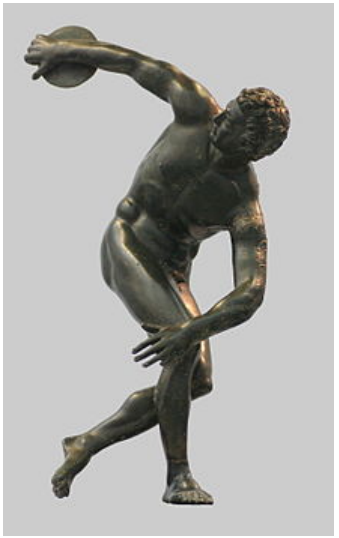
DISCUS,
Simulation and refinement of disordered crystal structures

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

Und



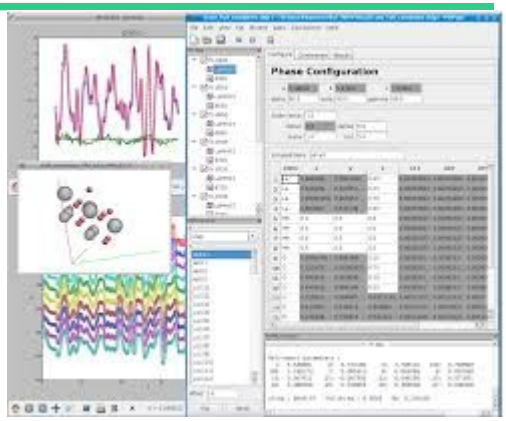
DISCUS Workshop 2018

Reinhard B. Neder
Kristallographie und Strukturphysik
Friedrich-Alexander-University Erlangen-Nürnberg

reinhard.neder@fau.de

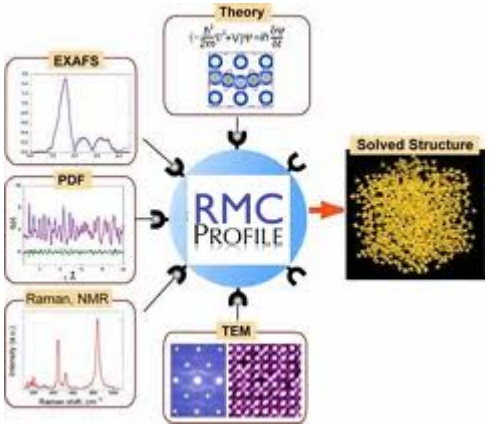
Small Box Modelling

PDFgui



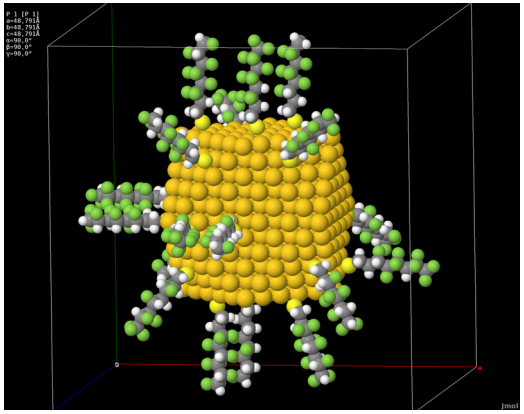
Large Box Modelling

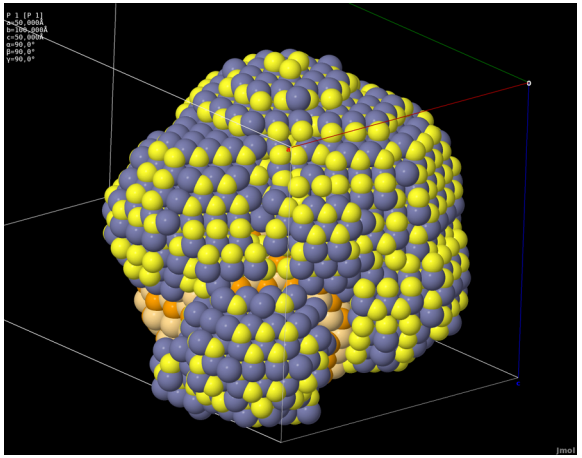
Reverse Monte Carlo
RMCprofile
RMC_POT++
DISCUS



Bottom Up Modelling

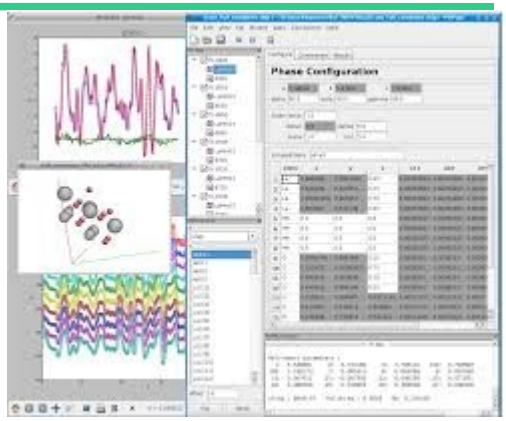
DISCUS





Small Box Modelling

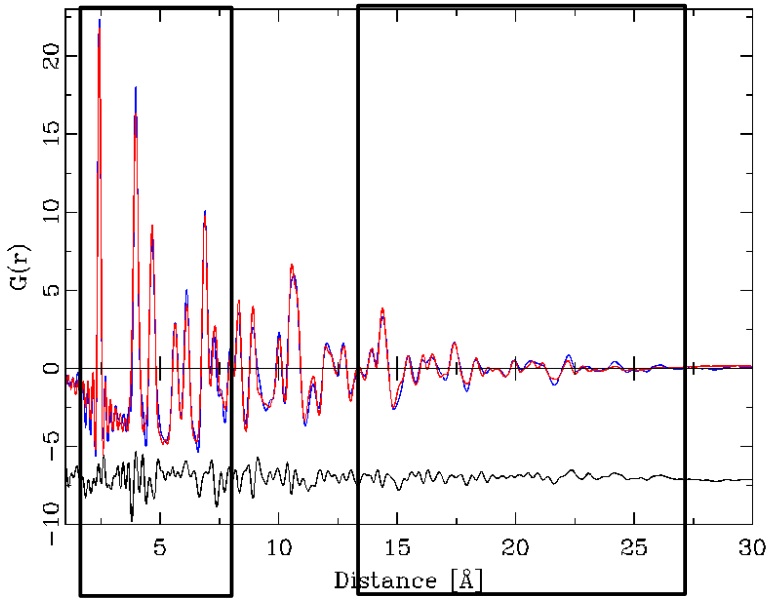
PDFgui



Rietveld type refinement

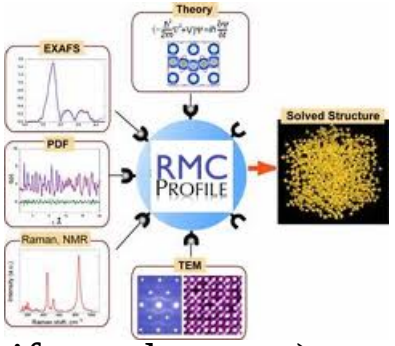
Calculate PDF from single unit cell or **small** block of cells

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

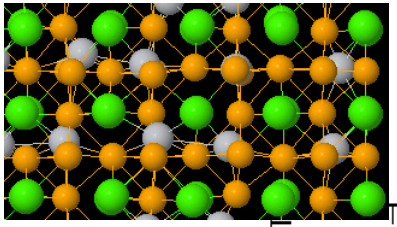


Large Box Modelling

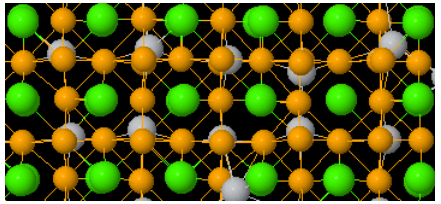
Reverse Monte Carlo
RMCprofile
RMC_POT++

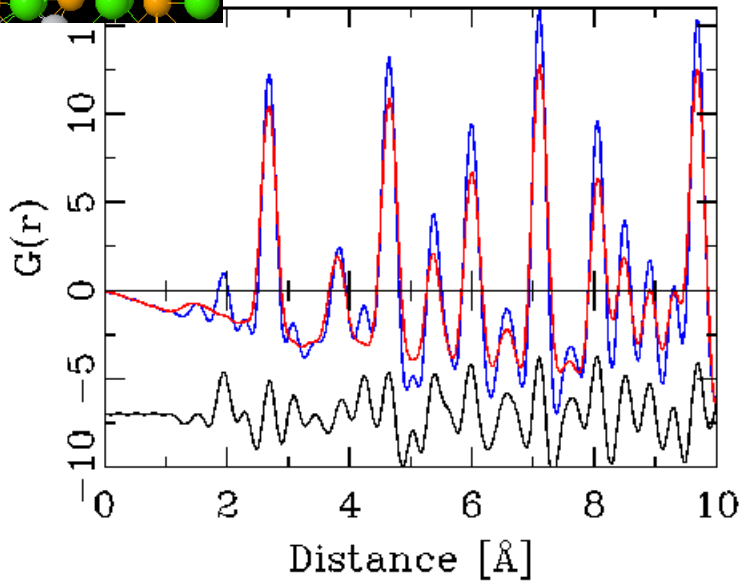


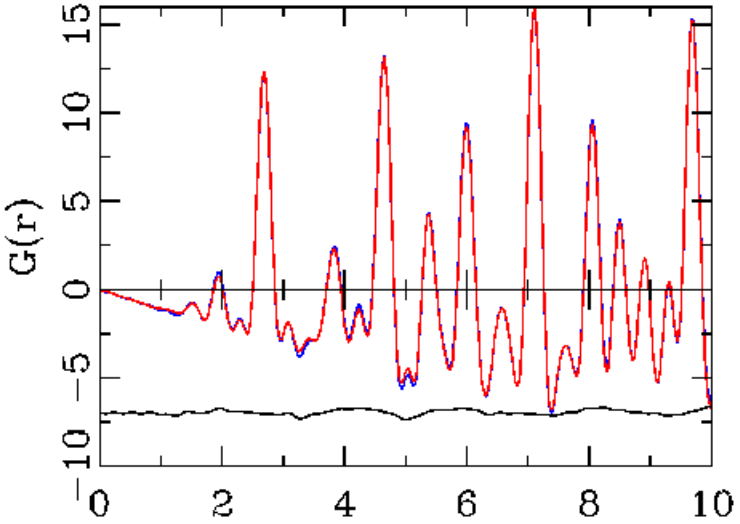
Model initial (random) **large** structure
Calculate PDF (+ powder + ...)



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

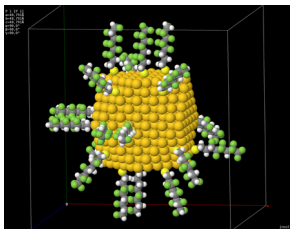


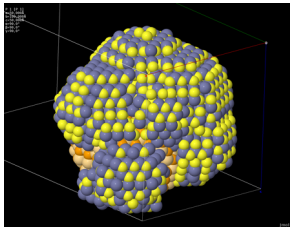




Analyze structure **afterwards**
Local coordination, shifts, etc.

