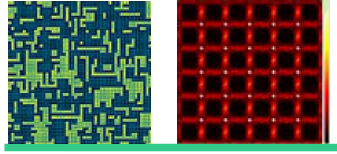
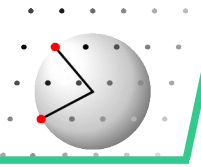


tutorial session II

diffraction by simulated crystal structures



The diffraction pattern is calculated as:

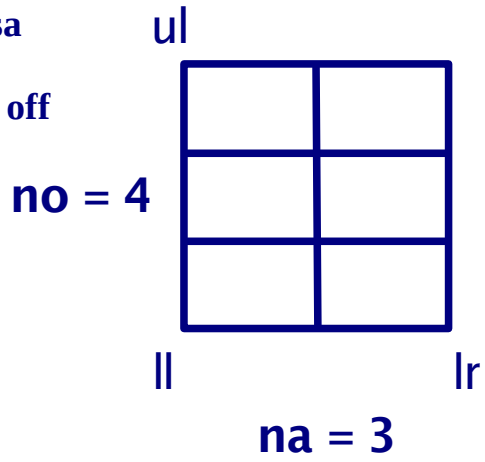
$$F(\vec{h}) = \sum_{j=1}^{N_{crystal}} f_j(|\vec{h}|) e^{2\pi i \vec{h} \vec{r}_j}$$

1D, 2D, 3D in reciprocal space	DISCUS	**fourier** menu
powder diffraction	DISCUS	**powder** menu
pair distribution function, pdf	DISCUS	**pdf** menu (Simulation III)
inverse Fourier transform	DISCUS	**inverse** menu
Patterson function	DISCUS	**patterson** menu

```
fourier
  neutron
  ll -2.5, 0.00, 0.00
  lr  2.5, 0.00, 0.00
  ul -2.5, 0.00, 0.00
  na  1001
  no     1
  abs    h
  ord    k
  temp  ignore
  disp  off
  show
  run
exit
#
output
  outf 1d.inte
  value intensity
  run
exit
```

Switch to fourier menu

- **calculate neutron diffraction pattern or xray or electron**
- **Lower Left corner in reciprocal space**
- **Lower Right corner**
- **Upper Left corner**
- **number of grid points along abscissa**
- **number of grid points along ordinate**
- **write H coordinate as abscissa**
- **write K coordinate as abscissa**
- **ignore thermal parameters**
- **switch anomalous dispersion off**
- **show settings**
- **run the calculation**



switch to the output menu

- **write output to file „1d.inte“**
- **write intensities**
- **run the actual write process**

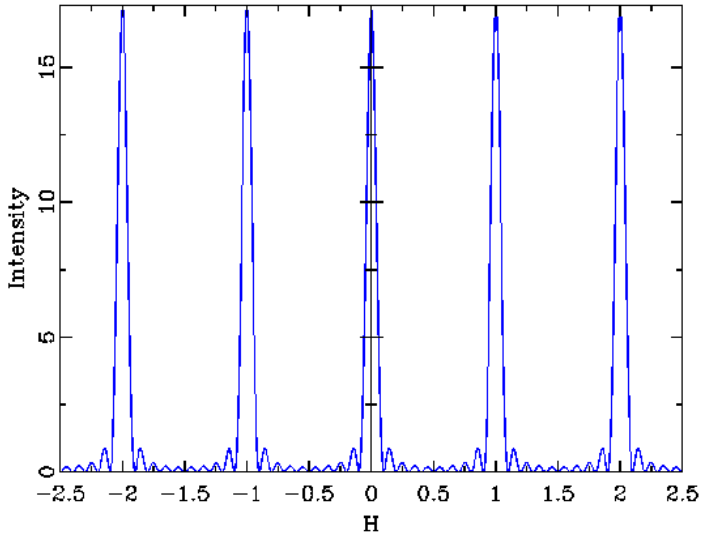
start discus_suite navigate to Lectures\02.Calculation_Scattering

