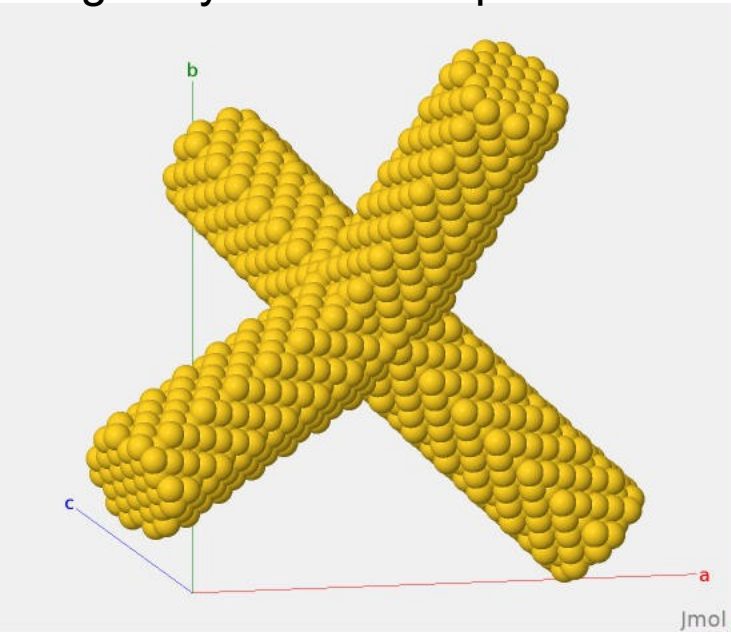


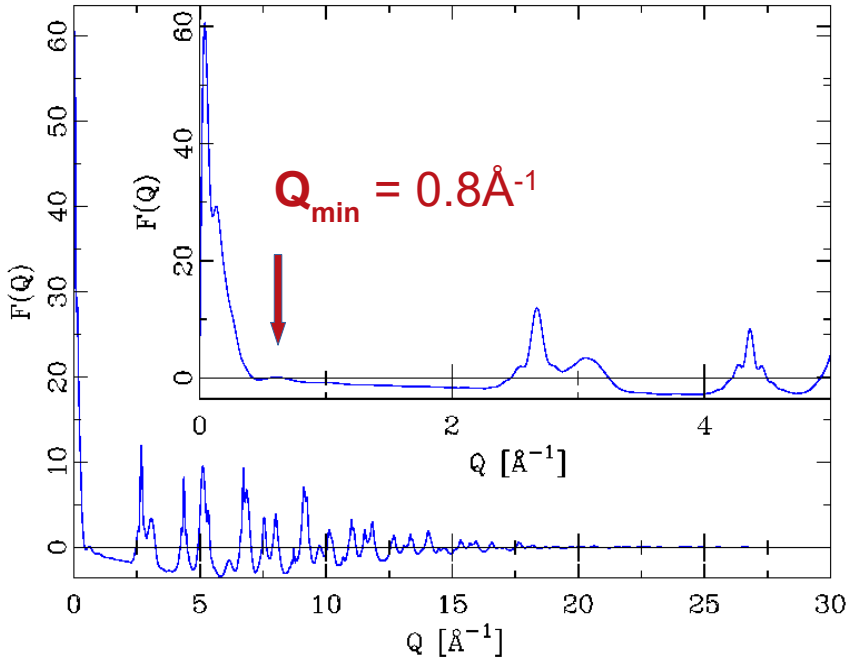
Baseline as Fourier of
-1 * small angle scattering signal