Bottom Up Modelling DISCUS



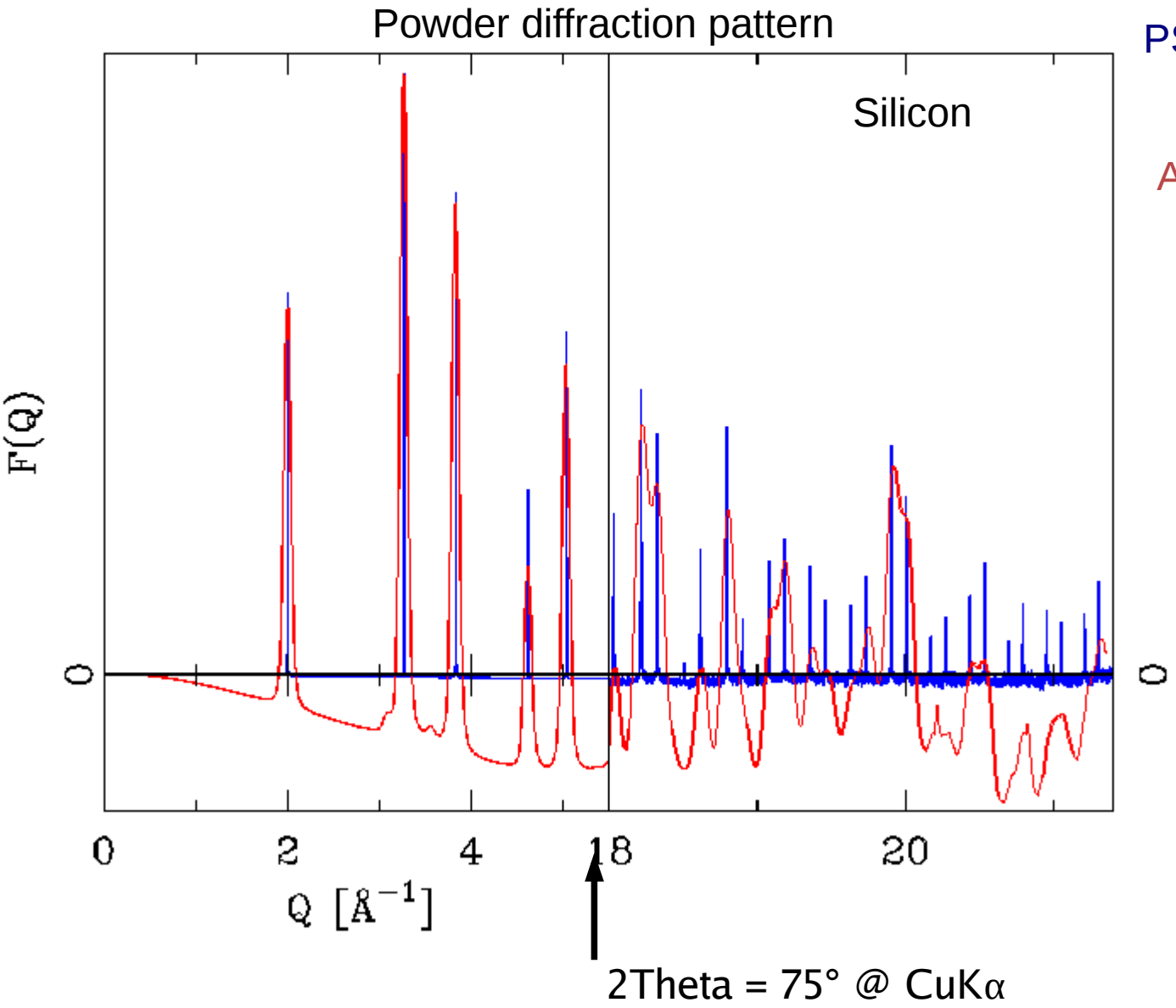


Define disorder rules to simulate complete structure

Non-periodic boundary conditions

Extended defect toolboxes

Experimental Determination of the PDF

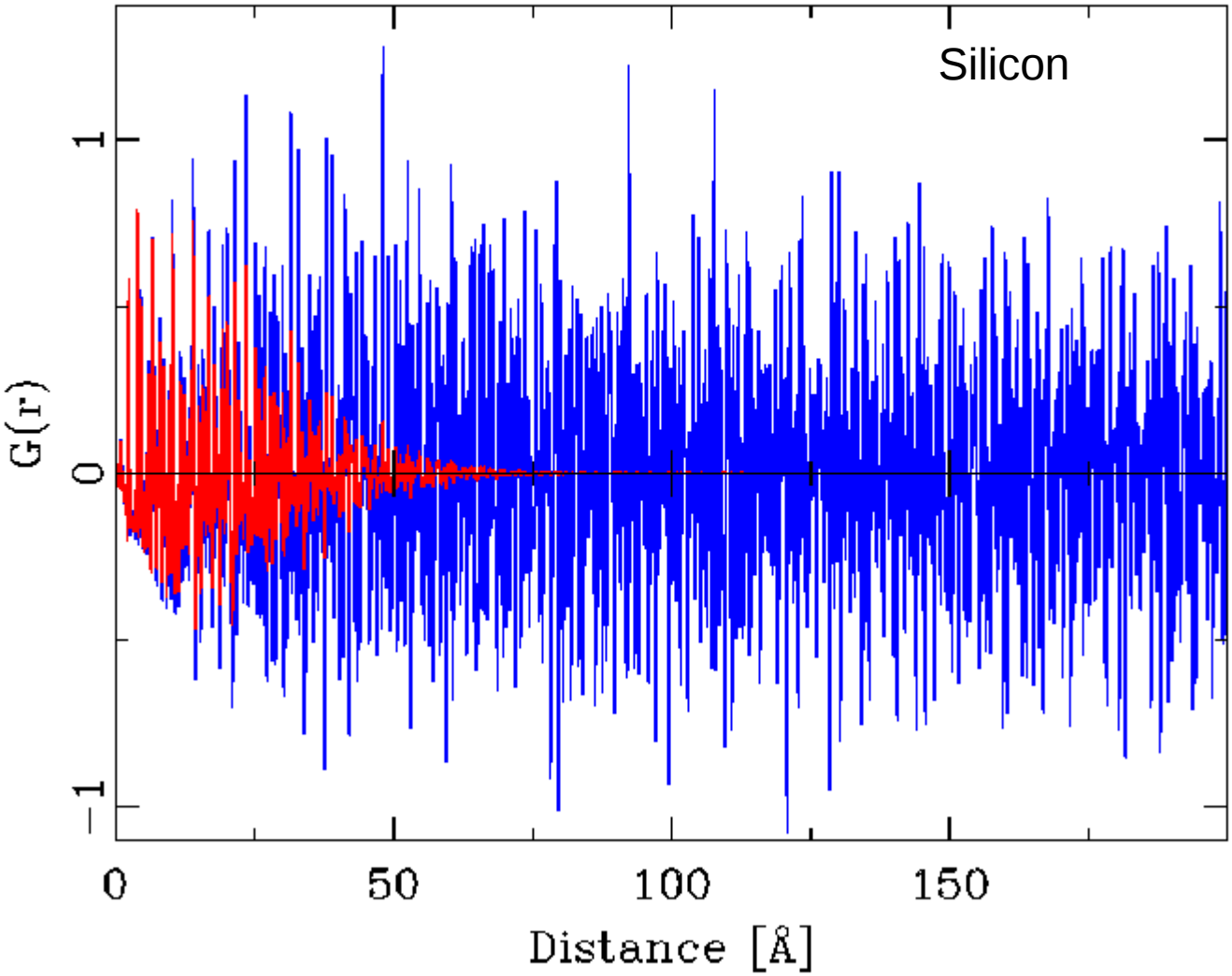


PSI high resolution data
~ 30 min

APS low resolution data
~ 1 min

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

Experimental Determination of the PDF



PSI high resolution data
~ 30 min

APS low resolution data
~ 1 min

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

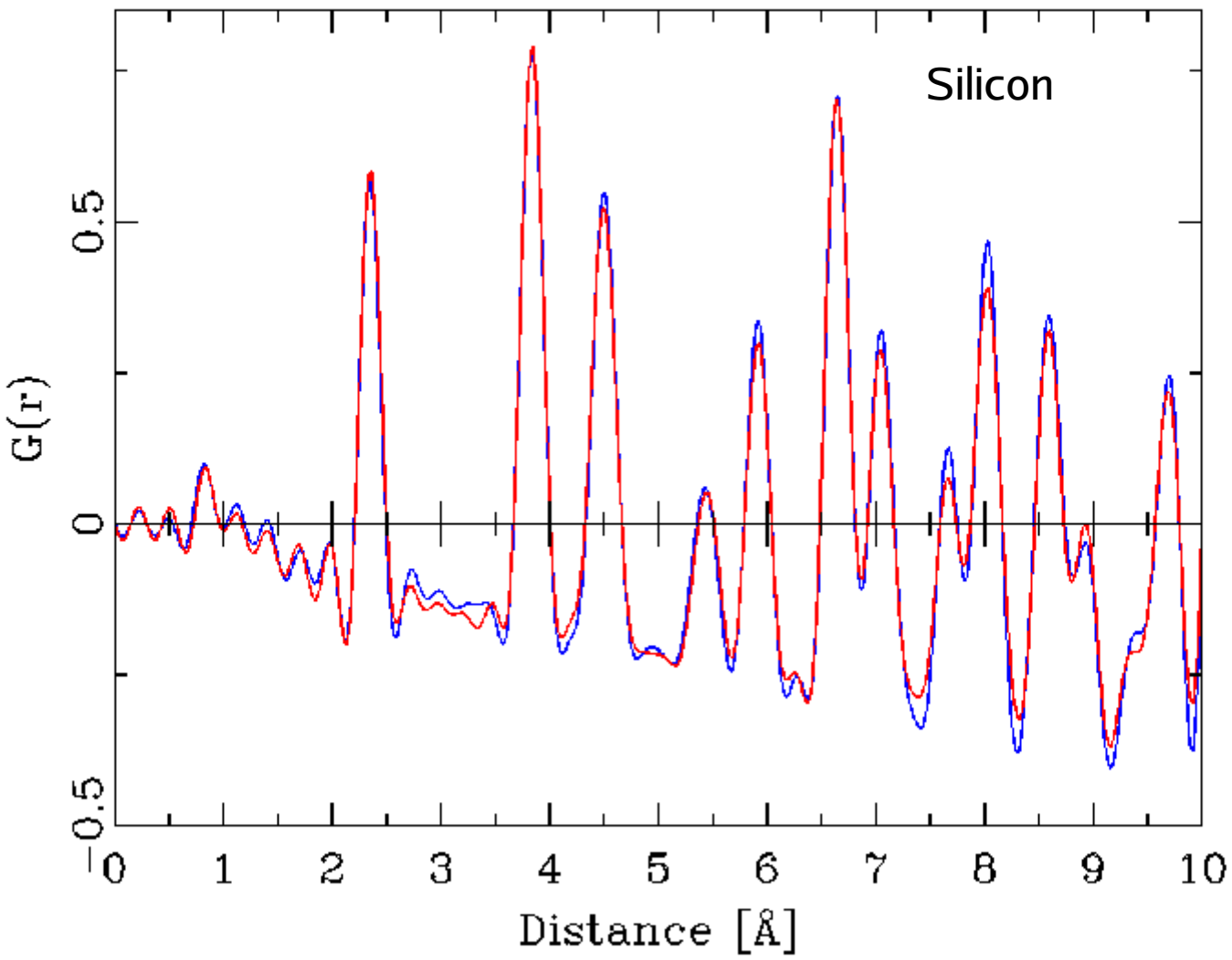
G(r) @ PSI extents well beyond 200 Å !

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



PSI high resolution data
~ 30 min

APS low resolution data
~ 1 min

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

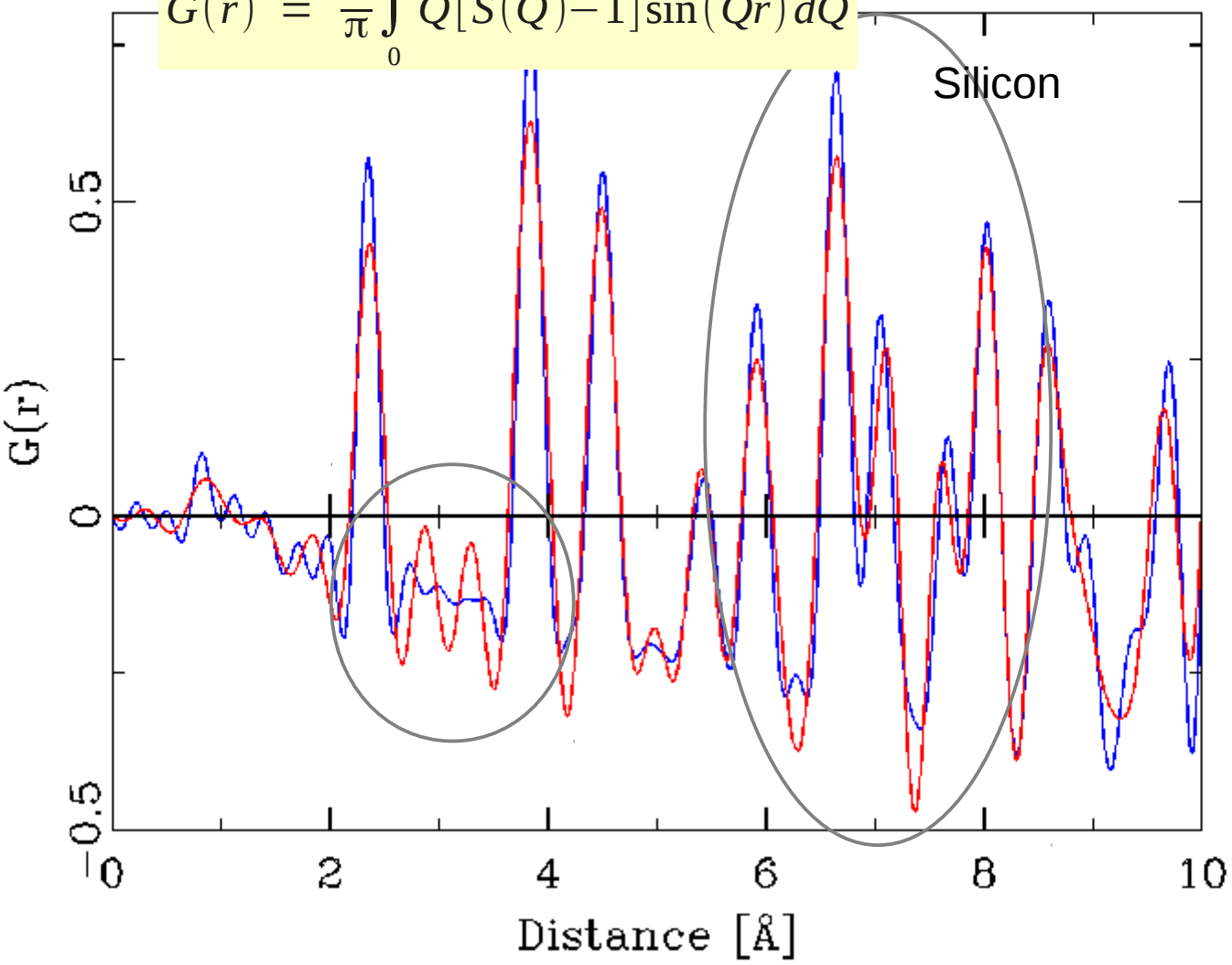
G(r) @ PSI extents well beyond 200 Å !

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

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



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!