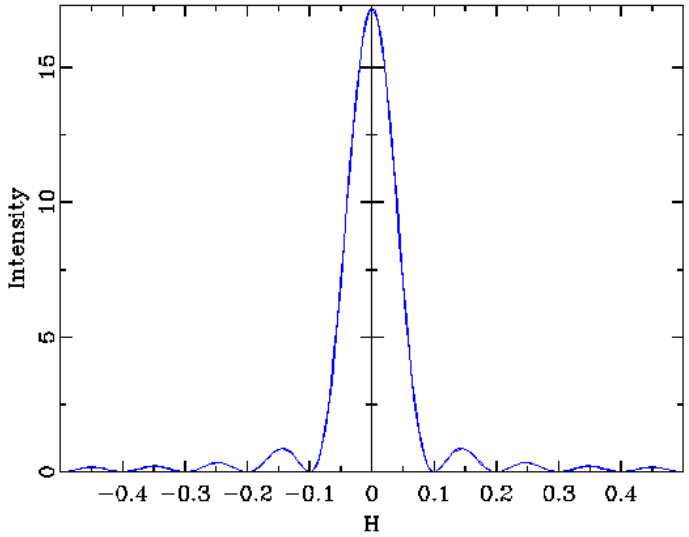
run macro 1d.mac with different numbers as input parameter:

suite> **@1d.mac 5 ! try different numbers**

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

```
fourier
  neutron
  ll -2.5, 0.00, 0.00
  lr  2.5, 0.00, 0.00
  ul -2.5, 0.00, 0.00
  na  1001
  no     1
  abs    h
  ord    k
  temp  ignore
  disp  off
  show
  run
exit
#
output
  outf 1d.inte
  value intensity
  run
exit
```

Switch to fourier menu
- **calculate neutron diffraction pattern**
- **Lower Left corner in reciprocal space**
- **Lower Right corner**
- **Upper Left corner**
- **number of grid points along abscissa**
- **number of grid points along ordinate**
- **write H coordinate as abscissa**
- **write K coordinate as abscissa**
- **ignore thermal parameters**
- **switch anomalous dispersion off**
- **show current settings**
- **run the calculation**

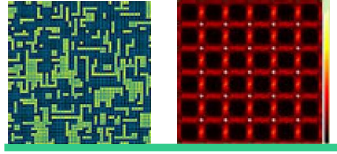
switch to the output menu
- **write output to file „1d.inte“**
- **write intensities**
- **run the actual write process**

make sure you have discus_suite started

change to directory Lectures/02.Calculation_Scattering

run macro 1d_shifted.mac with different numbers as input parameter:

suite> **@1d_shifted.mac 5**



Exercise 2

make sure you have started DISCUS_SUITE

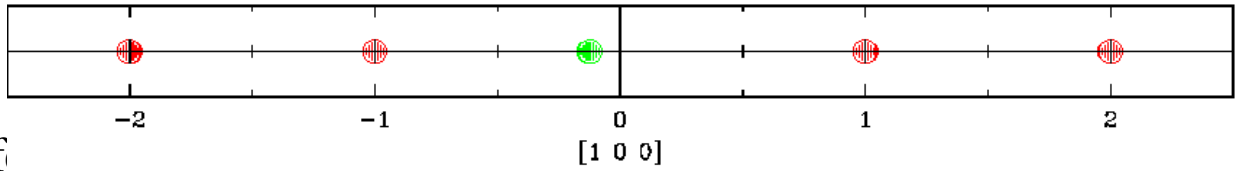
change to directory Lectures\02.Calculation_Scattering

