DISCUS,
Simulation and refinement of disordered crystal structures

DIffuse **SC**attering **A**nd **S**tructure simulation

Und

Active since 1990

ADD 2019

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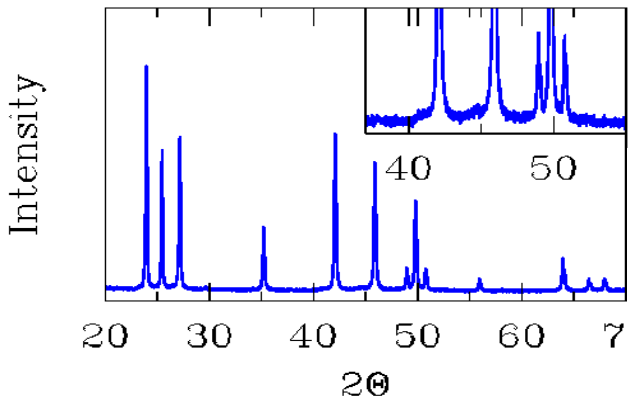
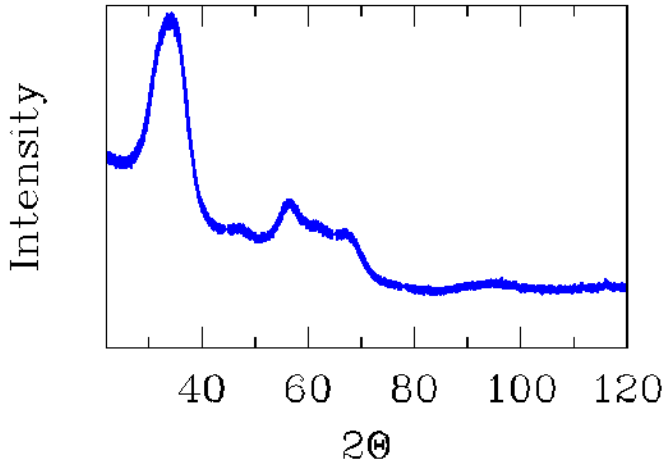
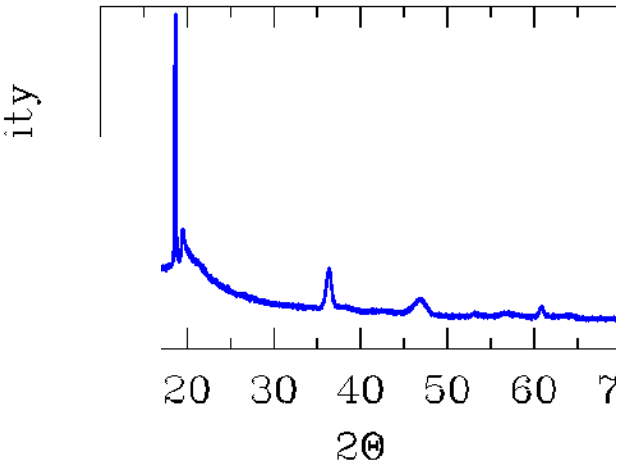
Powder Diffuse Scattering

CdSe crystalline material

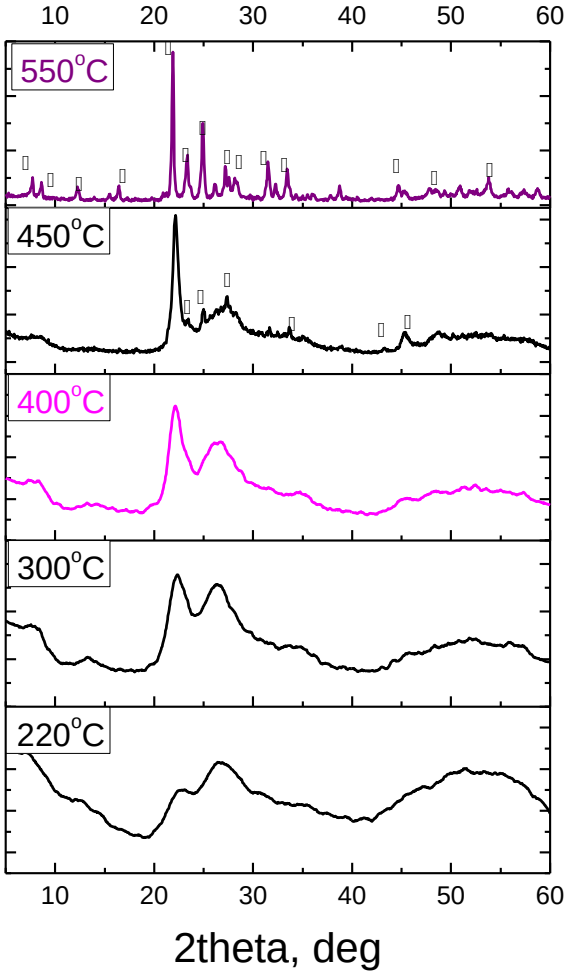




Nano crystalline ZnO



H_2TiO_3

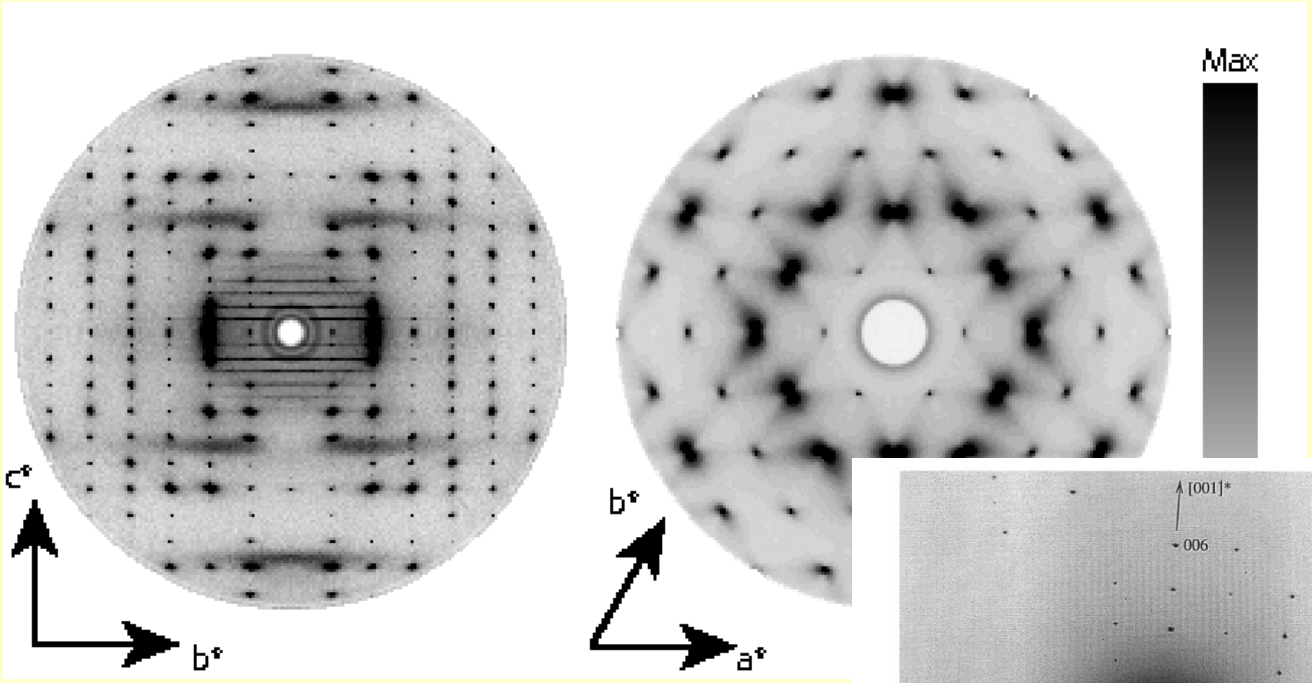


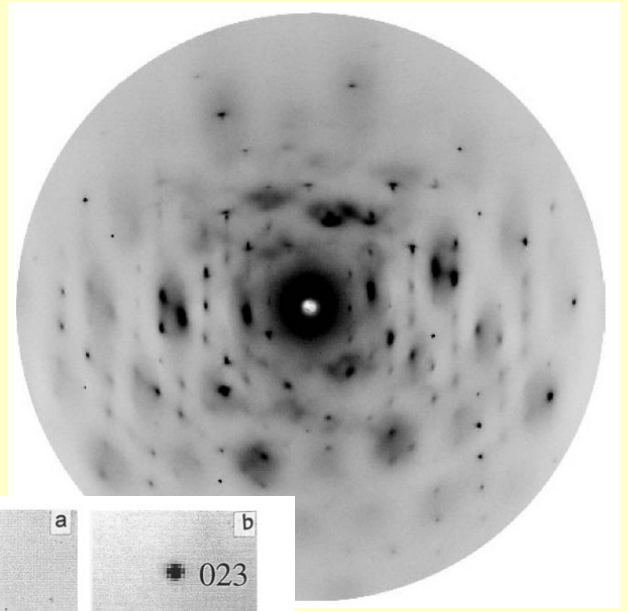
Mo-V-Nb oxides

Singe Crystal Diffuse Scattering

Pentachloronitrobenzene

Th Weber PhD München 1994





Alkane chains in Urea

Diffuse scattering by 0.05 μm^3
single crystal
Neder et al Clays & Clay Minerals 1999

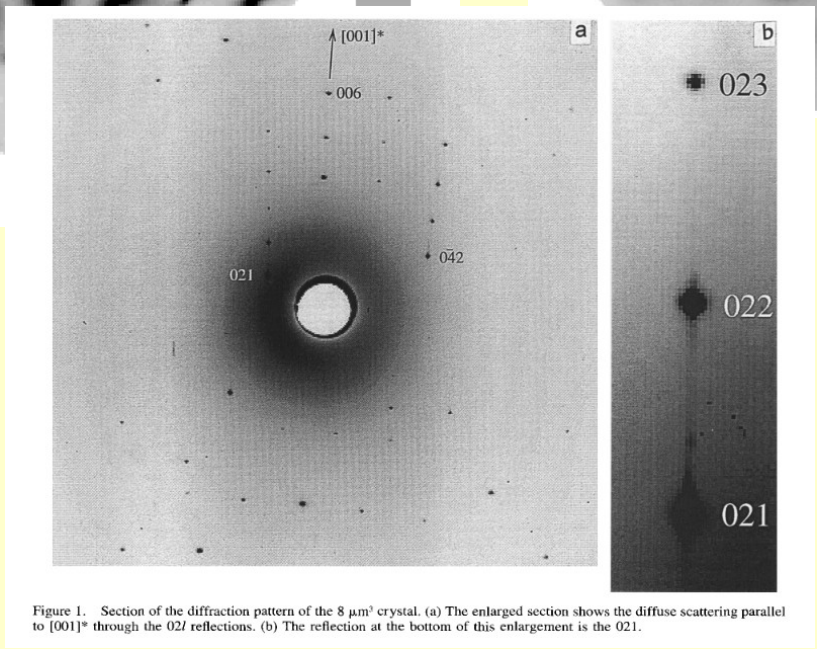
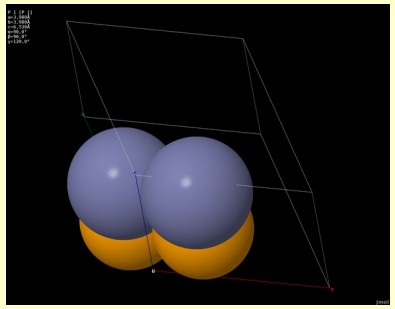