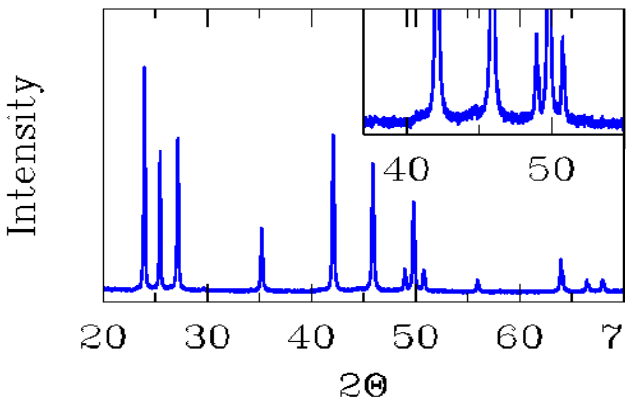
Local disorder in Si !?!

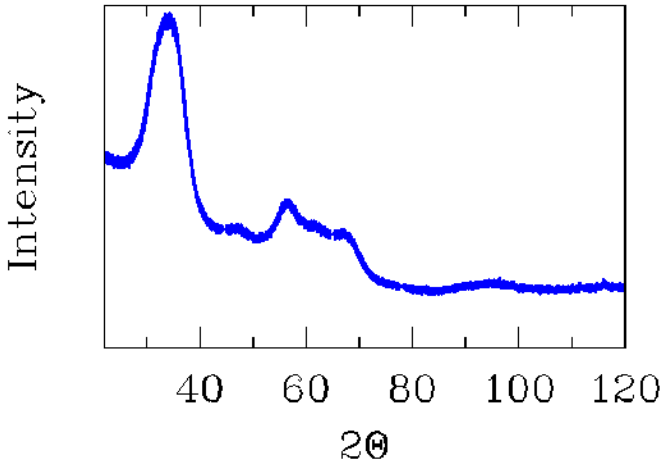
Anything that changes with Q_{max} is not real

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

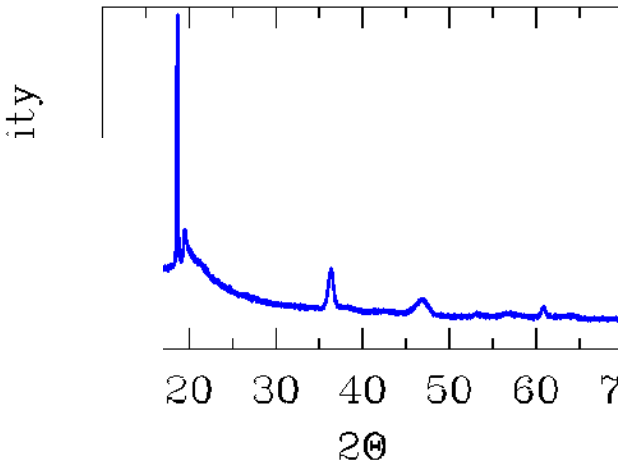
Powder Diffuse Scattering

CdSe crystalline material

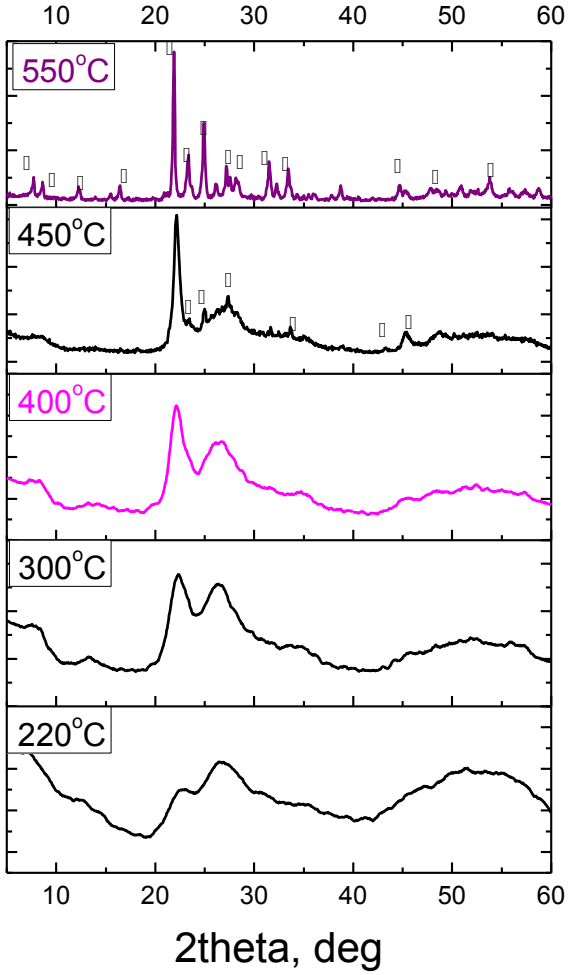




Nano crystalline ZnO



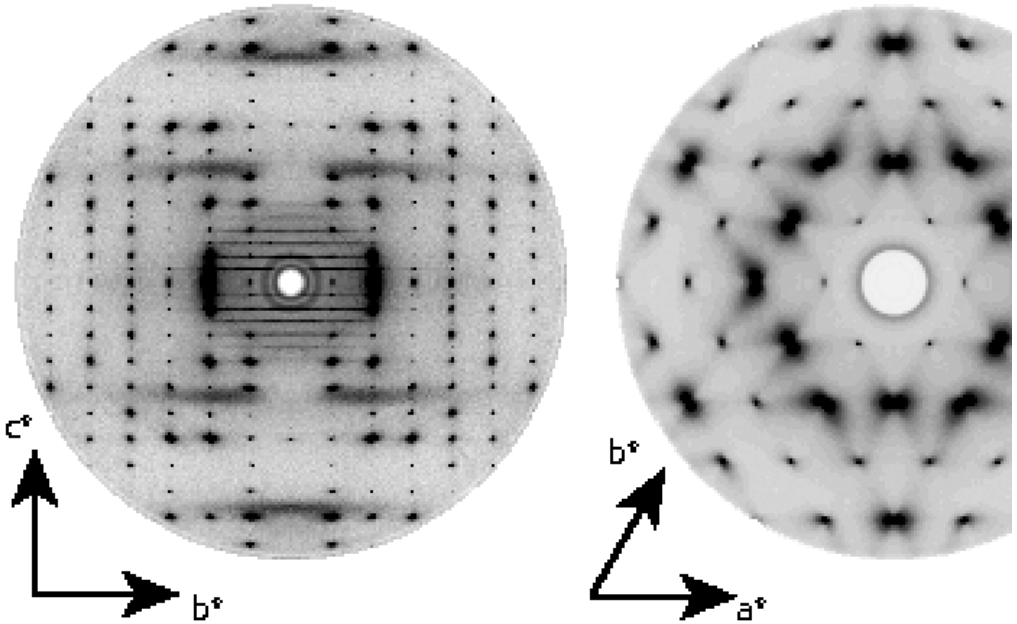
H_2TiO_3



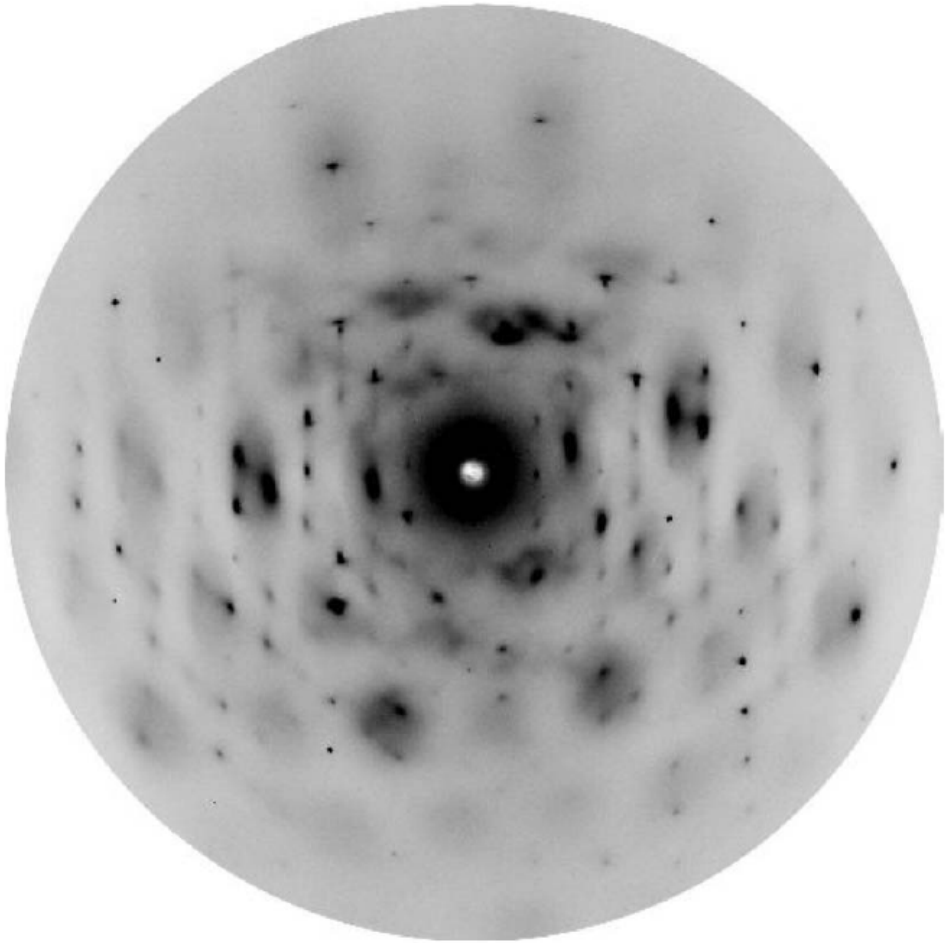
Mo-V-Nb oxides

Singe Crystal Diffuse Scattering

Th Weber PhD München 1994



Alkane chains in Urea

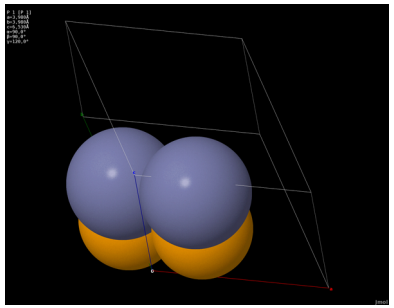


Pentachloronitrobenzene

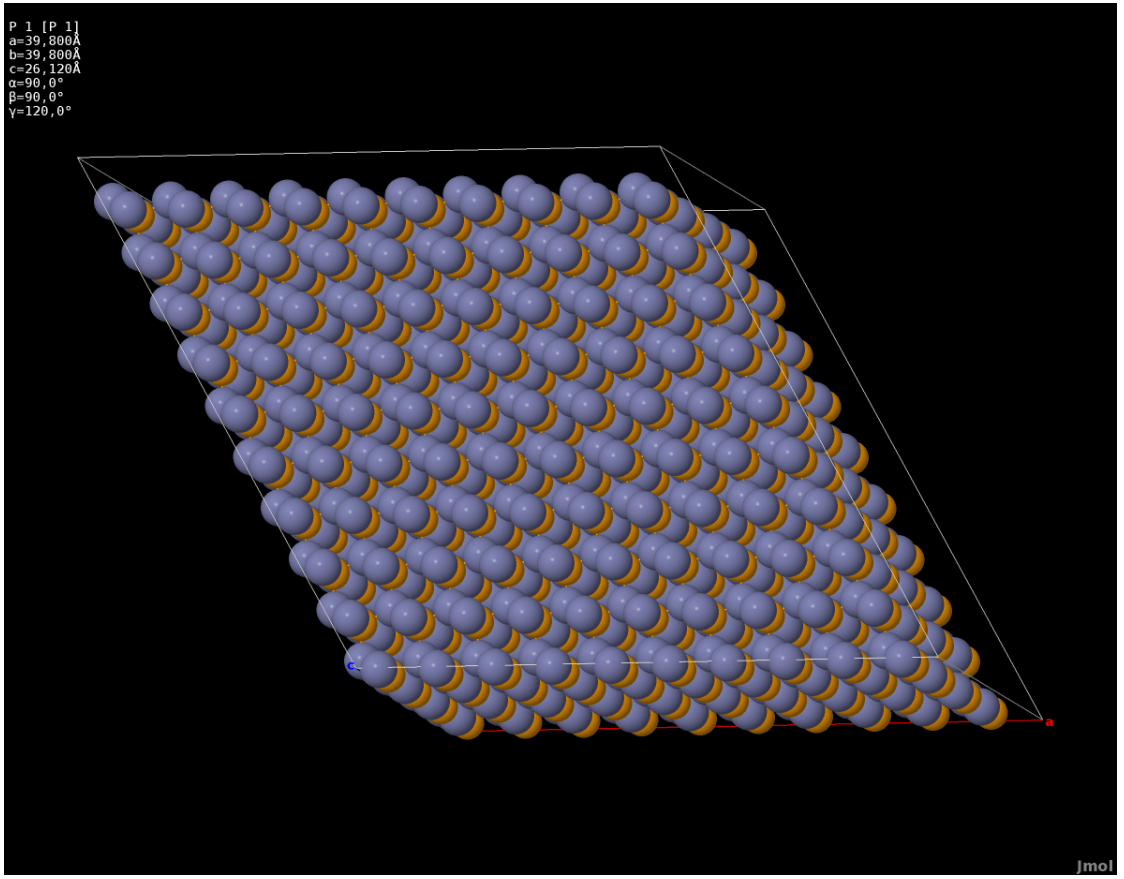
Diffuse scattering by 0.05 μm^3 single crystal
Neder et al Clays & Clay Minerals 1999