Neder & Proffen (2020) J.Appl. Cryst. **53**, 710

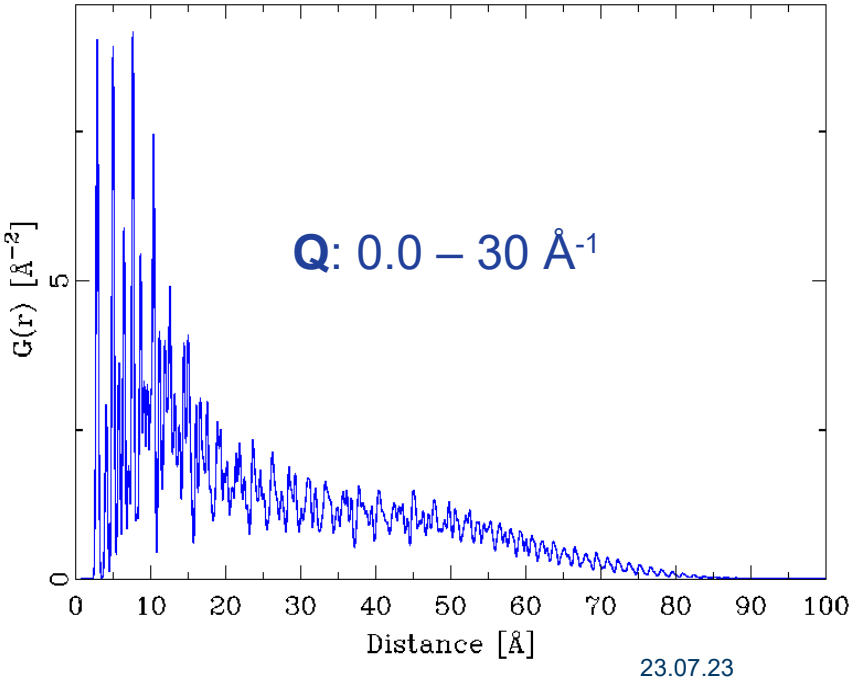
Complex Nanoparticle shape

Single crystal Au tetrapod





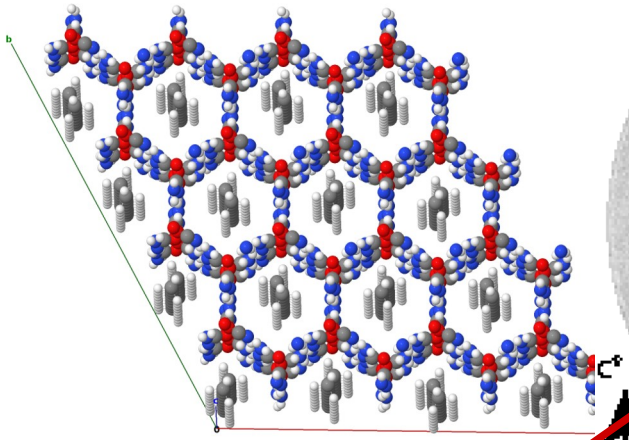
PDF as Fourier of diffraction pattern

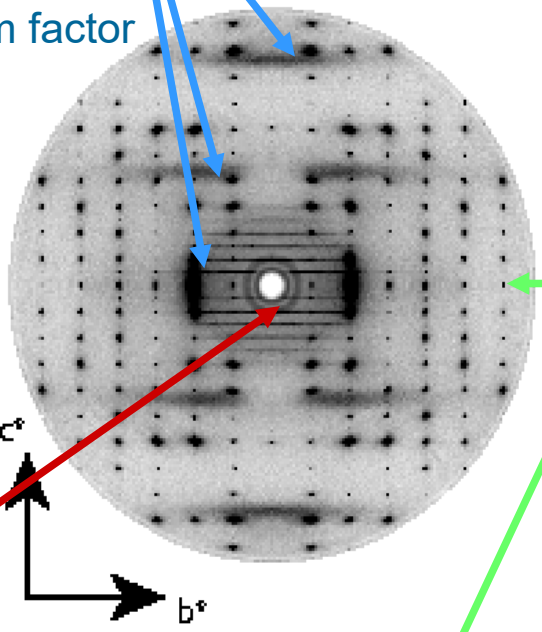


Baseline as Fourier of
-1 * small angle scattering signal

Very broad diffuse scattering,
no regularity in reciprocal space

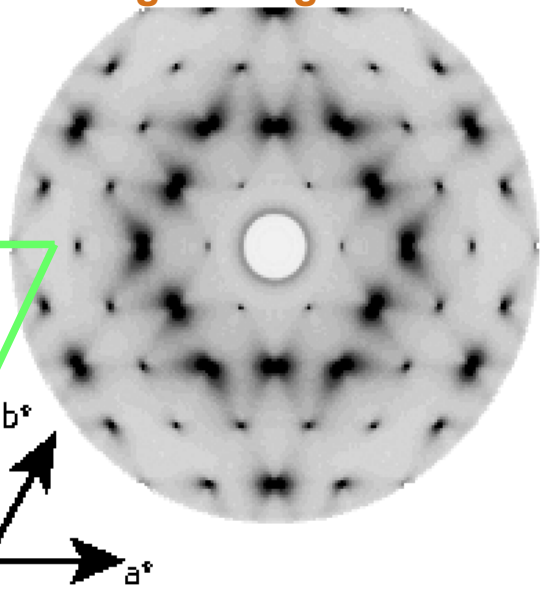
➡ **Scattering by single molecule ?**
Compare to molecular form factor





Modulated diffuse scattering
within planes

➡ **Correlations between neighboring channels**



Sharp diffuse layers
➡ **1-D disorder**

Distance between diffuse layers
➡ **1-D disorder of alkane chains**

Diffuse layers fade away from
reciprocal origin
➡ **Predominantly substitutional disorder: Orientation in channels**

No diffuse layer at L = 0 !