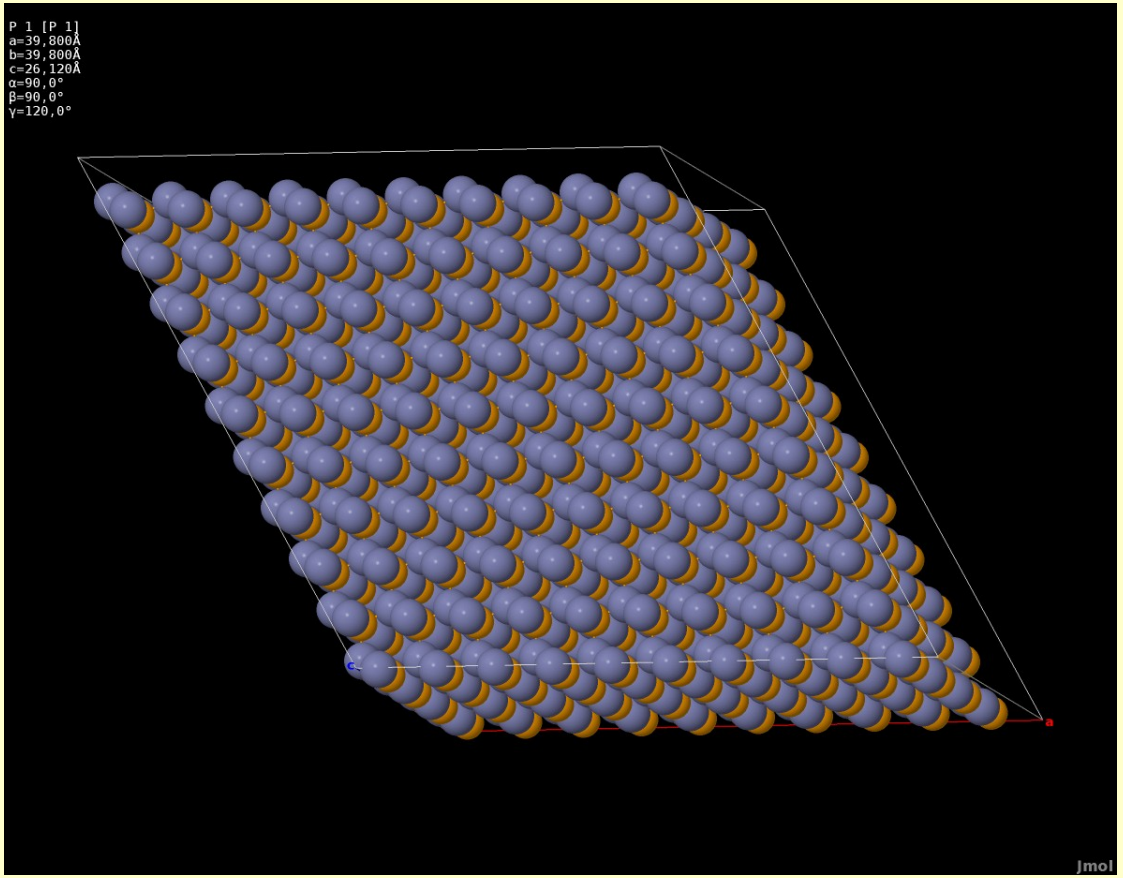
Figure 1. Section of the diffraction pattern of the 8 μm^3 crystal. (a) The enlarged section shows the diffuse scattering parallel to [001]* through the 02*l* reflections. (b) The reflection at the bottom of this enlargement is the 021.

Goal

Simulate all things



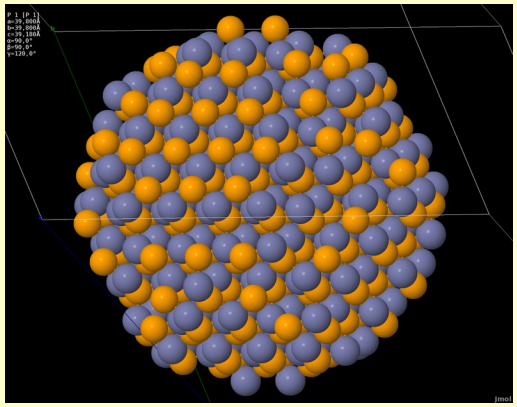
Small
like nanoparticles



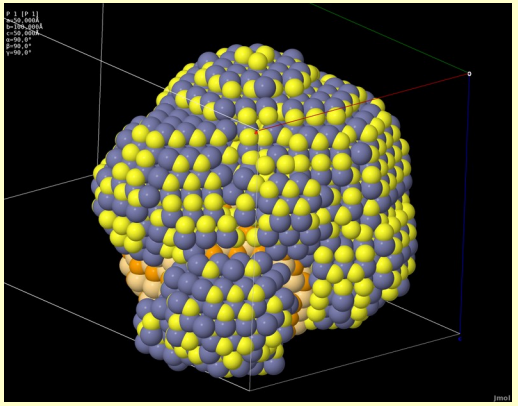
and large
which means periodic boundary conditions
like single crystals or glasses