Goal

Simulate all things



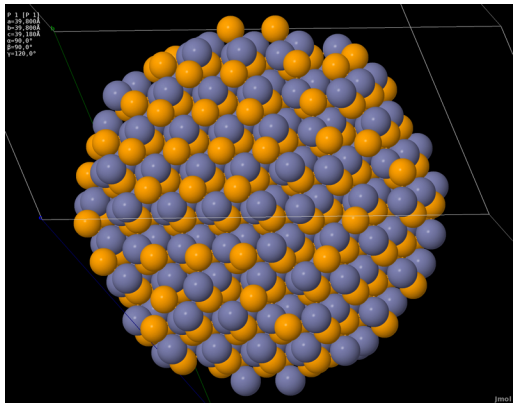
small



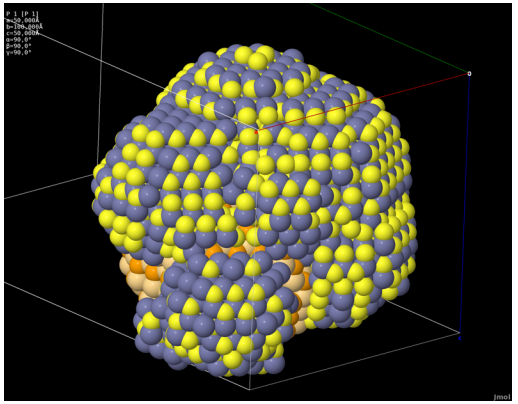
and large
which means periodic

Goal

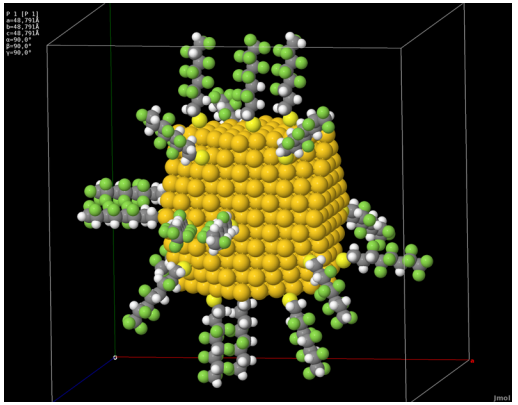
Simulate all things



simple

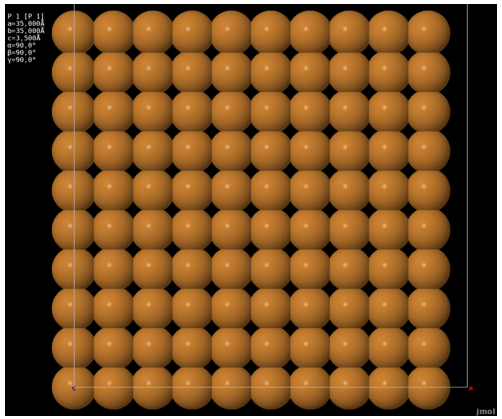


and complex

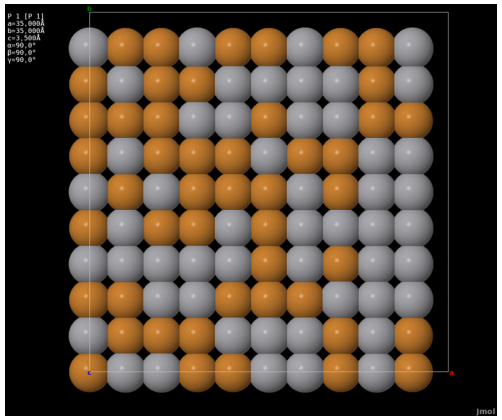


Goal

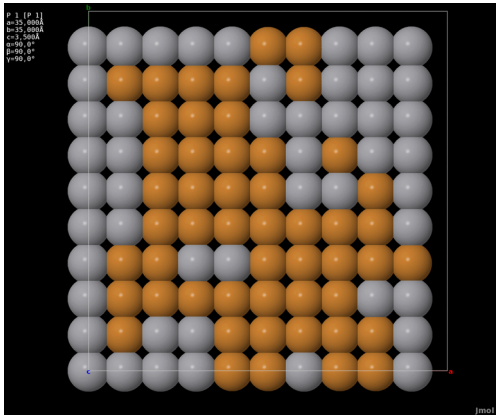
Simulate all things



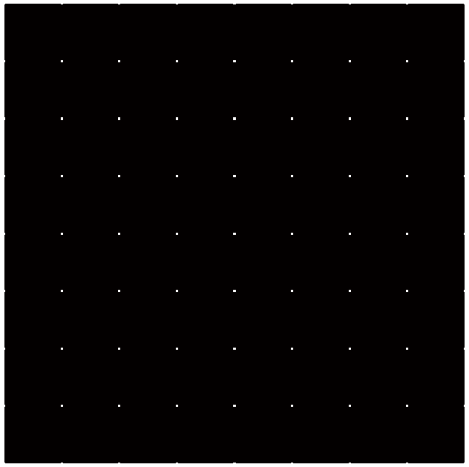
perfect

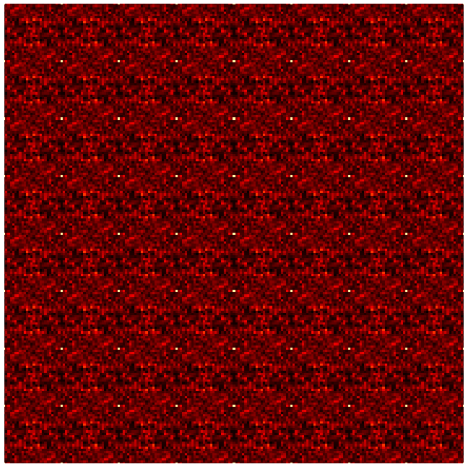


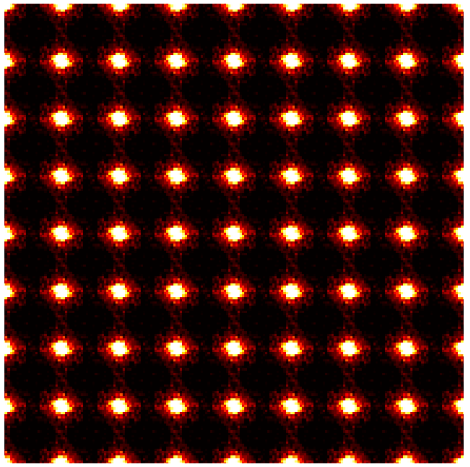
or random



and short range ordered







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

Basic information for a simulation

Chemical composition	ZnSe
Space group, lattice constants	$F\bar{4}3m$ # 216; 5.41 Å
symmetry operations, or; generators, asymmetric unit	4 * 24 symmetry operations
choose generators to reproduce sequence as in International Tables	(1) 1 (2) 2 0,0,z (3) 2 0,y,0 (5) 3^+ x,x,x (13) m x,x,z t(0, ½, ½); t(½, 0, ½) t(1,0,0); t(0,1,0); t(0,0,1)
atoms,positions	Zn 4 a 0,0,0 S 4 c ¼, ¼, ¼
atomic displacement parameters	

!