$$F(hk0) = \sum f_j e^{2\pi i(hx_j + ky_j + 0z_j)}$$

Independent of z coordinates
==> hk0 *sees* projected structure

➡ **No diffuse: projected structure is periodic**

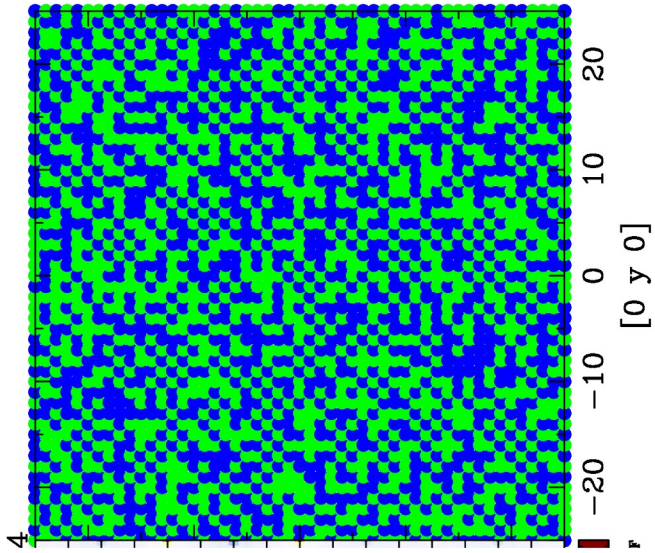
Th Weber PhD München 1994

Welberry & Mayo J. Appl. Cryst 29, 1996

Calculation of 3D (Δ)-Pair Distribution Function PDF

Calculation of 3D-PDF 3D-Delta-PDF from structural model

Structure

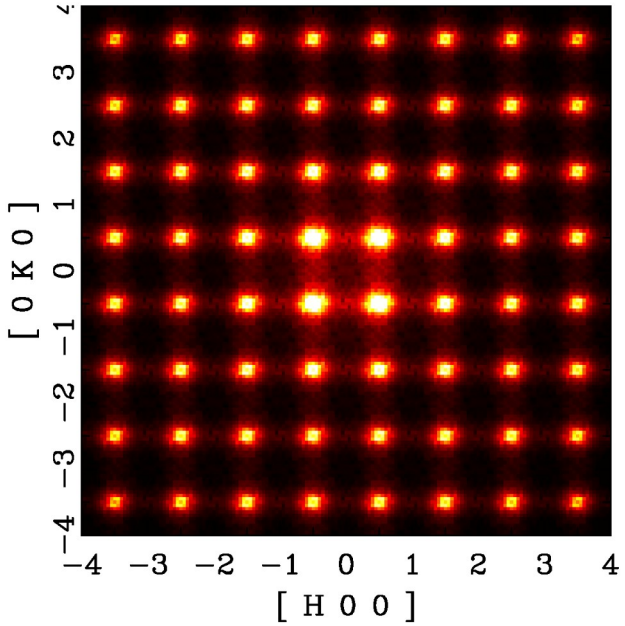


Negatice correlation **green** / **blue**
=> chess board pattern

Calculation of 3D (Δ)-Pair Distribution Function PDF

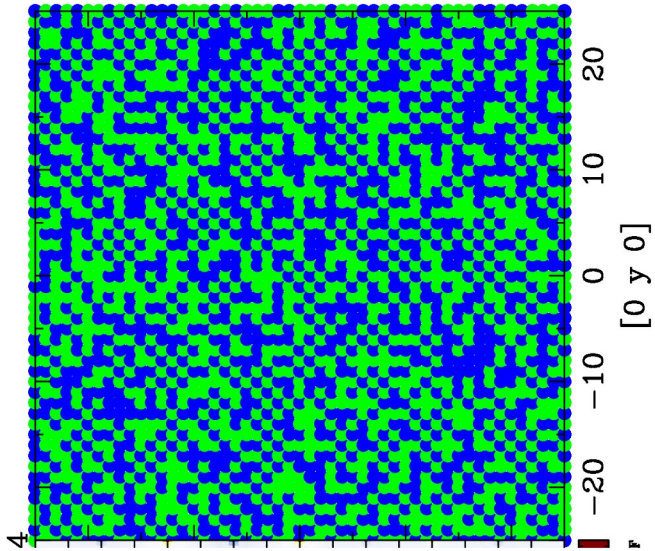
Calculation of 3D-PDF 3D-Delta-PDF from structural model

Diffuse intensity



$\mathcal{F}$

Structure



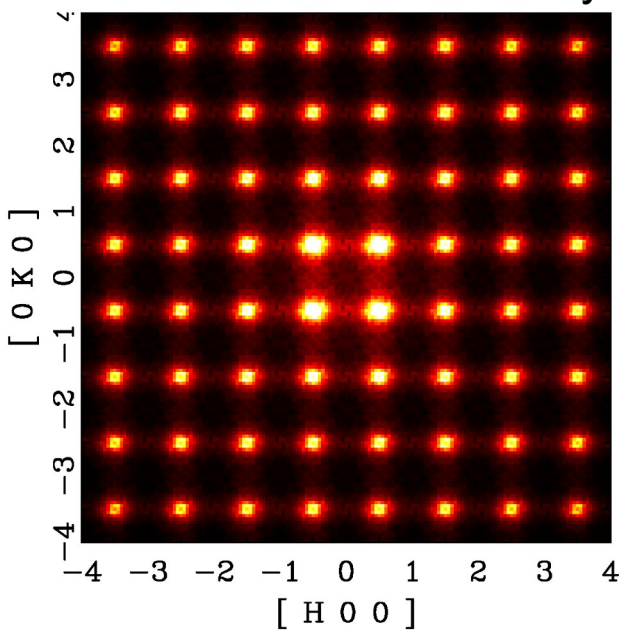
Negatice correlation **green** / **blue**
=> chess board pattern