Goal

Simulate all things

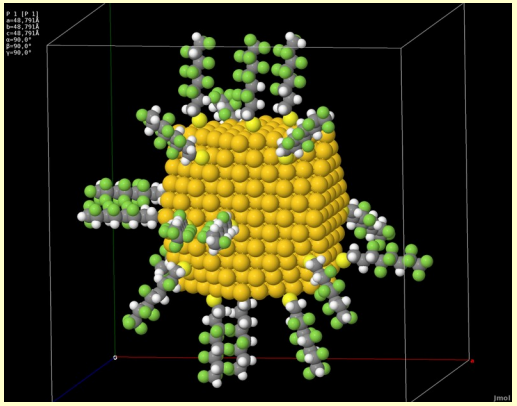


simple

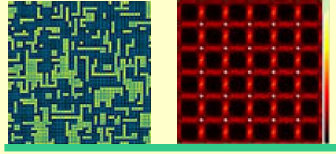


2005

and complex

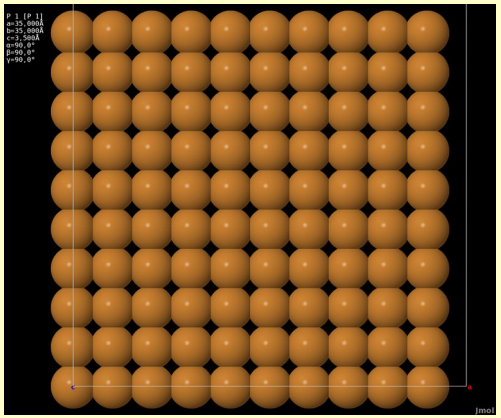


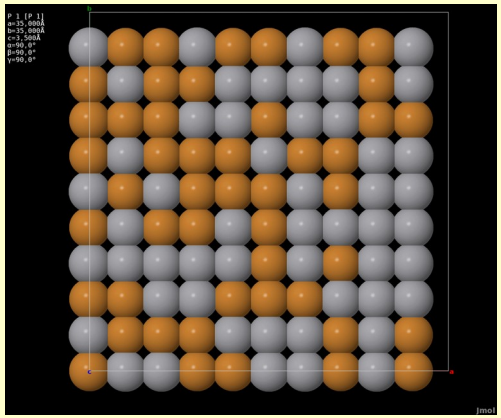
2011

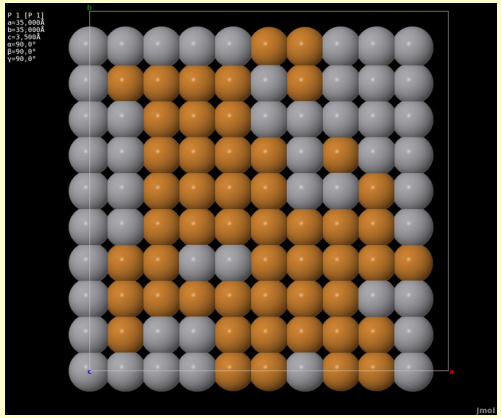


Goal

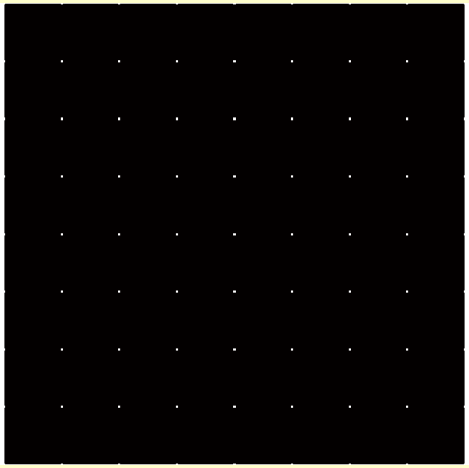
Simulate all things

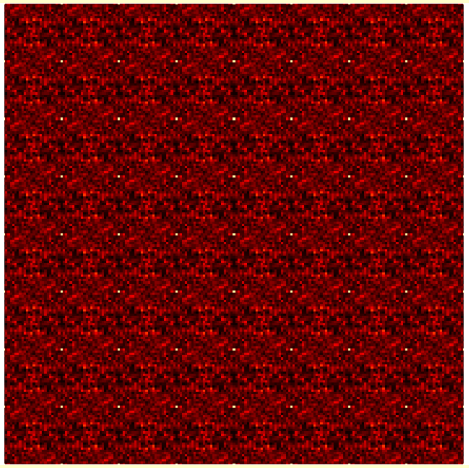


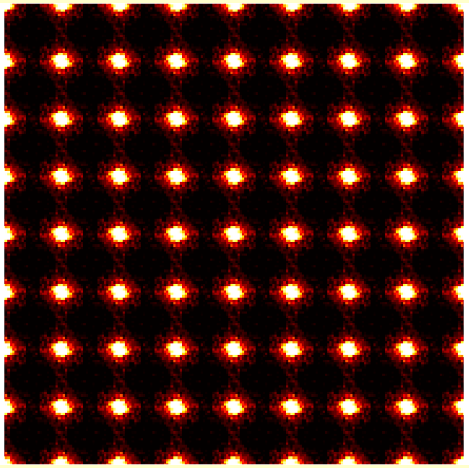




perfect **or random** **and short range ordered**

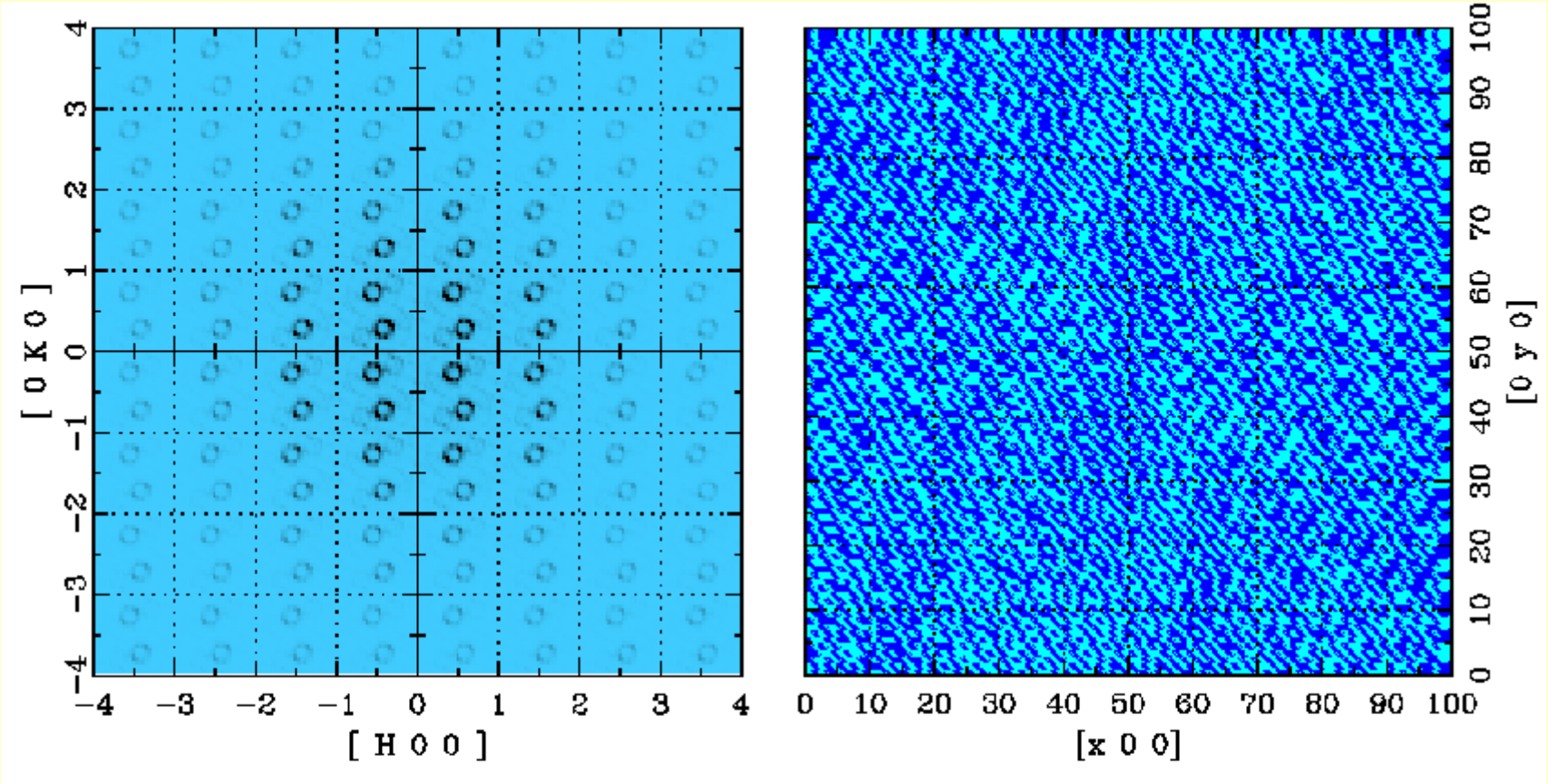






Goal

Simulate all things



or extremely complex

==> Ella M. Schmidt; Wed. 17:35

Differences to *Rietveld* or *single crystal Bragg work*

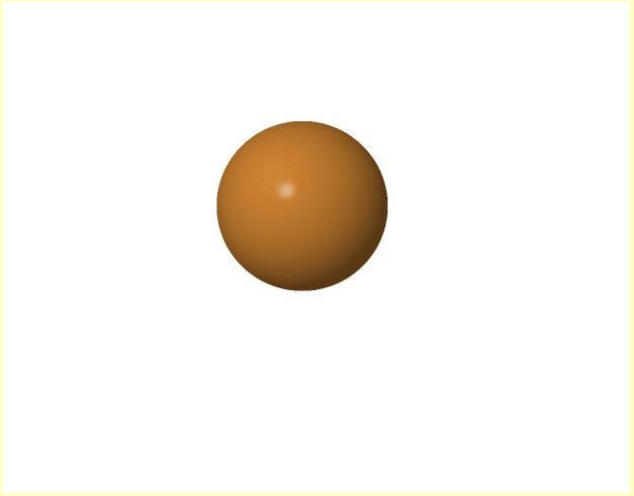
Rietveld / Single Crystal Bragg	Simulation of disorder
Just atoms in **one** asymmetric unit	list of ~ million atoms
sequence of atoms in computer memory irrelevant	very often one needs relations between „neighbors“ need to know sequence

Typical Simulation

Read asymmetric unit

```
title  primitive cubic
spcgr  Pm-3m
cell   5.00, 5.00, 5.00, 90.0, 90.0, 90.0
atoms
Cu   0.000000,  0.000000,   0.000000,  0.8
```

Alternative: import CIF
import SHELX
import RMCprofile

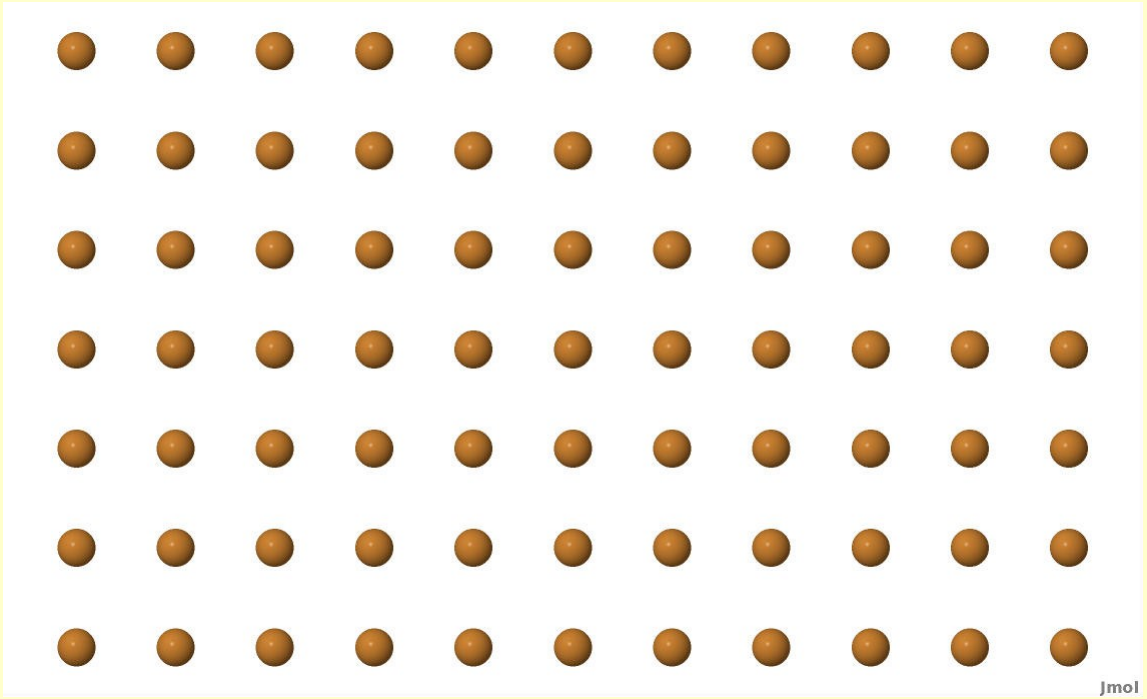


Typical Simulation

Read asymmetric unit

Expand to full unit cell
Expand to a block sized crystal

Keep shape simple!
Simulated crystal is small compared to real sample!



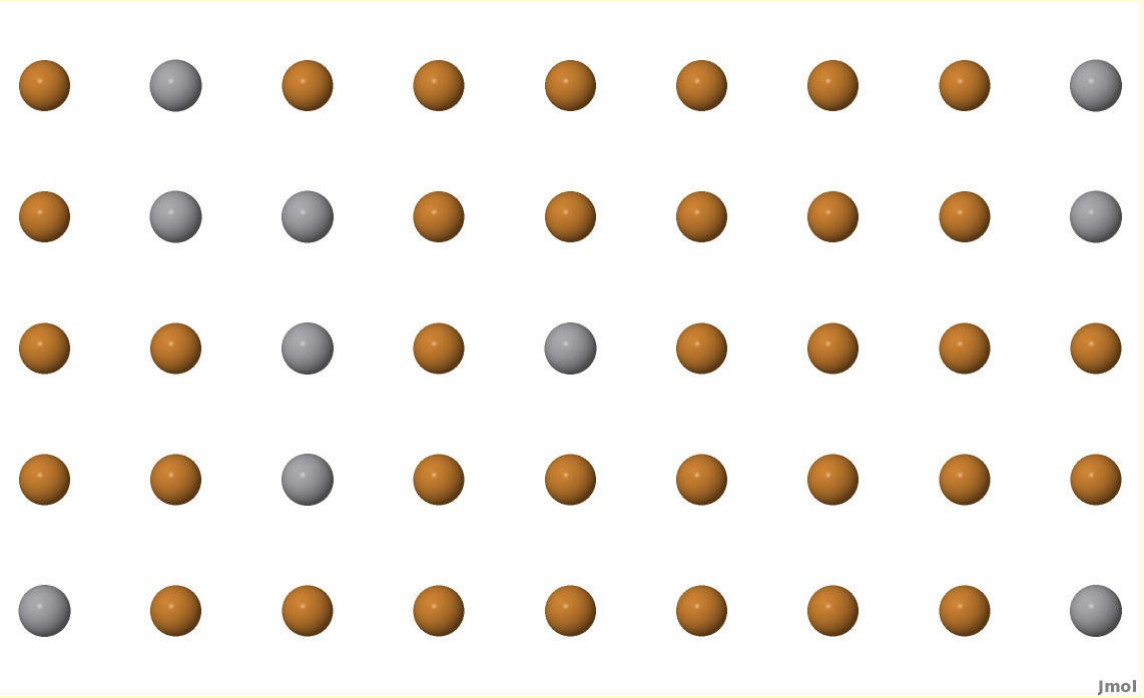
Typical Simulation

Read asymmetric unit

Expand to full unit cell
Expand to a block sized crystal

Introduce defects

- Randomly placed
  - atoms / molecules
  - domains
  - shift atoms
  - ...