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
```

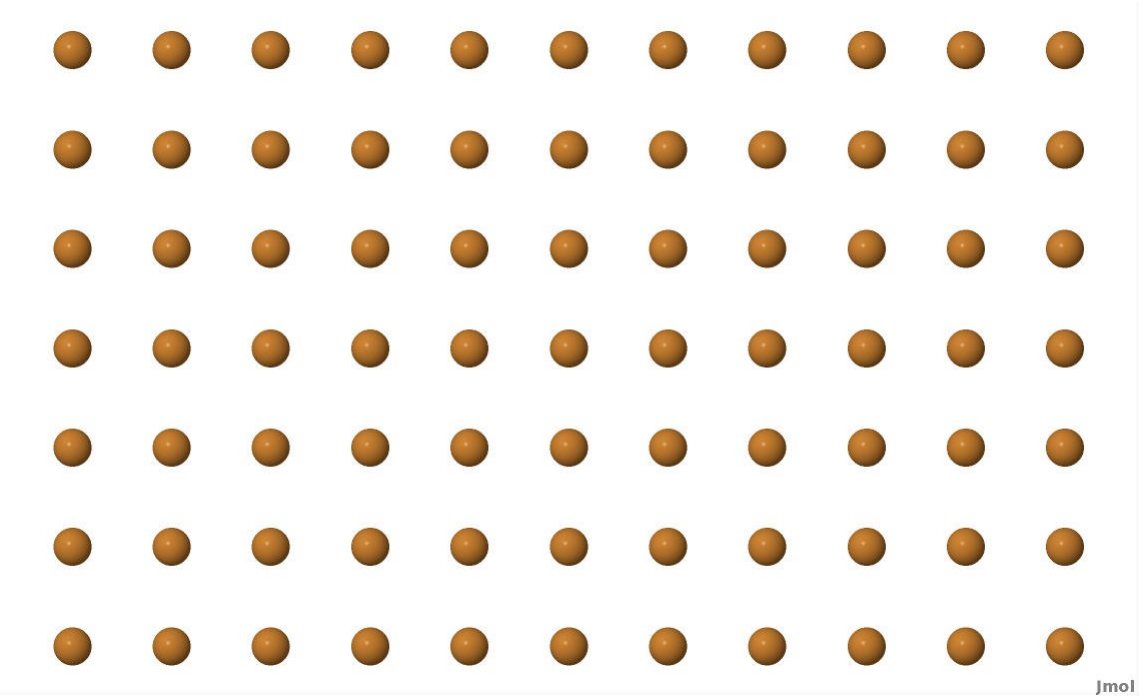
Alternative: import CIF file
import SHELX file

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!



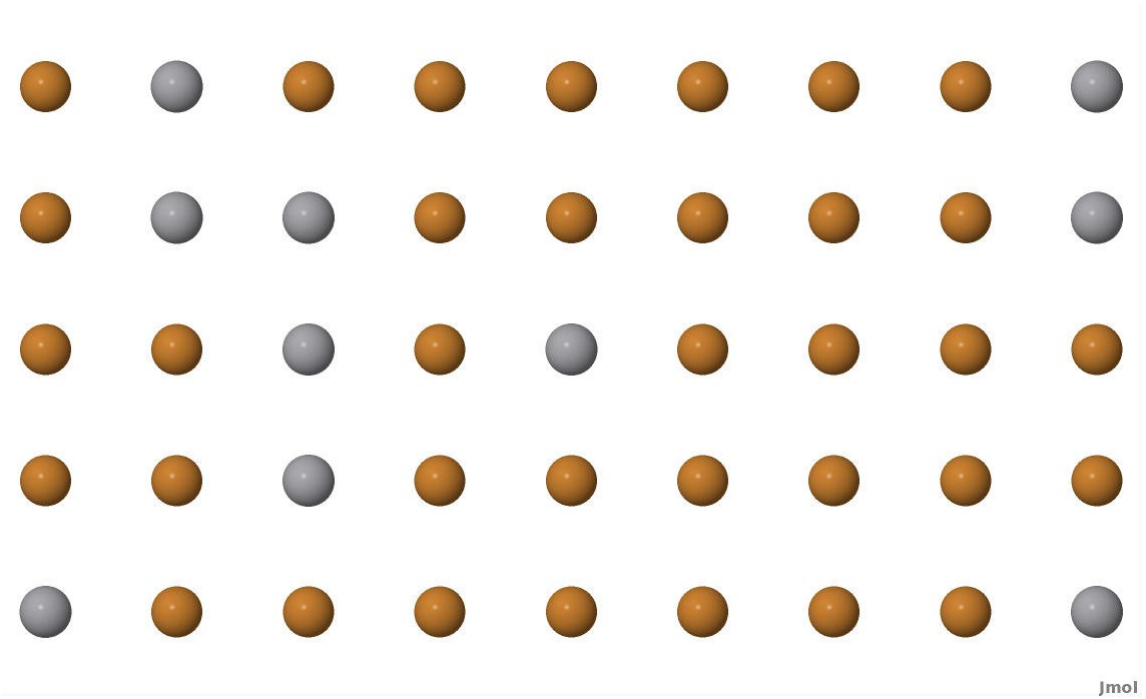
Typical Simulation

Read asymmetric unit

Expand to full unit cell
Expand to a block sized crystal

Introduce defects

- Randomly placed
  - atoms
  - domains
  - shift atoms
  - ...



Typical Simulation

Read asymmetric unit

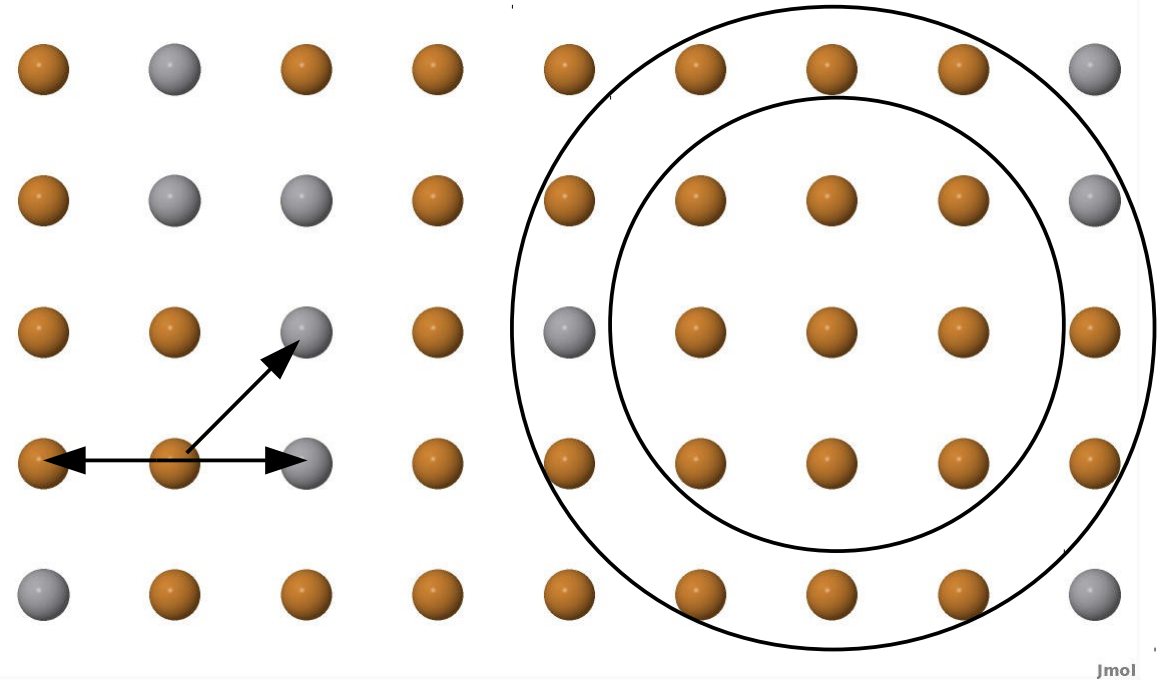
Expand to full unit cell
Expand to a block sized crystal

Introduce defects

- Randomly placed
  - atoms
  - domains
  - shift atoms
  - ...

Introduce correlations

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



Typical Simulation

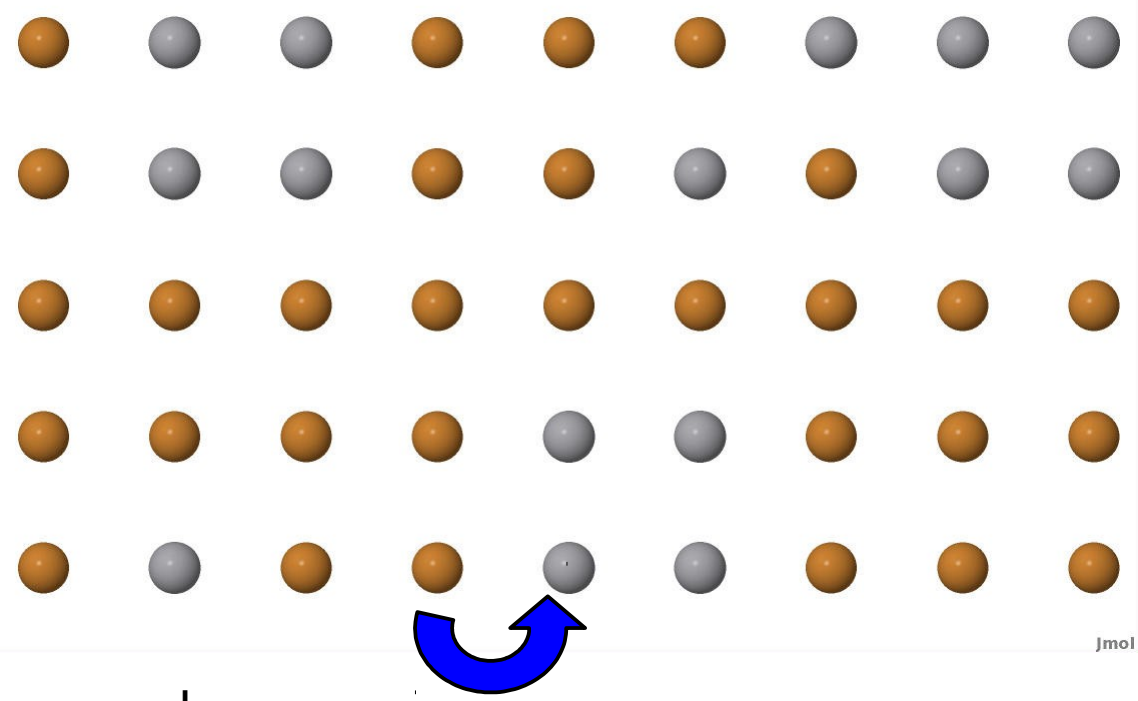
Read asymmetric unit

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

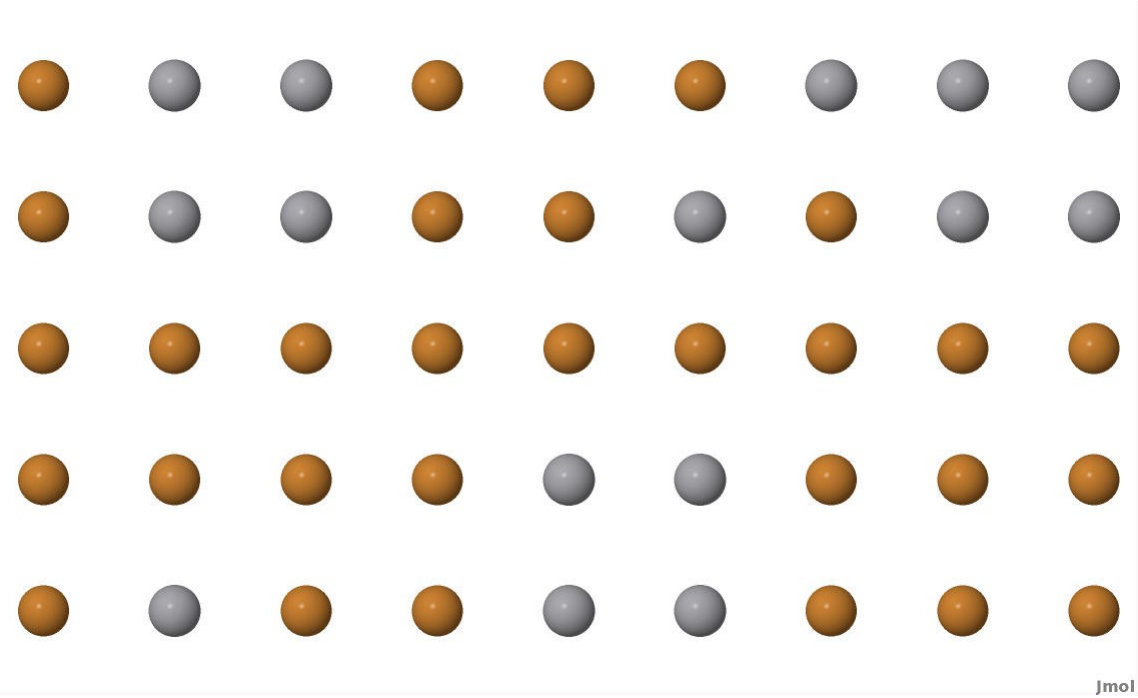
Read asymmetric unit

Expand to full unit cell
Expand to a block sized crystal

Introduce defects

Introduce correlations

Modify crystal

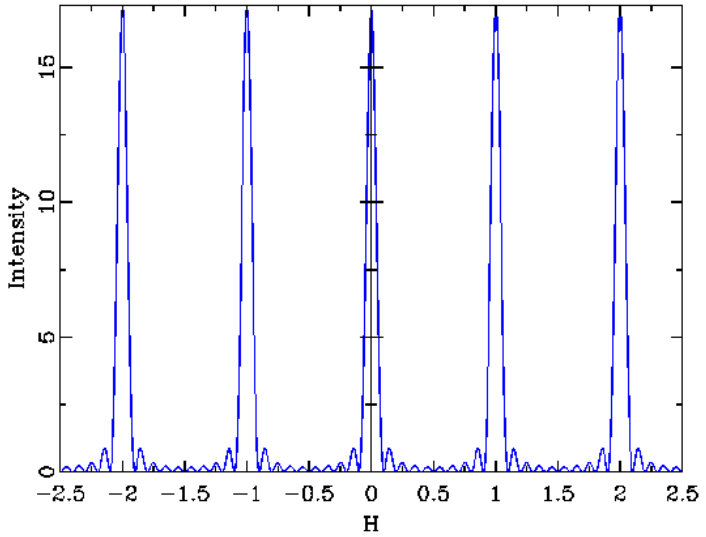


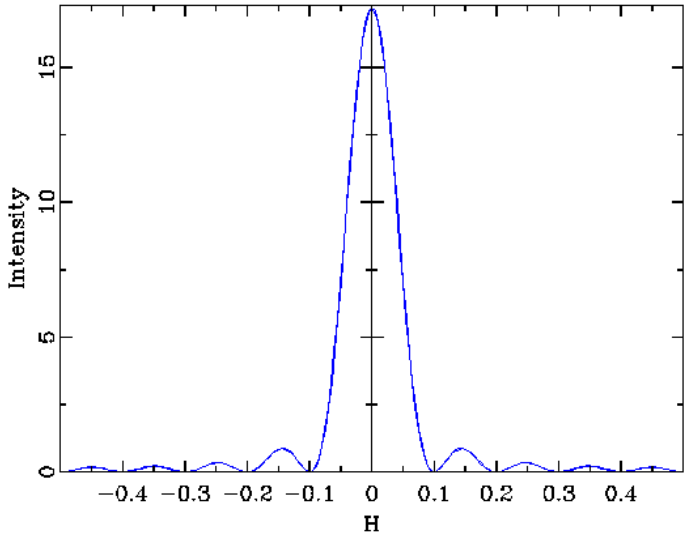
Calculate: single crystal diffraction pattern
powder diffraction pattern
powder PDF
3D PDF

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*

Hamlet: 2π or not 2π?

Typical Simulation

Read asymmetric unit

Expand to full unit cell
Expand to a block sized crystal

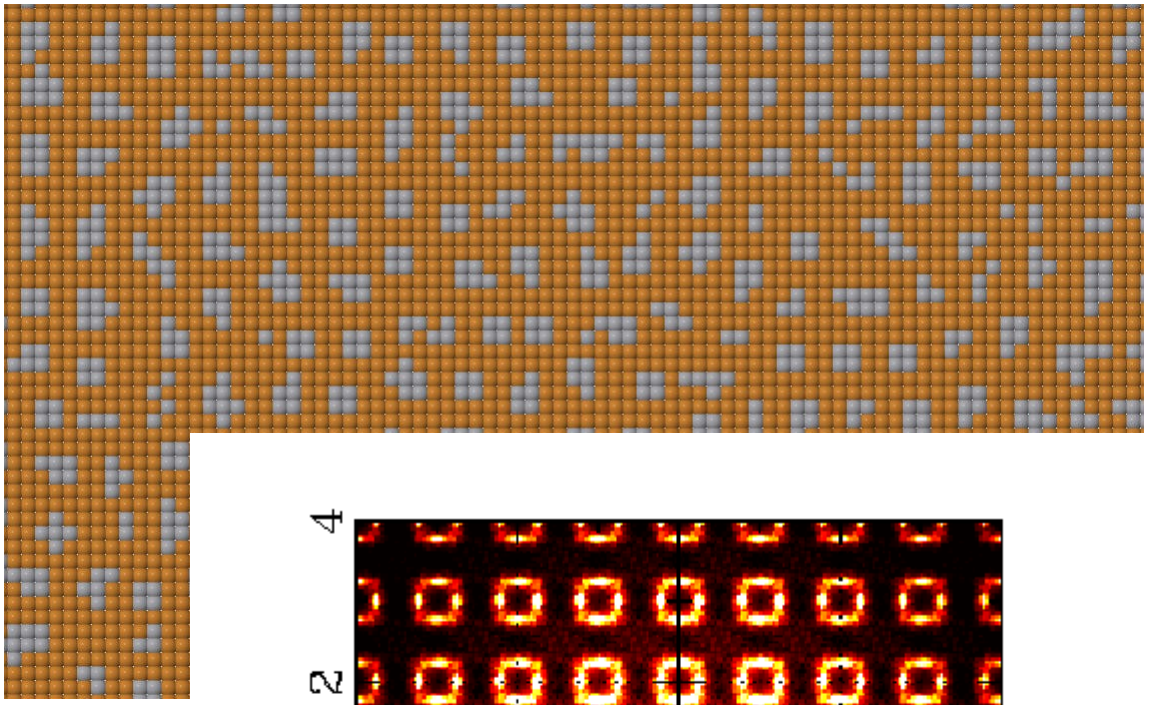
Introduce defects

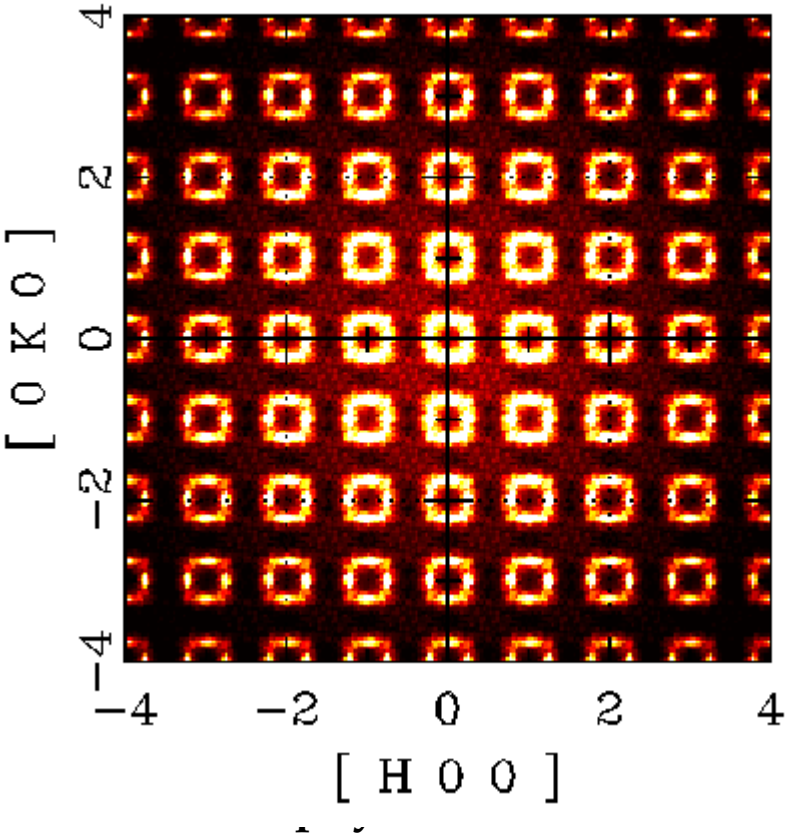
Introduce correlations

Modify crystal

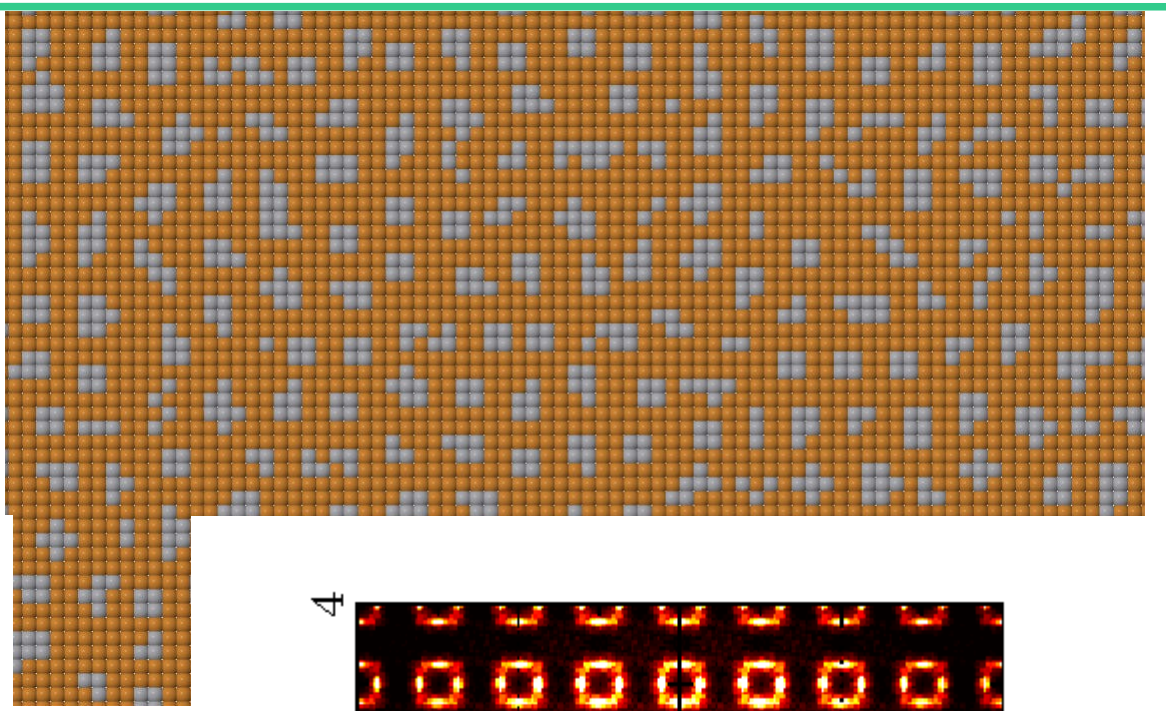
Calculate diffraction pattern / PDF