=> diffuse maxima at h/2; k/2

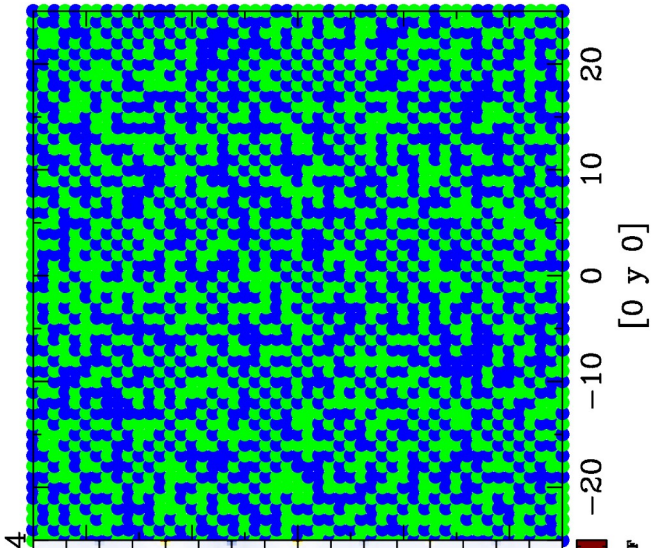
Calculation of 3D (Δ)-Pair Distribution Function PDF