Typical Simulation

Read asymmetric unit

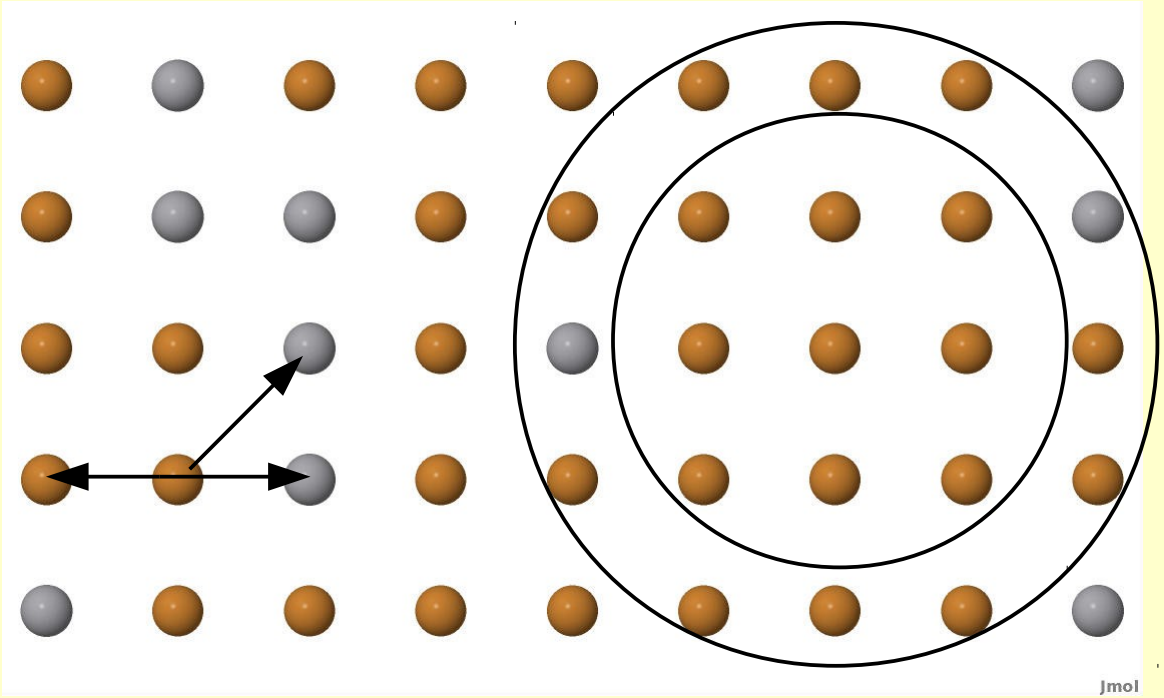
Expand to full unit cell
Expand to a block sized crystal

Introduce defects

- Randomly placed
  - atoms / molecules
  - domains
  - shift atoms
  - ...

Introduce correlations

- Neighbors in [100] or ...
- Neighbors in a shell
- Atoms type A and B or ...



Typical Simulation

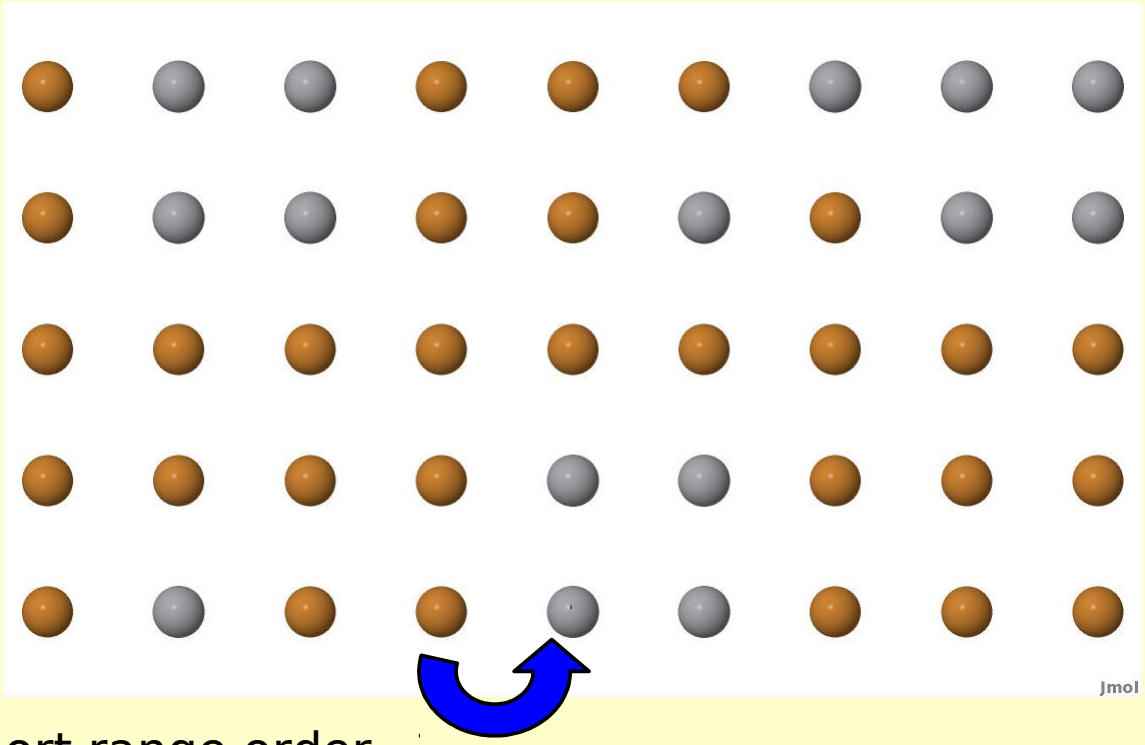
Read asymmetric unit

Expand to full unit cell
Expand to a block sized crystal

Introduce defects

Introduce correlations

Modify crystal while
minimizing energy
associated with correlations



Ising models for chemical short range order
Distance potentials
Angular potentials
...

Typical Simulation

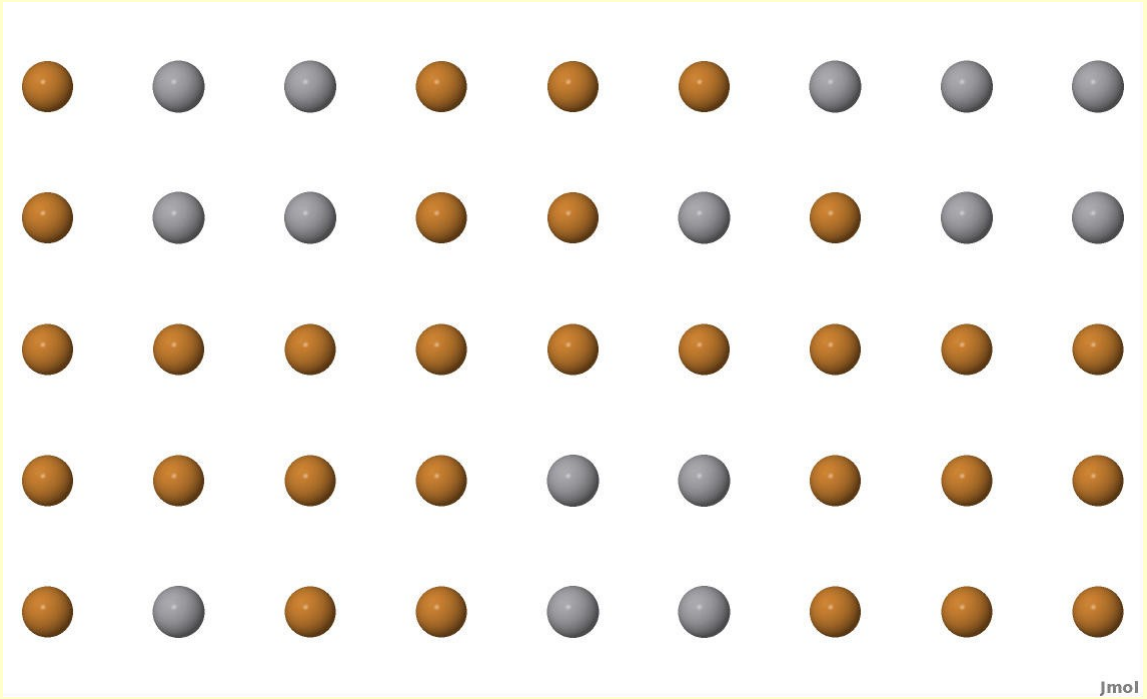
Read asymmetric unit

Expand to full unit cell
Expand to a block sized crystal

Introduce defects

Introduce correlations

Modify crystal

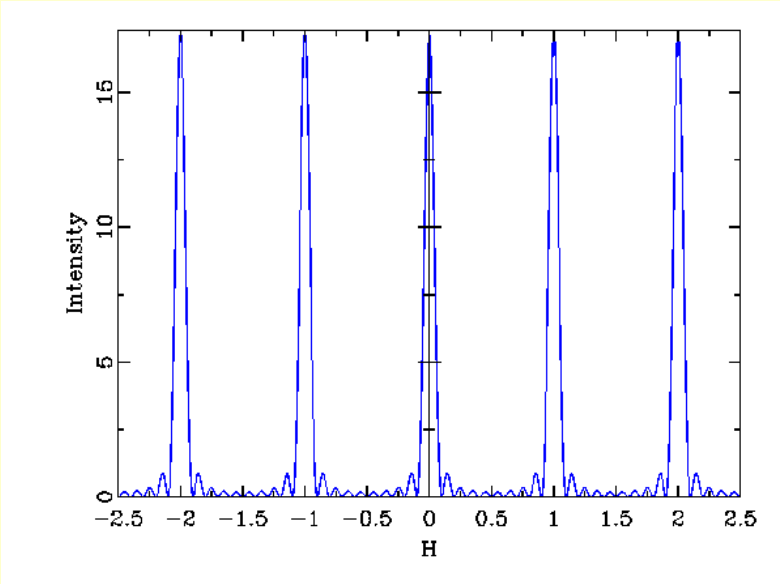


Calculate: single crystal diffraction pattern
powder diffraction pattern
powder PDF
3D PDF

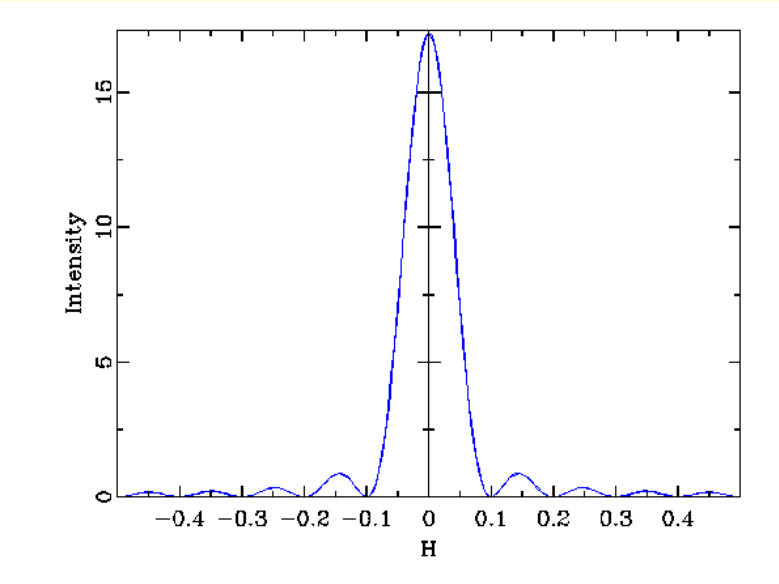
Refine: structure and disorder against experimental pattern

chain of 10 Si atoms

Calculated neutron diffraction pattern (intensity)



periodic reflections spaced at 1/(Si-Si)



detail of a reflection

zero points at 1/10 reziprocal lattice constants

Simulated crystals are small !!