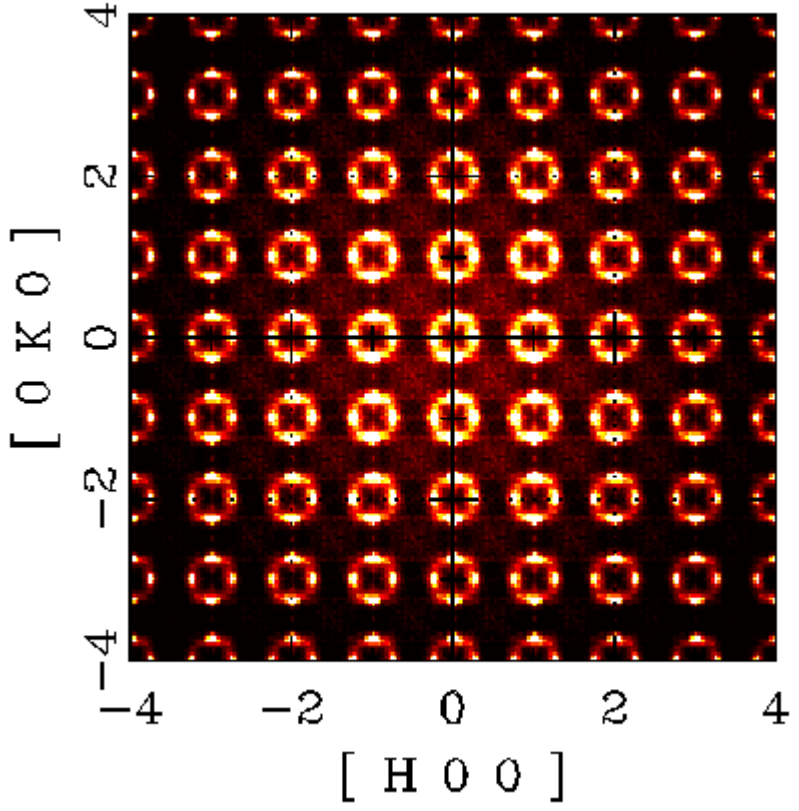
Compare to experimental data
Refine disorder parameters

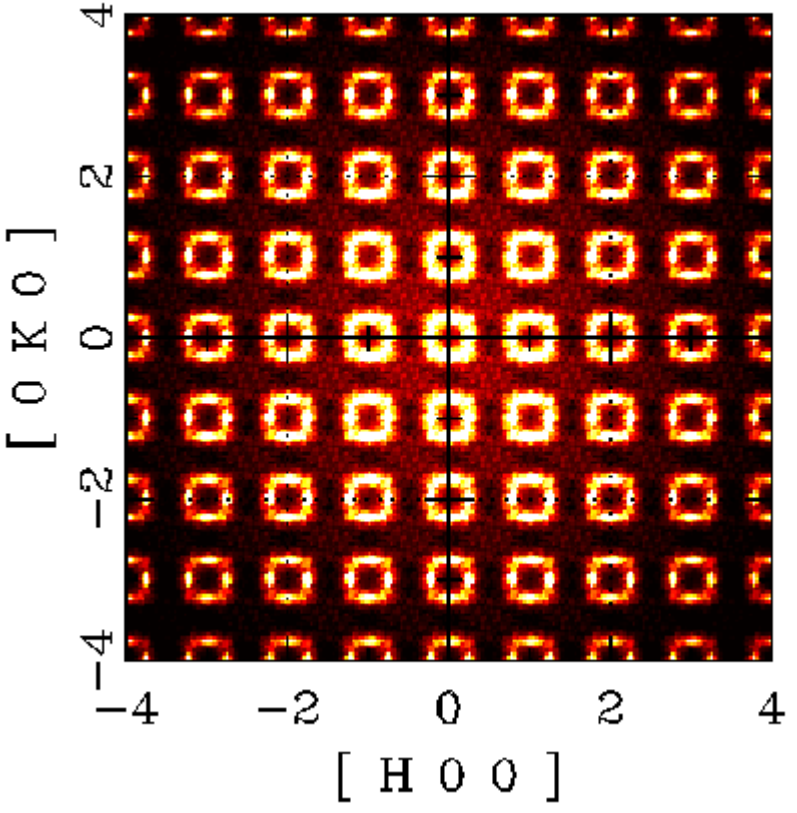




A word of CAUTION



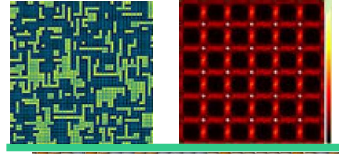


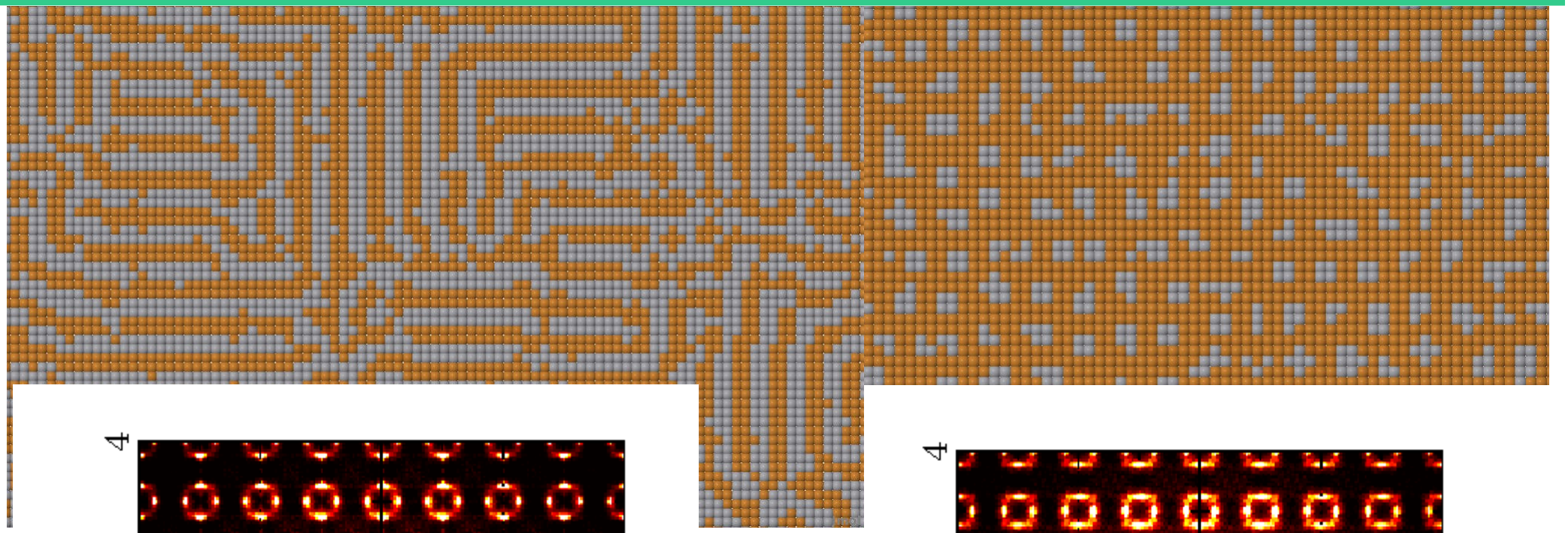


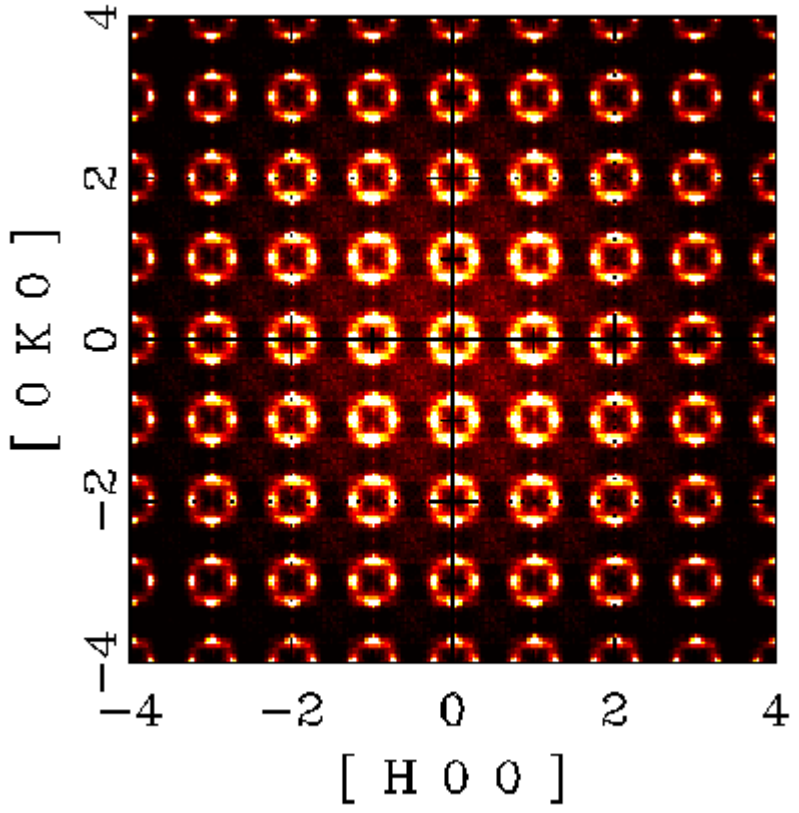
lographi

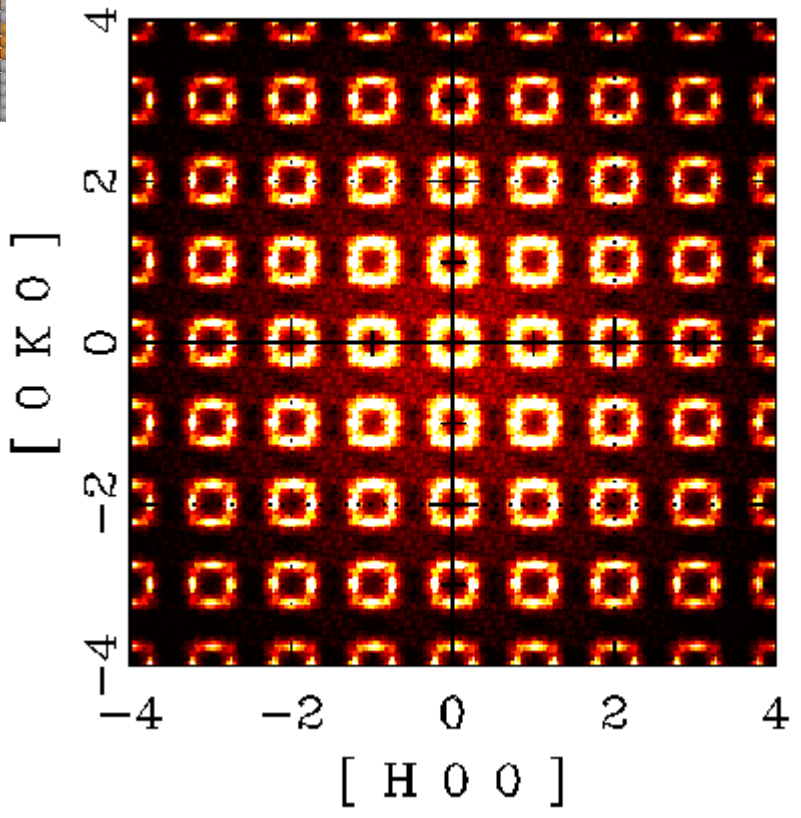
t Erlange

A:B = 1:1 Identical Correlations A:B = 3:1









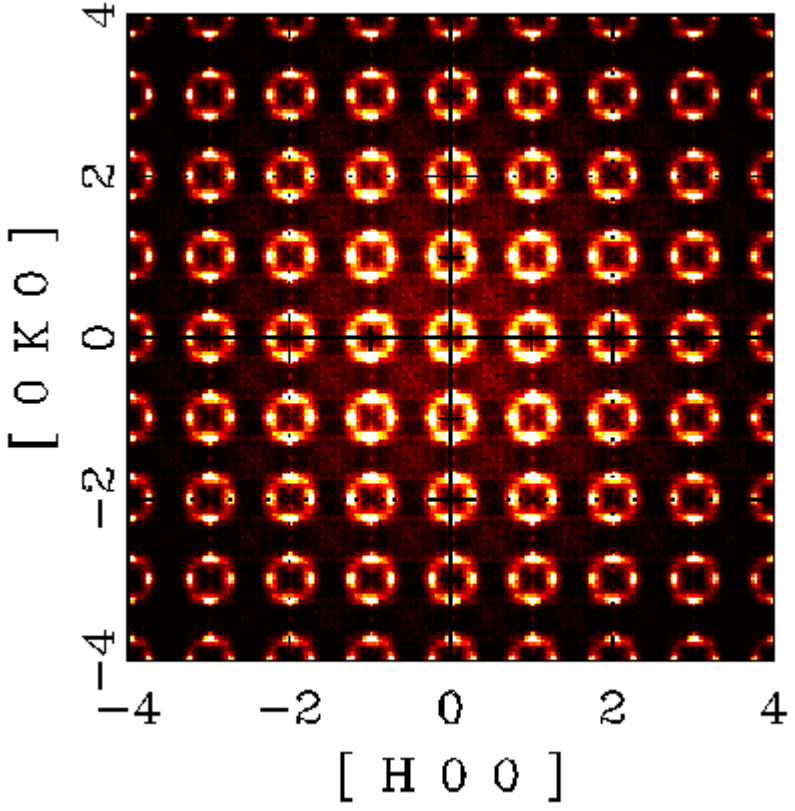
lographi

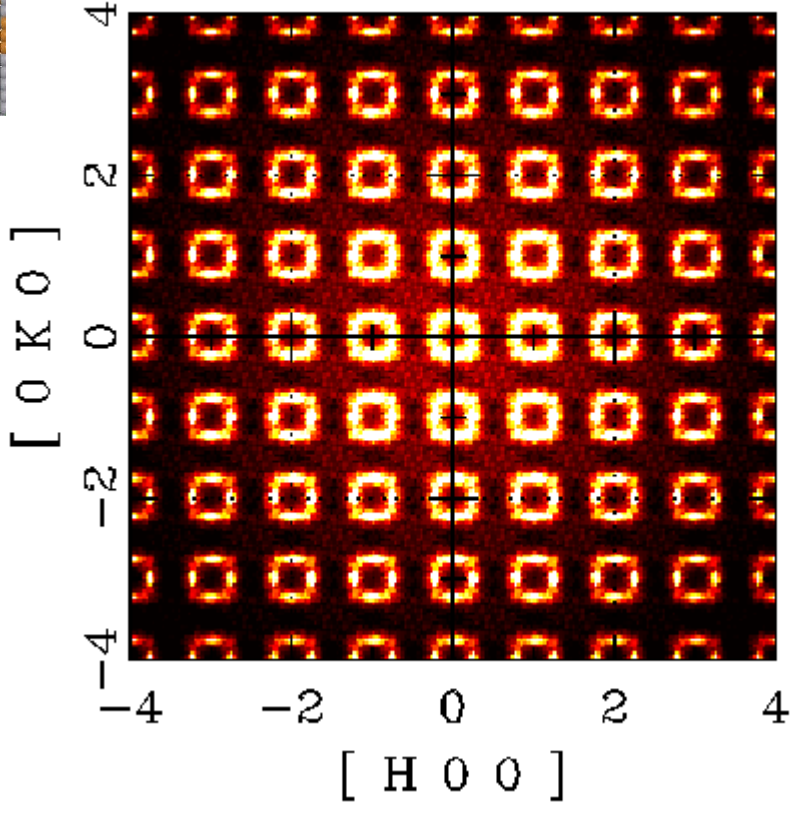
t Erlange

A word of CAUTION

Analyze single crystal refinement
Obtain complementary information:
HRTEM, SAXS, SANS, PDF, Chemistry

Helps to define correct starting model





lographi
t Erlange

DISCUS_SUITE

Command line driven program

you type individual commands

main commands must be memorized

Extensive on-line help /Manual / Book

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
extended defects

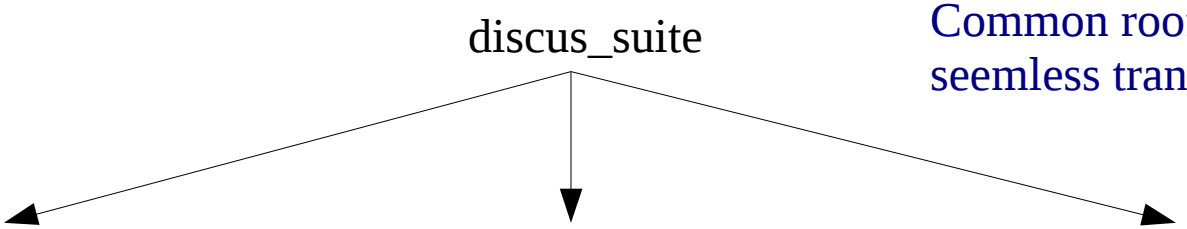
SRO, strain, stacking faults, domains, waves
nanoparticle builder
surface decoration

Refinement

Flexible global optimizer

Define disorder model
Simulate structure
calculate diffraction pattern / PDF

DISCUS Program package



Common roof to provide seemless transitions

crystal builder

graphics, assesment

General optimizer

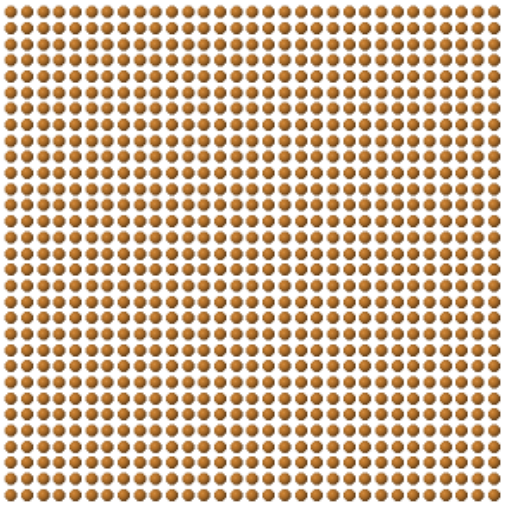
Build in parallel options

Availability:

Linux, Unix,Mac-OS, Windows

Single computer
Massive parallel farms

DISCUS / short range order menu

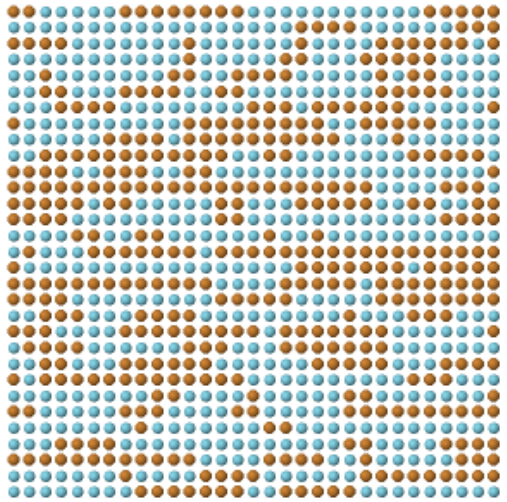


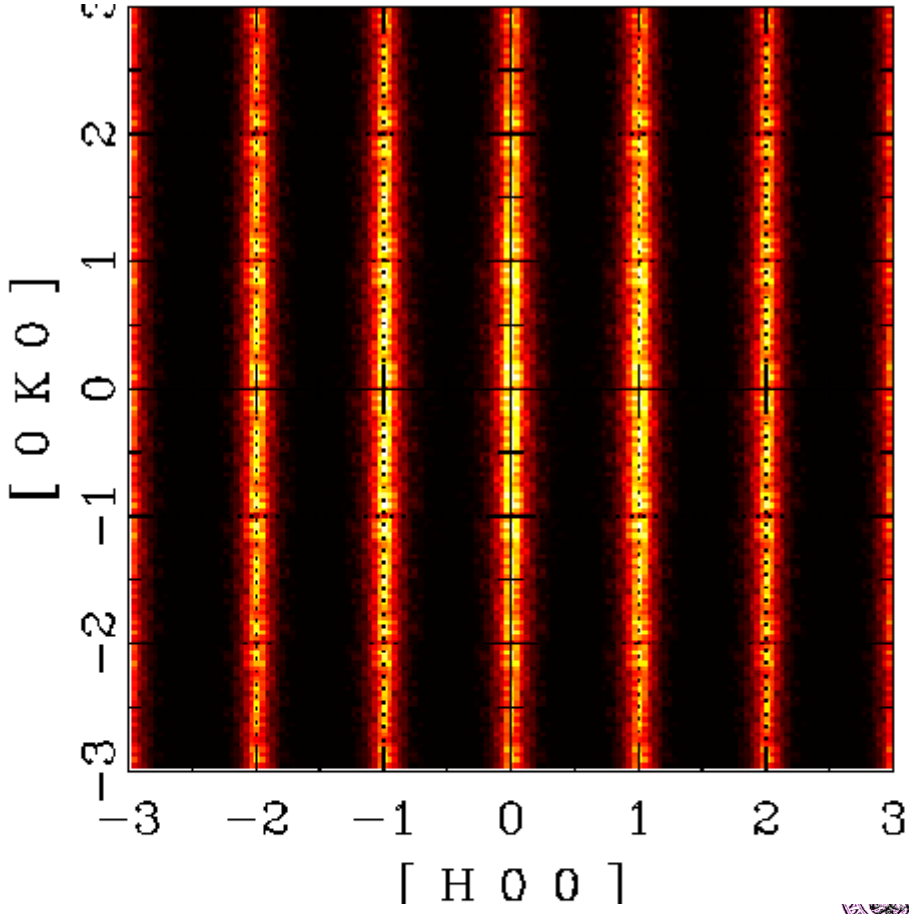
Example

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

DISCUS / short range order menu