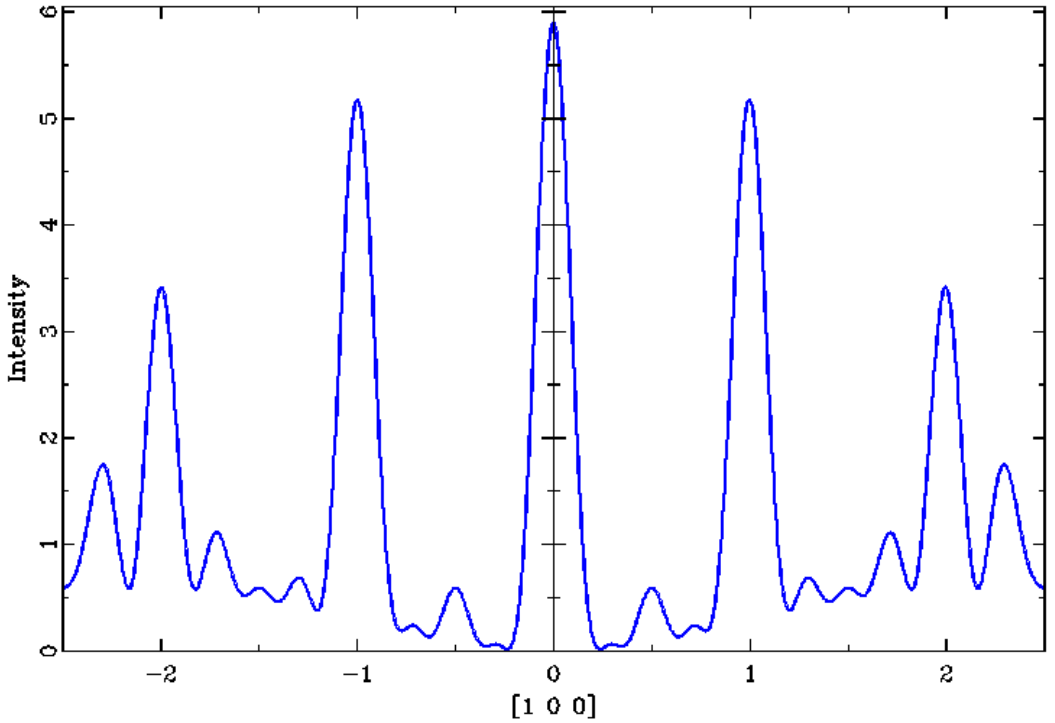
run macro 1d_periodic.mac with diff

suite> **@1d_shifted 5**

What are finite size effects and

what is diffuse scattering ???