Calculate diffraction pattern while avoiding finite size effects

Simulate Block of N unit cells; calculate in reciprocal space at 1/N • a*

Typical Simulation

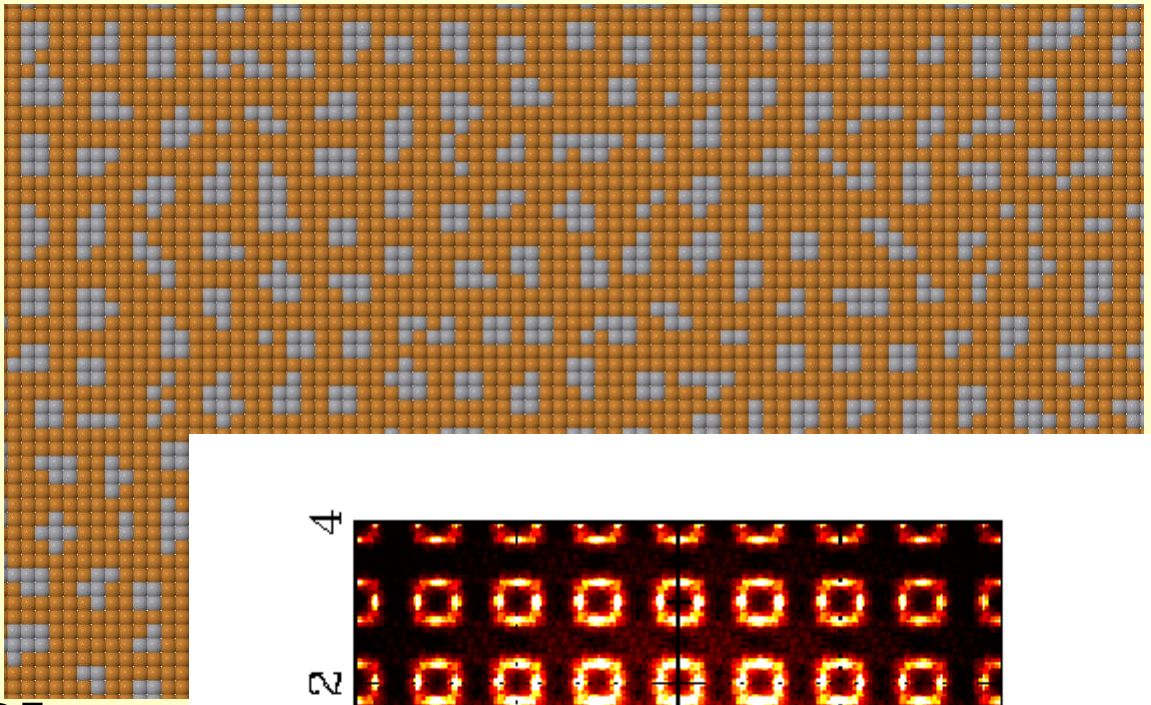
Read asymmetric unit

Expand to full unit cell
Expand to a block sized crystal

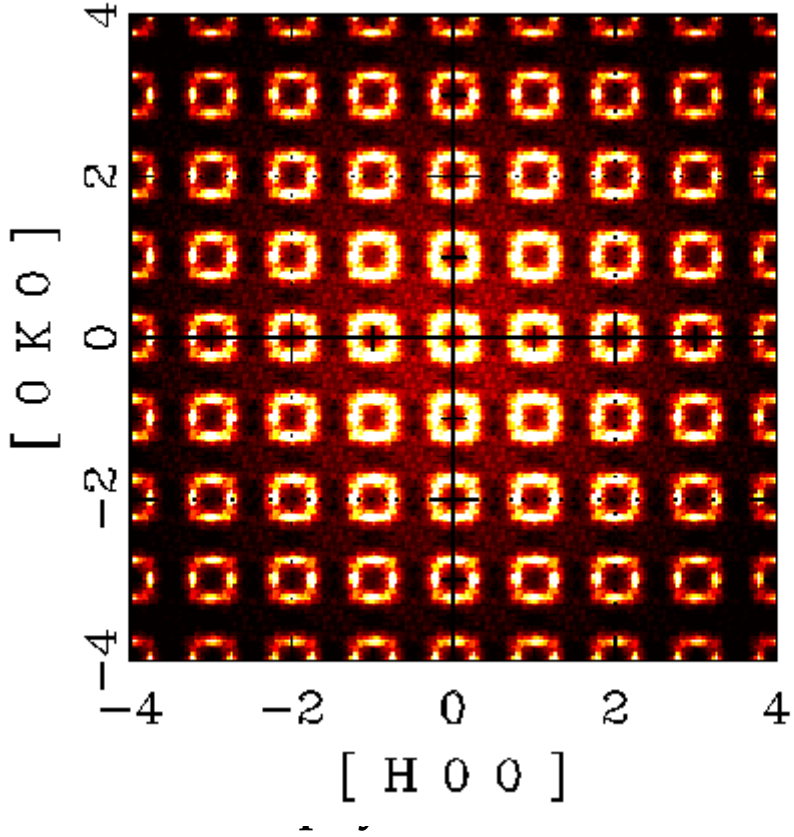
Introduce defects

Introduce correlations

Modify crystal



Calculate diffraction pattern / PDF



Compare to experimental data
Refine disorder parameters

DISCUS

Command line driven program

you type individual commands

main commands must be memorized

Extensive on-line help

very flexibel

includes a programming language

allows simulation of any atom configuration

crystal, glass, nanoparticles, quasicrystals, ...

Structured into menus

combine several main tasks

read a unit cell / a structure
calculate diffraction pattern / PDF
plot the structure
analyze structure
extended defects

SRO, strain, stacking faults, domains, waves

nanoparticle builder

surface decoration

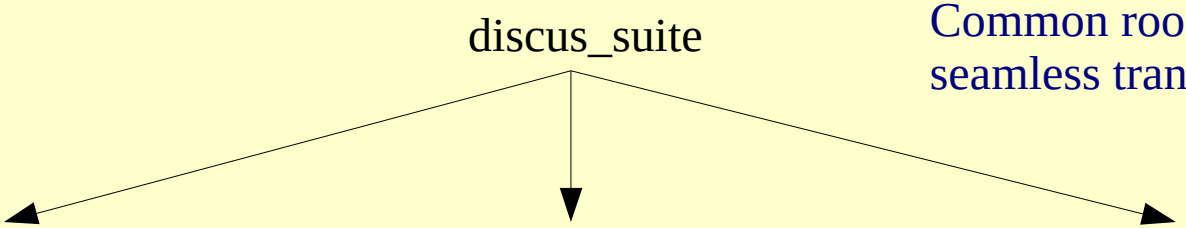
Refinement

Flexible global optimizer

Define disorder model
Simulate structure
calculate diffraction pattern / PDF

RMC single crystal / powder

DISCUS Program package



Common roof to provide seamless transitions

crystal builder

graphics, assesment

General optimizer

Build in parallel options

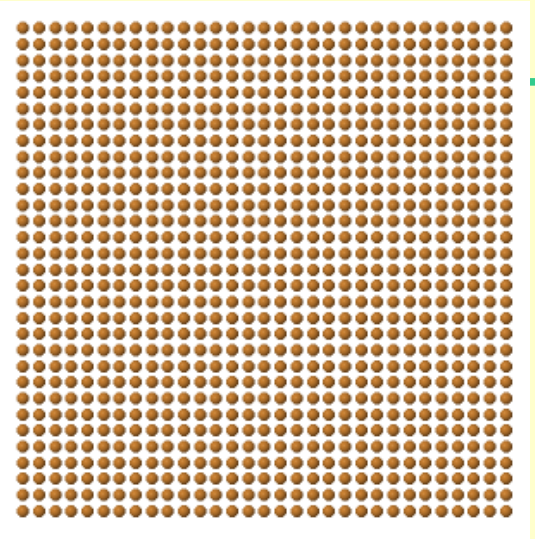
Availability:

Linux, Unix, Mac-OS, Windows,
Windows Subsystem for Linux

Single computer
Massive parallel farms

Example

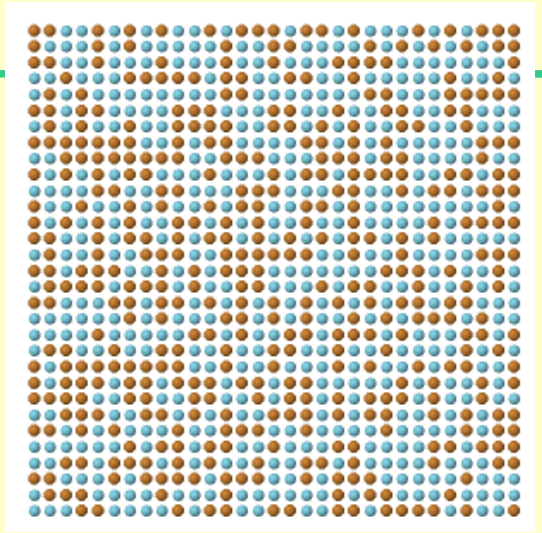
```
#
read
     cell crystal.cell,200, 200,1
#
plot
     program cif
     select all
     outfile crystal_plot.cif
     run
exit
#
```