Calculation of 3D-PDF 3D-Delta-PDF from structural model

Diffuse intensity

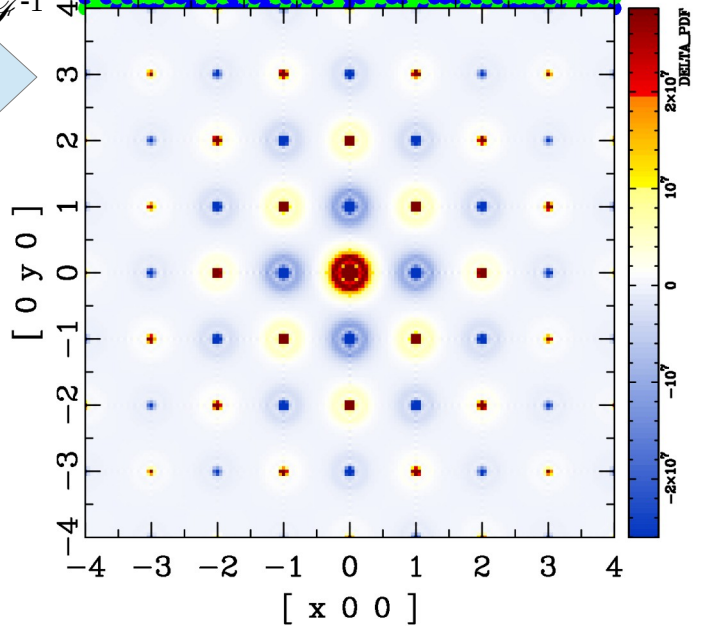


Structure



$\mathcal{F}$

$\mathcal{F}^{-1}$



3D-ΔPDF

Negatice correlation **green** / **blue**
=> chess board pattern

=> diffuse maxima at h/2; k/2

=> chess board distribution of
positive / **negative** maxima
in 3D-Δ-PDF

Calculation of 3D (Δ)-Pair Distribution Function PDF