modify macro 1d_shifted to take two input parameters

the second parameter shall be the position of the copper atom

run the macro with different positions; different number of atoms

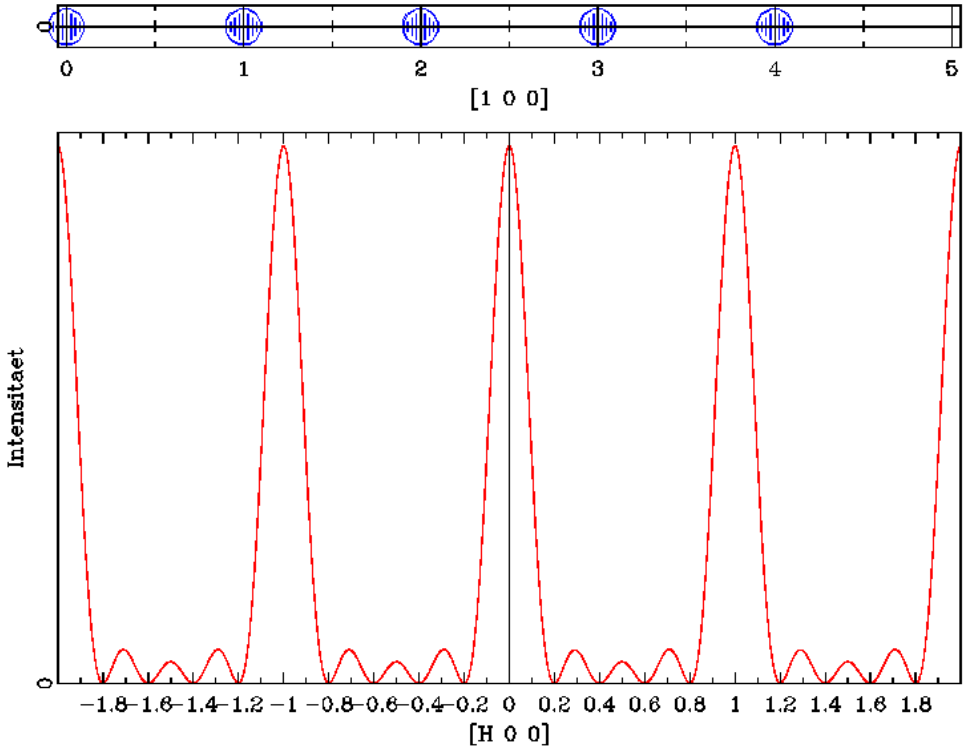
suite> **@1d_shifted.mac 5, 0.123**

How to avoid finite size effects

solution A: **periodic boundary conditions**

crystal of M=5 unit cells

→ zero points at h = j/5



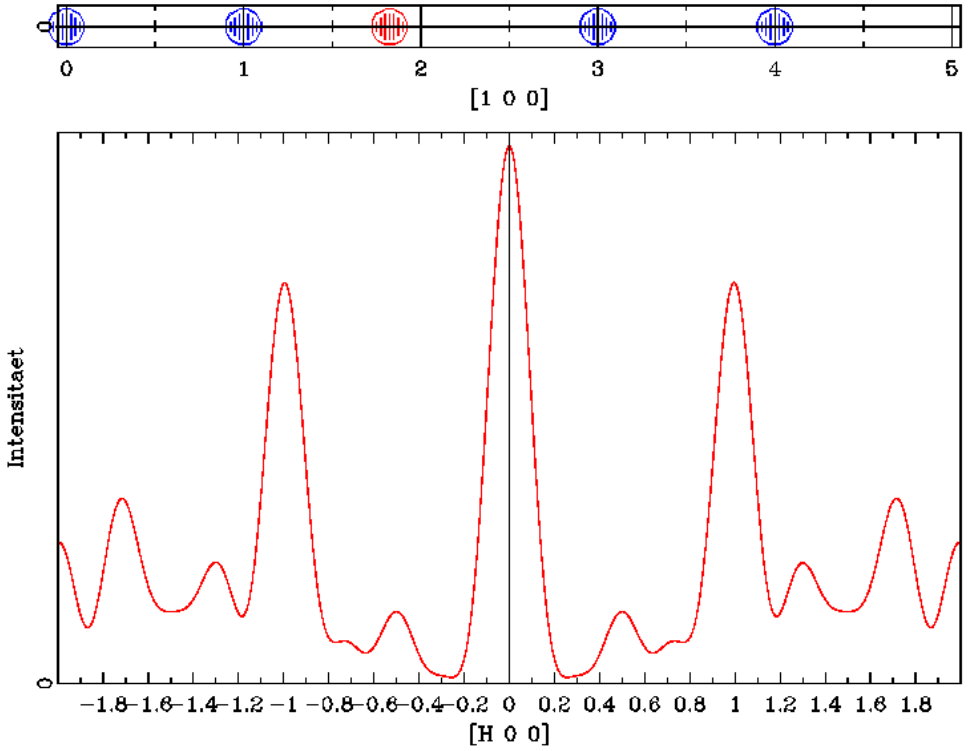
Diffraction by simulated crystal structures

how to avoid finite size effects solution A: **periodic boundary conditions**

crystal of 5 unit cells with disorder

→ zero points of the finite size effects at h = j/5

additional diffuse scattering



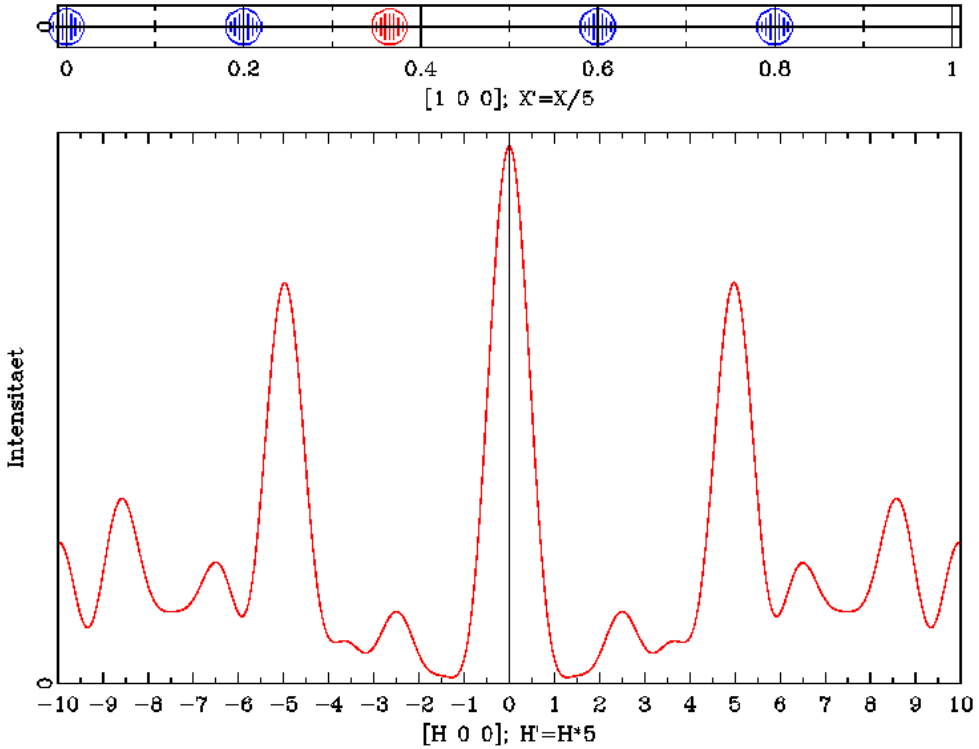
Diffraction by simulated crystal structures