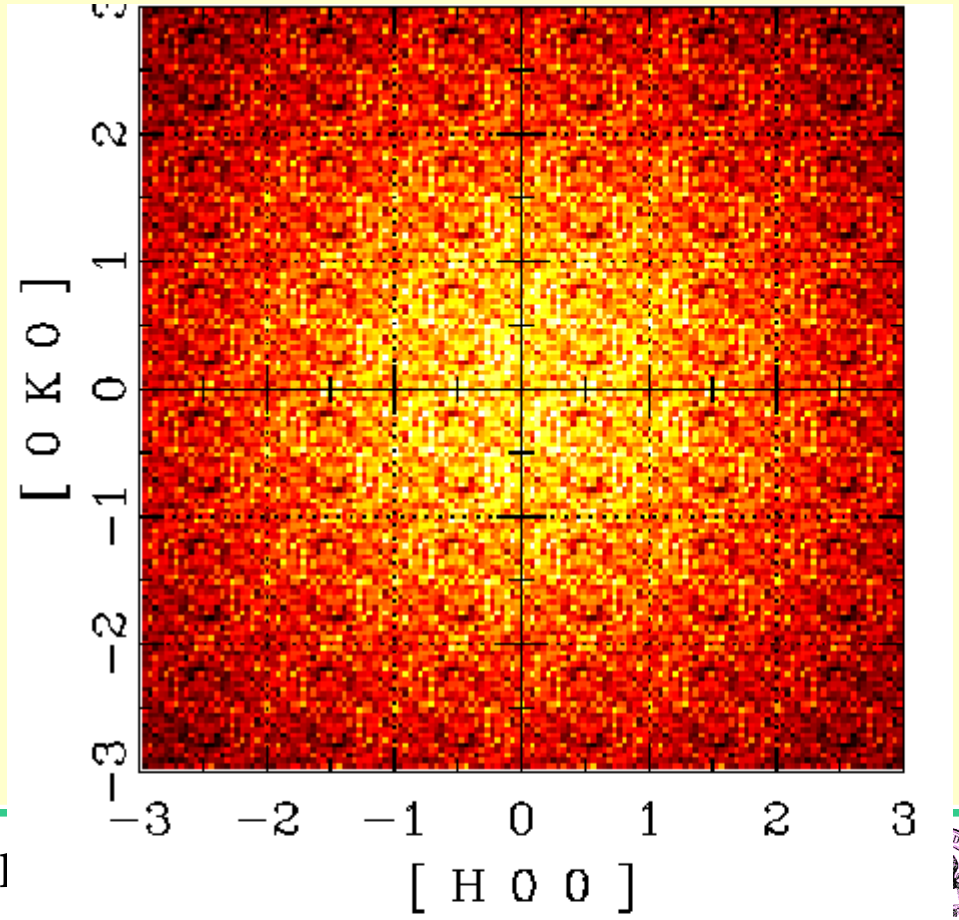


DISCUS / short range order menu

Example

```
#
read
     cell crystal.cell,200, 200,1
#
replace cu,au,all,0.50
#

#



#

#
fourier
     xray
     ll  -3.00, -3.00, 0.00
     lr  -3.00, -3.00, 0.00
     ul  -3.00, -3.00, 0.00
     na  151
     no  151
     run
exit
```

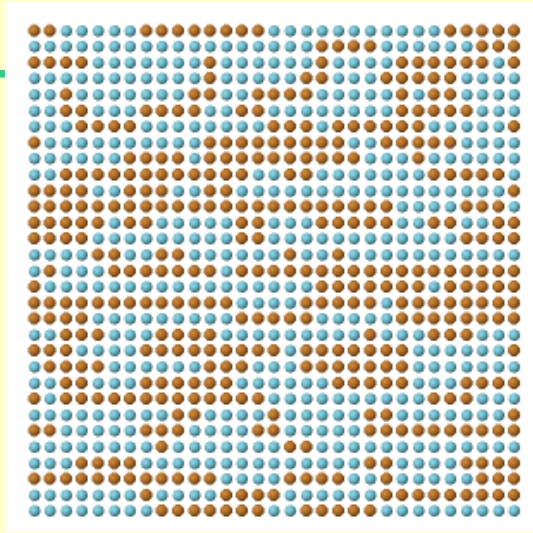


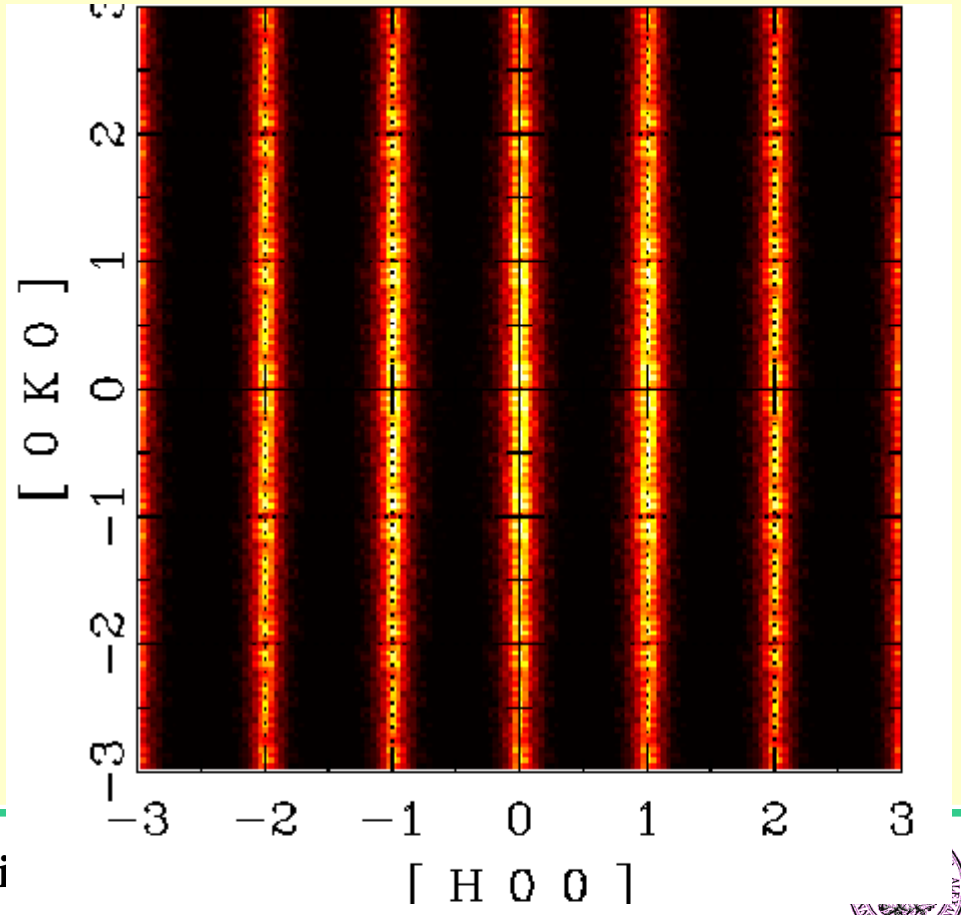


DISCUS / short range order menu

Example

```
#
read
     cell crystal.cell,200, 200,1
#
replace cu,au,all,0.50
#
mmc
#
     set vec,1, 1,1,  1, 0, 0
     set vec,2, 1,1, -1, 0, 0
     set neig,vec,1,2
#
     set mode, 1.0, swchem,all
     set targ,1,corr,cu,au, 0.80, 0.0,CORR
     set cyc, 100*n[1]
     set feed,  5*n[1]
     set temp,  2.5
     run
exit
#
fourier
     xray
     ll  -3.00, -3.00, 0.00
     ll  -3.00, -3.00, 0.00
     ll  -3.00, -3.00, 0.00
     na  151
     no  151
     run
exit
```



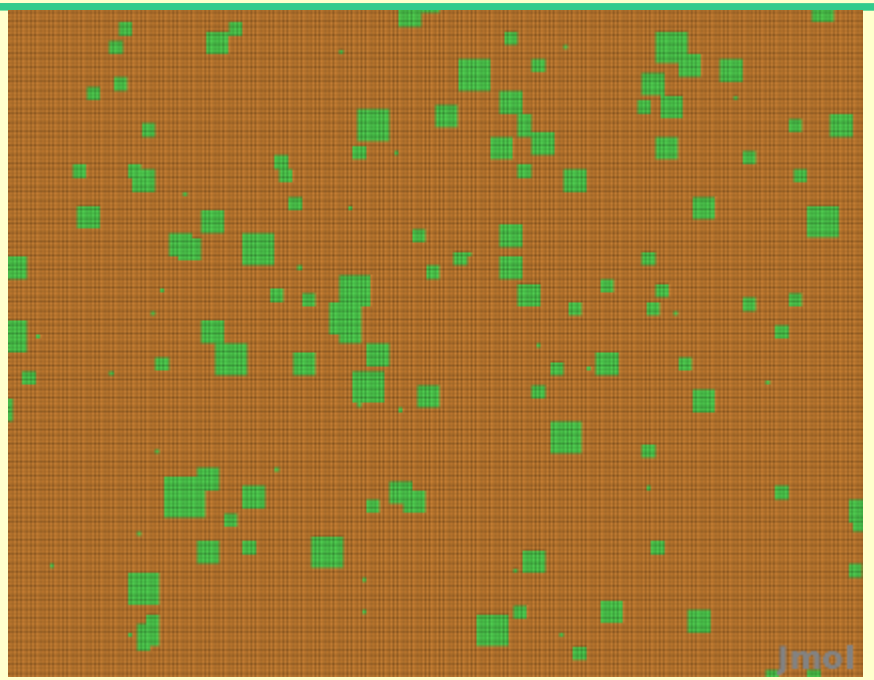


DISCUS / domain concept

```
#        Example
read
     cell host.cell,200, 200,1
#
domain
#
    mode pseudo
    input domain.list  !Domain origins
#
    assign character, SI, cube
    assign fuzzy,     SI, 1.5
    assign content,   SI, guest.stru
    assign orient,    SI,1,  1,0,0,  0
    assign orient,    SI,2,  0,1,0,  0
    assign orient,    SI,3,  0,0,1,  0
    assign shape,     SI,1,  2,0,0,  0, 0.5
    assign shape,     SI,2,  0,2,0,  0, 0.5
    assign shape,     SI,3,  0,0,1,  0, 0.0

    run
exit
#
plot . . .
```

A regular DISCUS file with Domain coordinates

use any tool to distribute the origins

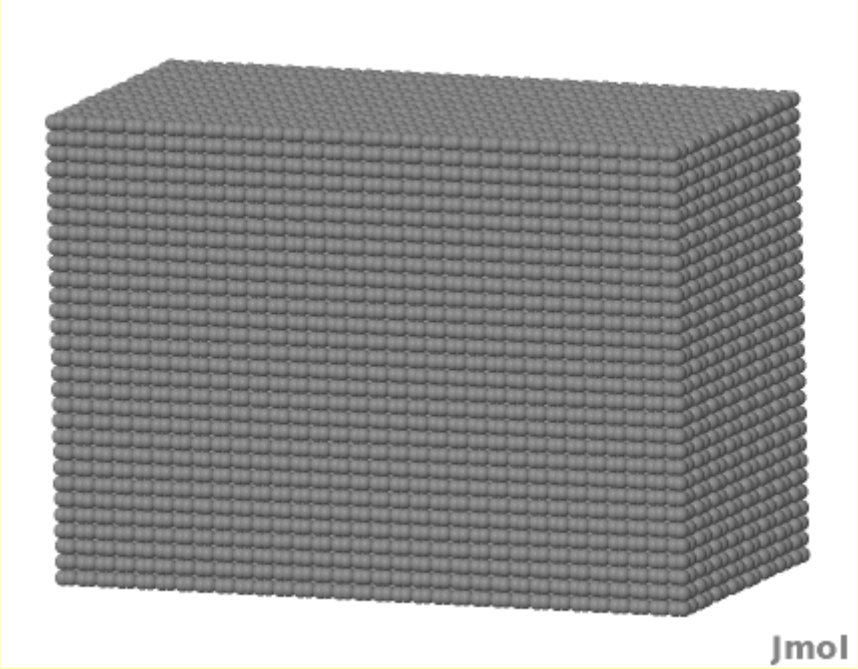


domain.list

```
title Primitive host structure
spcgr P4
cell  2.50, 2.50, 2.50, 90., 90., 90.
atoms
SI    71.0,-100.00,   0.00,  0.05, 1
SI   -22.0, -98.00,   0.00,  0.05, 1
. . .
SI   -19.0,   2.00,   0.00,  0.05, 1
SI    75.0,   2.00,   0.00,  0.05, 1
SI   -20.0,   5.00,   0.00,  0.05, 1
. . .
```