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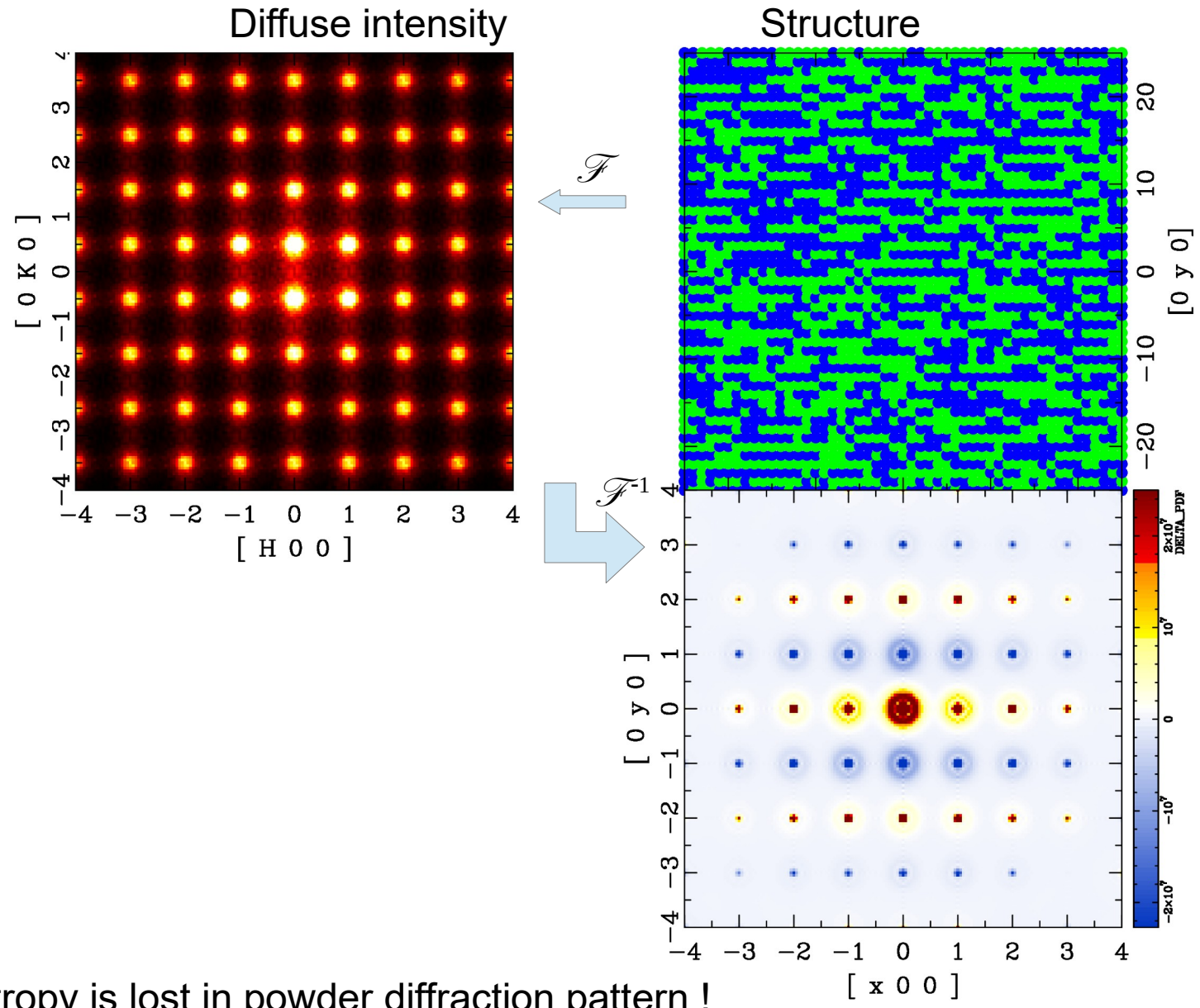
FACULTY OF SCIENCES

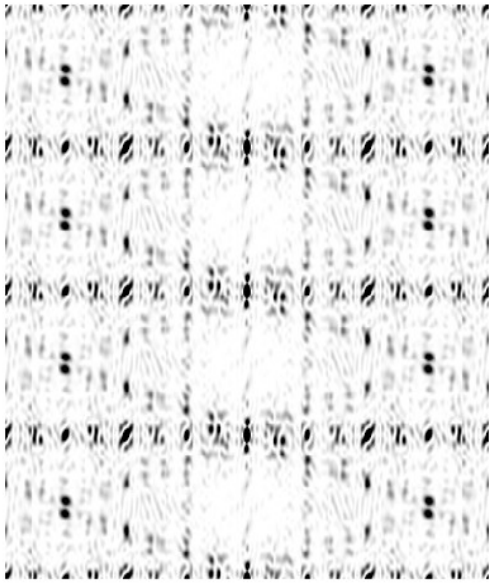
Calculation of 3D-PDF 3D-Delta-PDF from structural model



3D-ΔPDF

Anisotropy is lost in powder diffraction pattern !

And finally



$\mathcal{F}^{-1}$

Fourier

Full DISCUS workshop:

July 24 to July 28, 2023 Erlangen; Germany

https://www.icsp.nat.fau.eu/neder-group/discus-home/

http://tproffen.github.io/DiffuseCode/