```
#
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
```





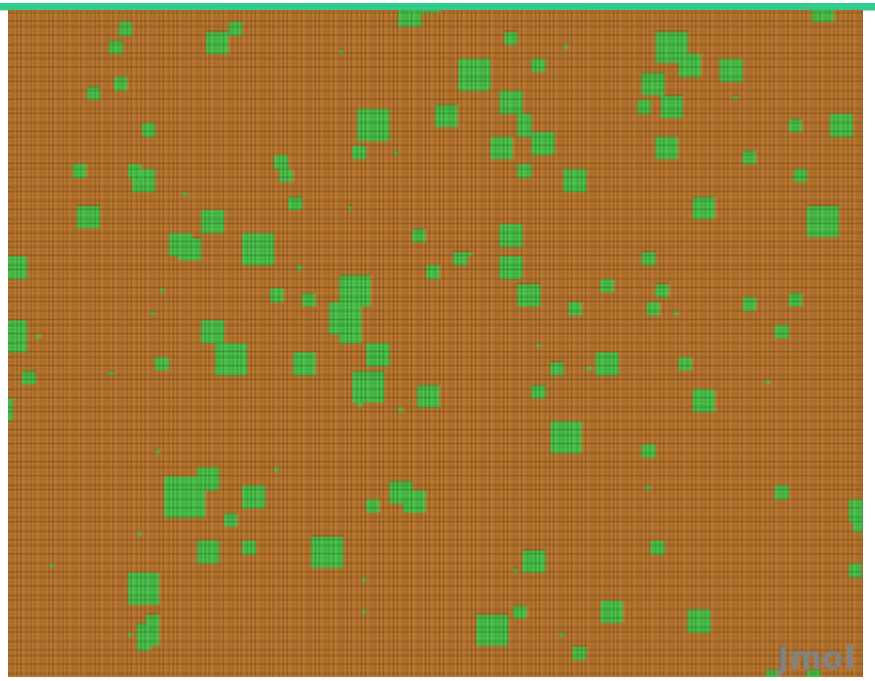
DISCUS / domain concept