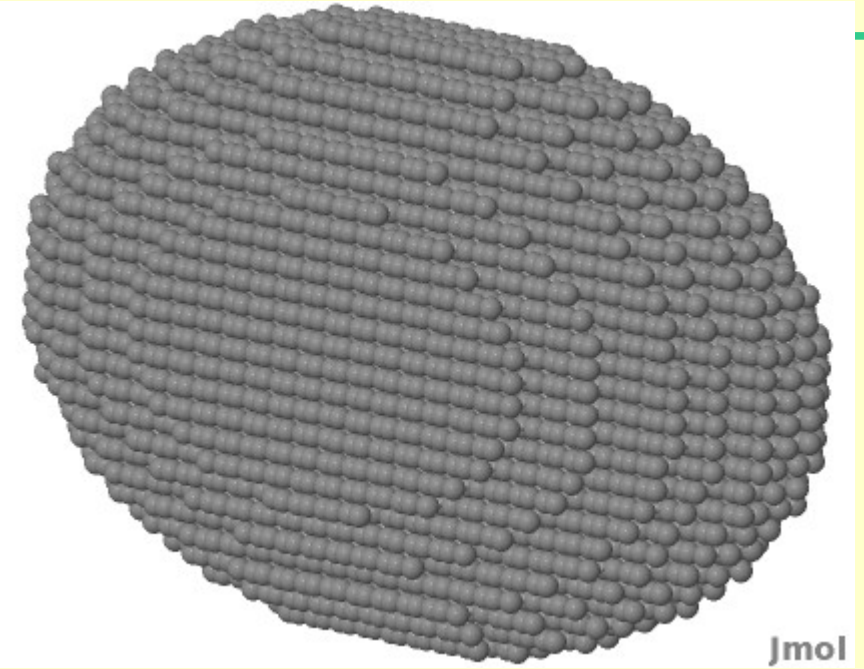
DISCUS / nanoparticle

```
variable real, diam_a
variable integer, ncellx
#
diam_a = $1
#
read
     cell 2,3,4, 90,90,90, Pmmm
#
ncellx = int(diam_a/lat[1]) + 2
#
read
   cell diamond.cell, ncellx, ncelly, ncellz
#
@plot.mac block
```



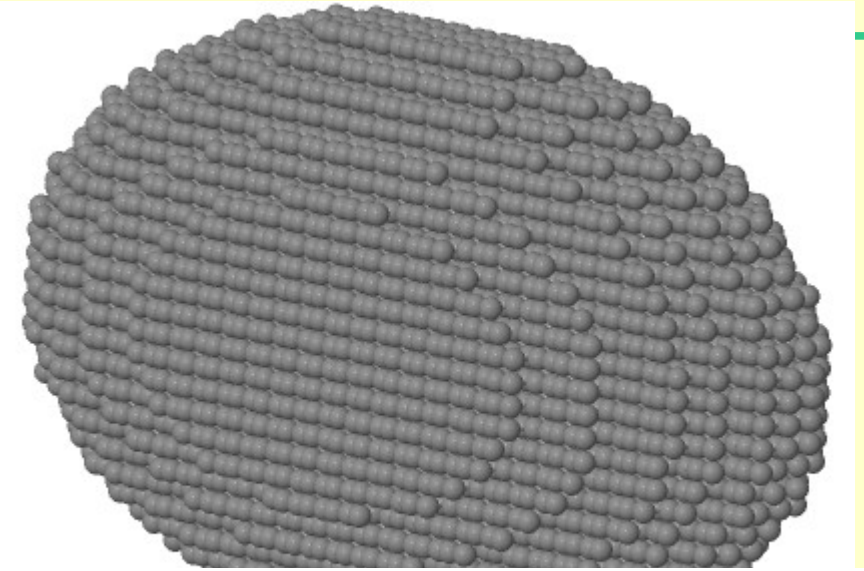
DISCUS / nanoparticle

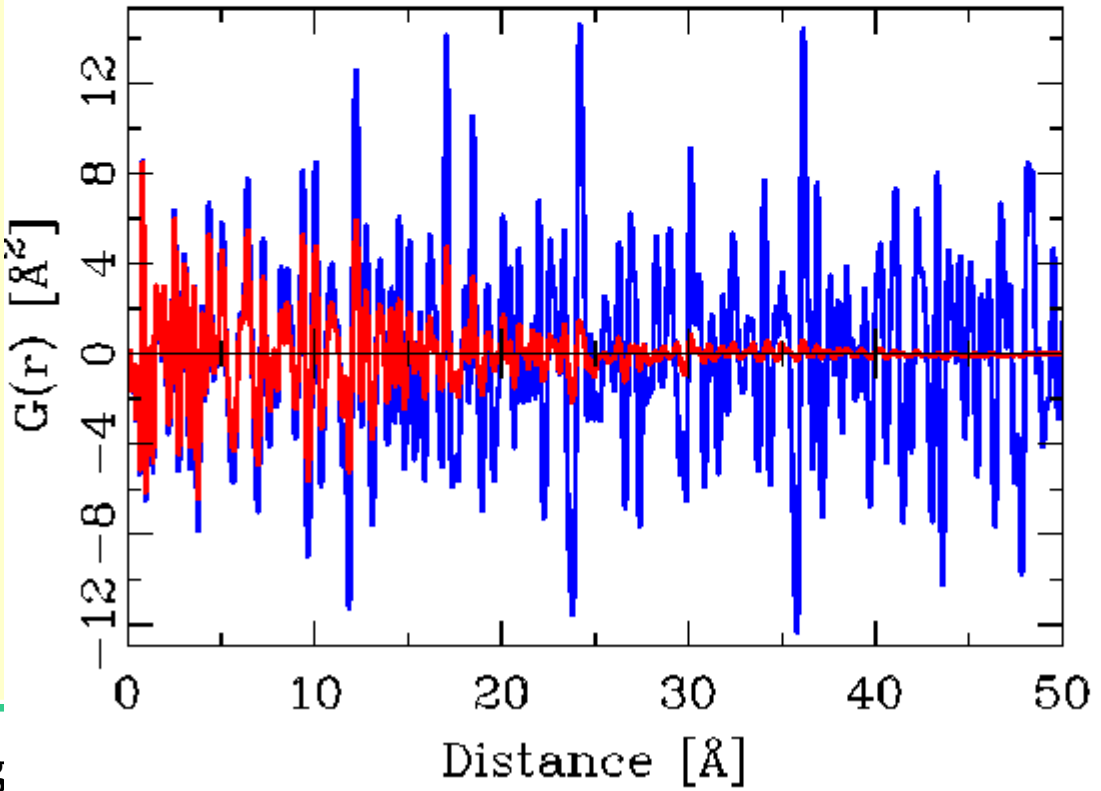
```
variable real, diam_a
variable integer, ncellx
#
diam_a = $1
#
read
     Cell diamond.cell
#
ncellx = int(diam_a/lat[1]) + 2
#
read
   cell diamond.cell, ncellx, ncelly, ncellz
#
@plot.mac block
#
surface
   boundary  ellipsoid, diam_a, diam_b, diam_c
Exit
#
purge
@plot.mac ellipsoid
```



DISCUS / nanoparticle

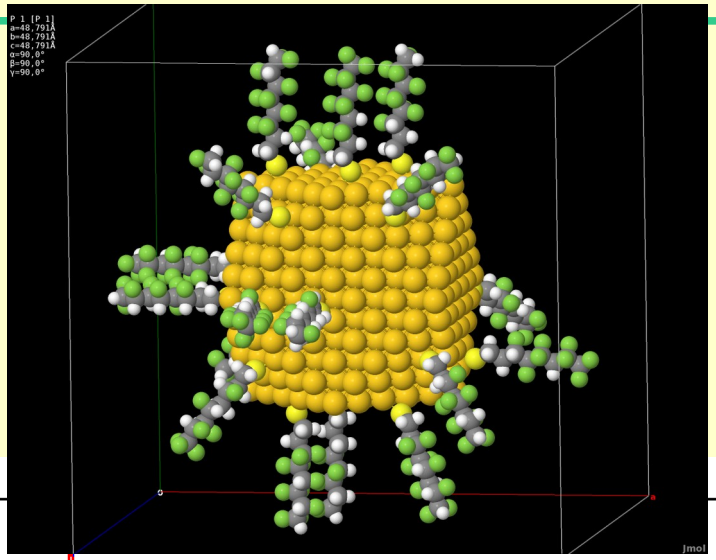
```
variable real, diam_a
variable integer, ncellx
#
diam_a = $1
#
read
     Cell diamond.cell
#
ncellx = int(diam_a/lat[1]) + 2
#
read
   cell diamond.cell, ncellx, ncelly, ncell
#
@plot.mac block

surface
   boundary  ell, diam_a, diam_b, diam_c
exit
#
purge
@plot.mac ellipsoid
@pdf.mac  ellipsoid
```

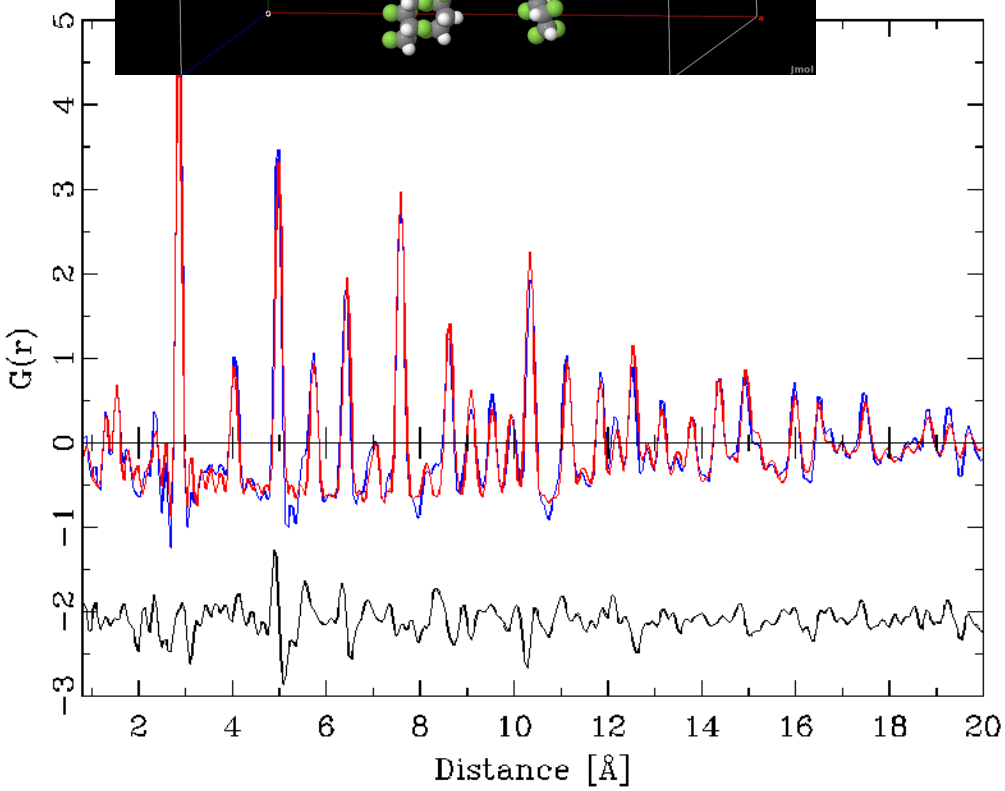




DISCUS / nanoparticle

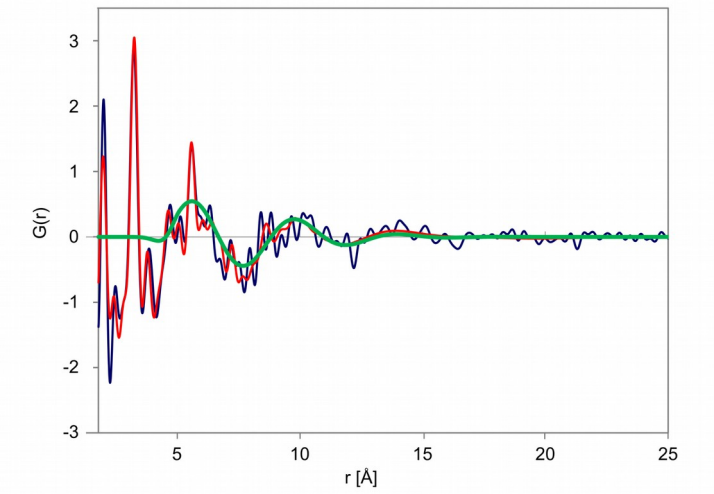
```
variable real, diam_a
variable integer, ncellx
diam_a = $1
read
     cell gold.cell
ncellx = int(diam_a/lat[1]) + 2
read
   gold diamond.cell, ncellx, ncelly, ncellz
@plot.mac block
#
surface
   boundary  cubeoct, diam_a
exit
#
purge
decorate
   add thio, normal
   set thio, ligand, thiooct.stru, 0.05
   set bond, Au, 1, 2.42
   run
exit
@plot.mac cubeoct
@pdf.mac  cubeoct
```



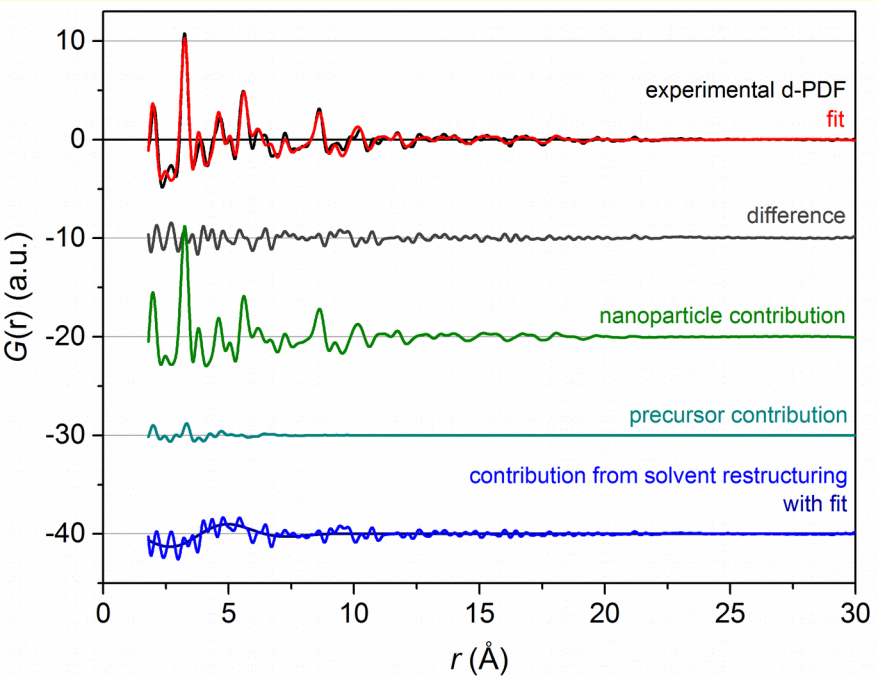


K. Page et al. J.Appl.Cryst 2011

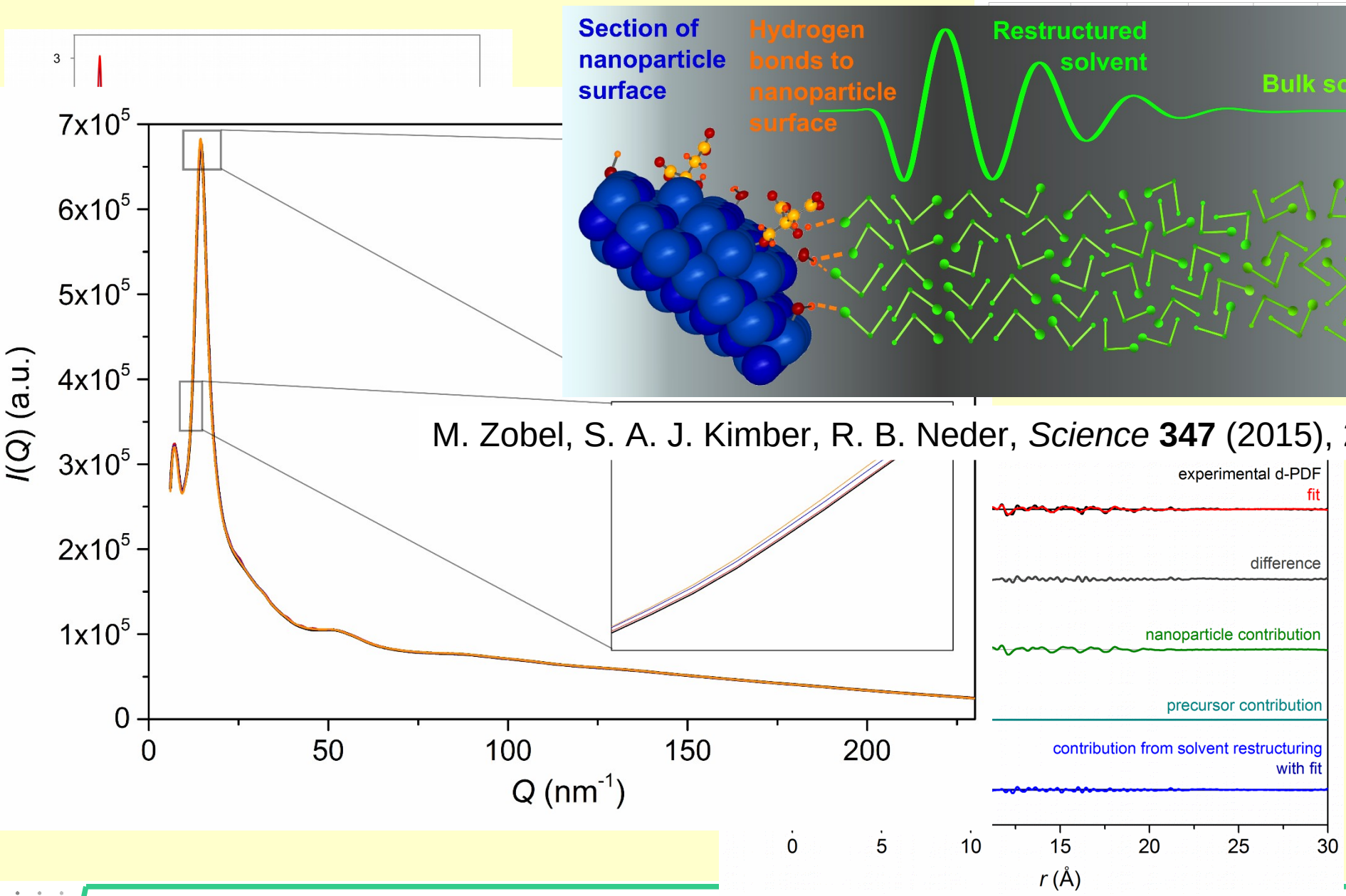
DISCUS / nanoparticles in a solvent



Additional dampened sinusoidal oscilla



DISCUS / nanoparticle



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Literature

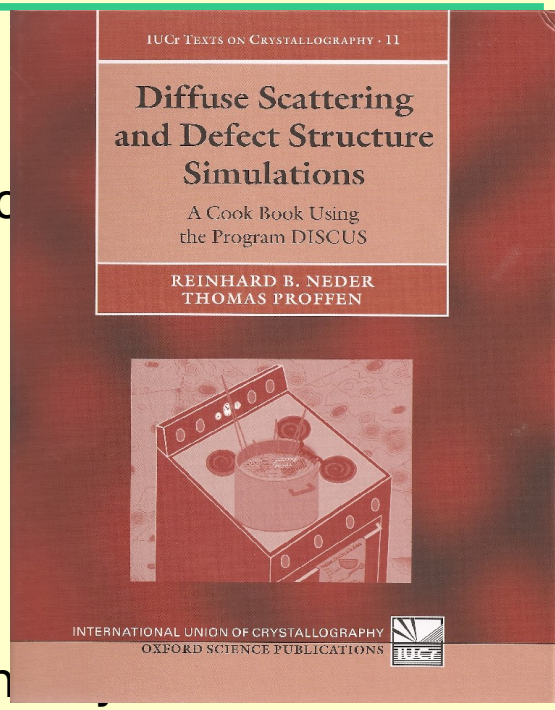
Neder & Proffen, (Oxford, 2008)
Diffuse Scattering and Defect Structure Simulation
Simulation and refinement of disordered structures, coc

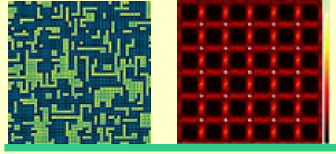
T.R. Welberry (Oxford,2004)
Diffuse X-ray Scattering and Models of Disorder
Limited to X-ray diffraction, short experimental part,
otherwise extensive theory, many examples

V.M. Nield & D.A. Keen (Oxford, 2001)
Diffuse Neutron Scattering from Crystalline Materials
Limited to neutronen diffraction, otherwise extensive th
experimental methods, some simulations, many examples

T. Egami & S.J.L. Billinge (Pergamon 2003)
Underneath the Bragg Peaks
Extensive description of PDF Method

S.J.L. Billinge & M.F. Thorpe Eds. (Plenum, 1997)
Local Structure from Diffraction
Collection of papers on PDF and disorder in general





Literature

Interactive Tutorial on Diffraction

www.lks.physik.uni-erlangen.de/diffraction/index.html

DISCUS source code at:

Releases	github.com/tproffen/DiffuseCode/releases
Source Code	github.com/tproffen/DiffuseCode

DISCUS workshop

August, 2016 prior to ECM @ Vienna, Austria
October 21-24 @ORNL, USA: Total Scattering Analysis School

Looking forward to seeing you at the tutorial!

Learn to

Simulate a disordered single crystal
Refine model to experimental data

Tue: ILL 1 7/8
Wed: ILL 1 7/8