```
#        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

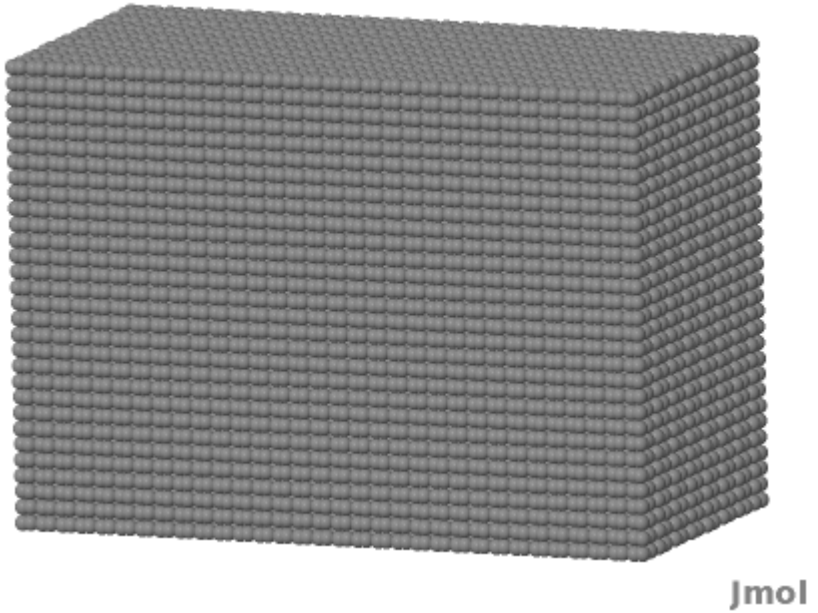


domain.list

```
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
. . .
```

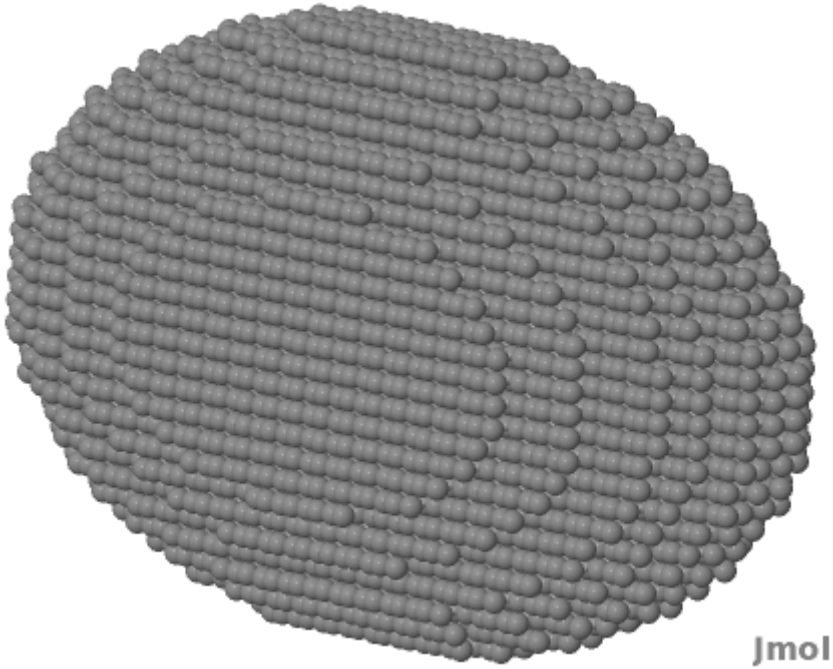
DISCUS / nanoparticle

```
variable real, diam_a
variable integer, ncellx
#
diam_a = $1
#
read
     free 2,3,4, 90,90,90, Pmmm
insert C, 0.3, 0.25,0.3, 0.5
#
ncellx = int(diam_a/lat[1]) + 2
#
save
   outf internal.cell
   run
exit
#
read
   cell internal.cell, ncellx, ncelly, ncellz
@plot.mac block
```



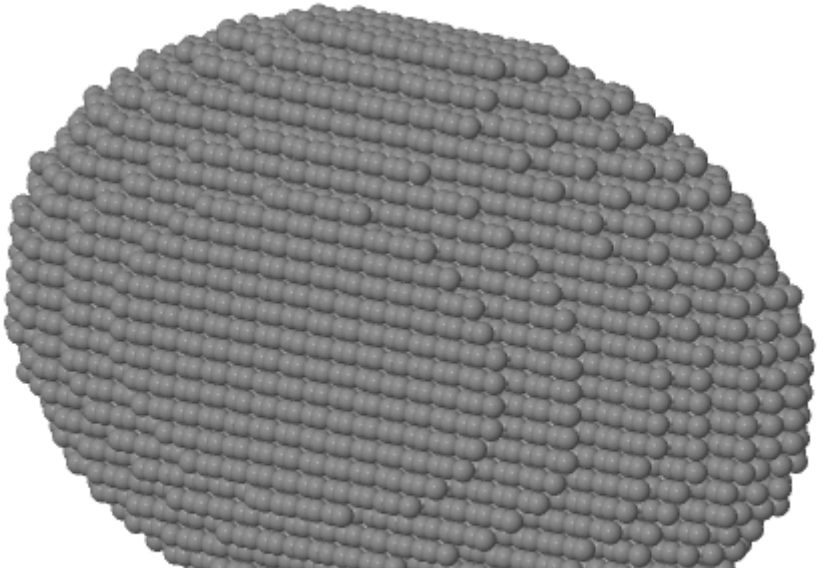
DISCUS / nanoparticle

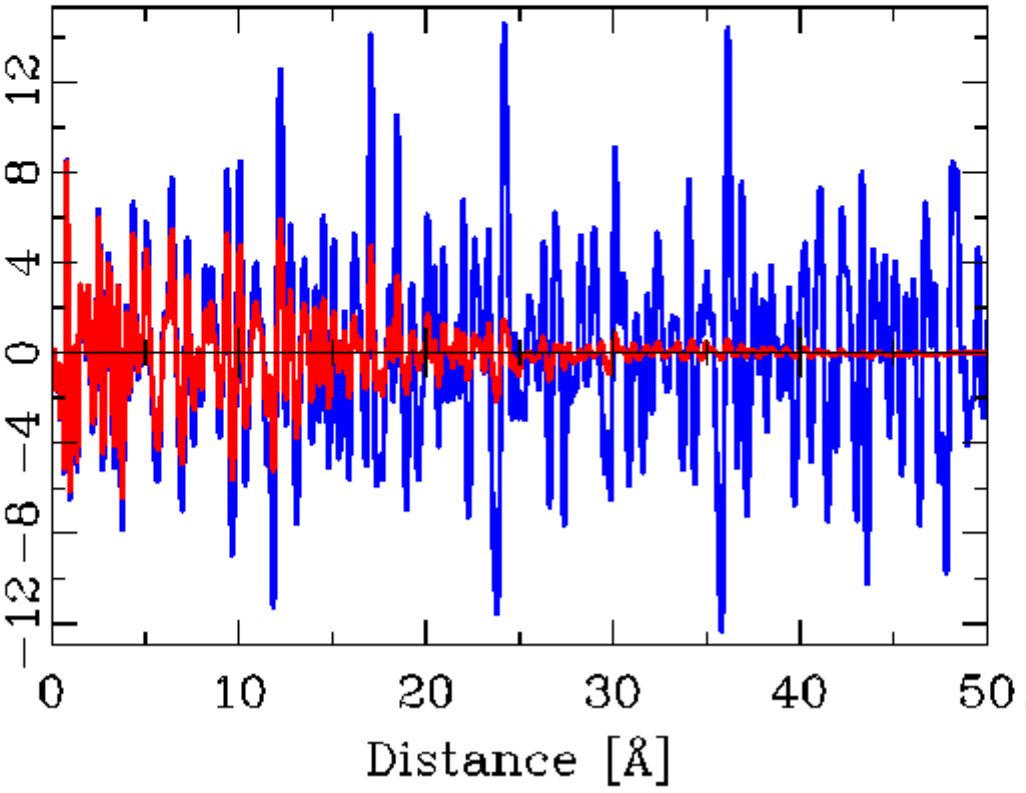
```
variable real, diam_a
variable integer, ncellx
...
#
diam_a = $1
diam_c = $2
diam_b = $3
#
read
     free 2,3,4, 90,90,90, Pmmm
insert C, 0.3, 0.25,0.3, 0.5
#
ncellx = int(diam_a/lat[1]) + 2
...
#
save
   outf internal.cell
   run
exit
#
read
   cell internal.cell, ncellx, ncelly, ncellz
@plot.mac block
surface
   boundary, ellip, diam_a, diam_b, diam_c
exit
purge
@plot.mac ellipsoid
```



DISCUS / nanoparticle

```
variable real, diam_a
variable integer, ncellx
...
#
diam_a = $1
diam_c = $2
diam_b = $3
#
read
     free 2,3,4, 90,90,90, Pmmm
insert C, 0.3, 0.25,0.3, 0.5
#
ncellx = int(diam_a/lat[1]) + 2
...
#
save
   outf internal.cell
   run
exit
#
read
   cell internal.cell, ncellx, ncelly, ncellz
@plot.mac block
surface
   boundary, ellip, diam_q, diam_b, diam_c
exit
purge
@plot.mac ellipsoid
@pdf.mac  ellipsoid
```





Literature

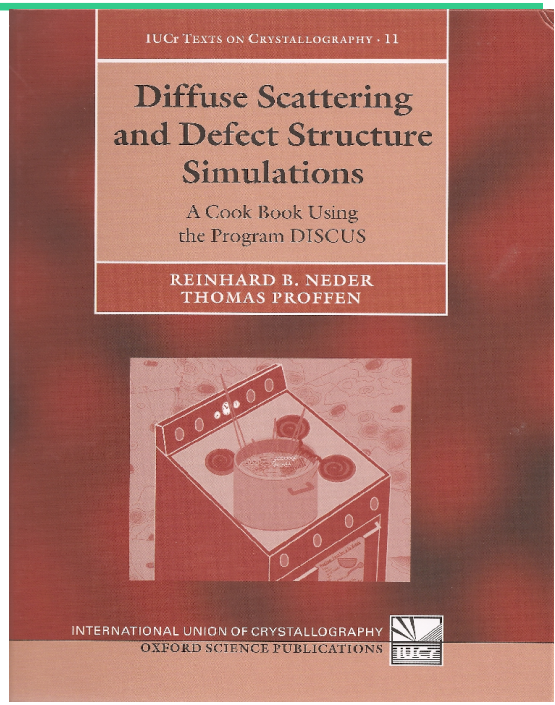
Neder & Proffen, (Oxford, 2008)
Diffuse Scattering and Defect Structure Simulation
Simulation and refinement of disordered structures, cook book

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 theory,
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

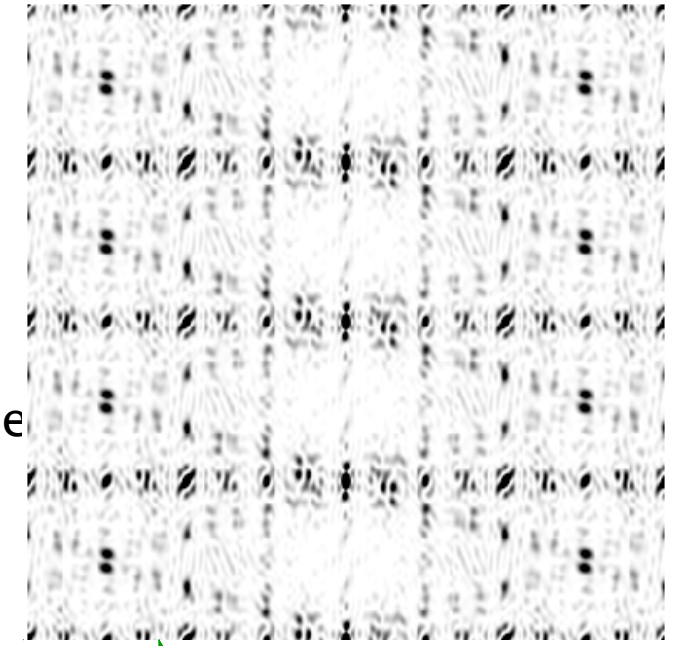
www.lks.physik.uni-erlangen.de/diffraction/index.html

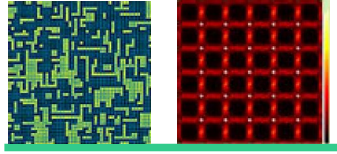
DISCUS source code at:

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

DISCUS Workshop July 16 to July 20, 2018
Erlangen, Germany

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





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 July 16 to July 20, 2018
Erlangen, Germany

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