how to avoid finite size effects solution A: **periodic boundary conditions**

crystal of 5 unit cells with disorder

→ Zero points of finite size effects at h = j/5

additional diffuse scattering



Transformation:

direct space

a_0 ⇒ a_0 * M

x ⇒ x / M

reciprocal space

a* ⇒ a* / M

h ⇒ h * M

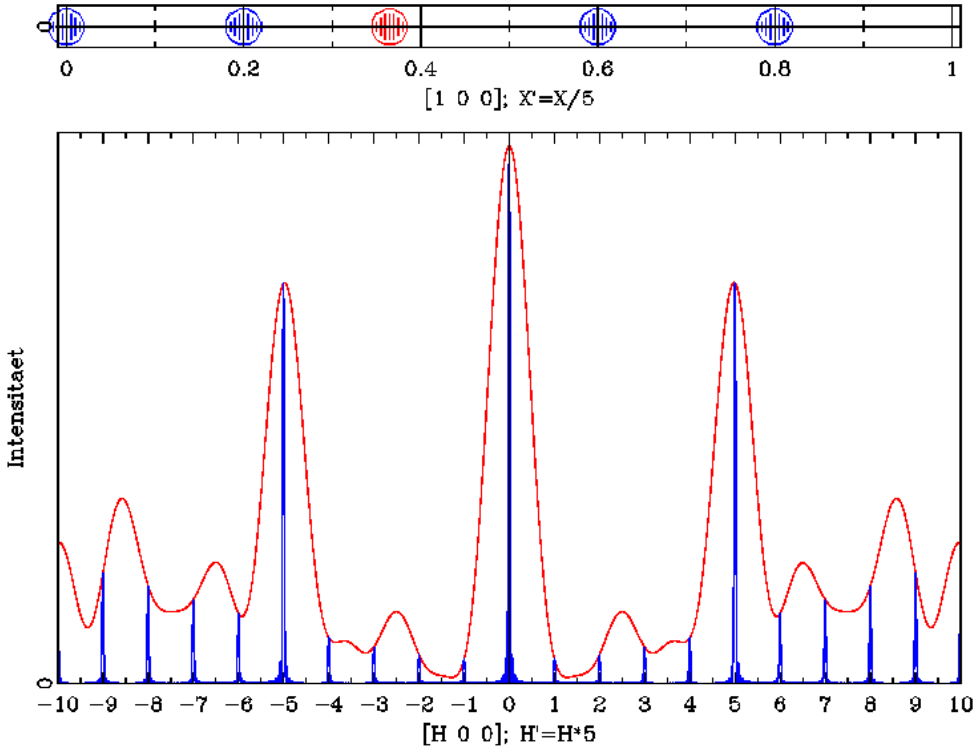
Diffraction by simulated crystal structures

how to avoid finite size effects solution A: **periodic boundary conditions**

crystal of 5 unit cells with disorder

→ zero points of finite size effects at h = j/5

additional diffuse scattering



Transformation:

direct space

$a_0 \Rightarrow a_0 * M$

$x \Rightarrow x / M$

reciprocal space

$a^* \Rightarrow a^* / M$

$h \Rightarrow h * M$

Bragg reflections of a periodic super structure with M-fold unit cell

Diffraction by simulated crystal structures

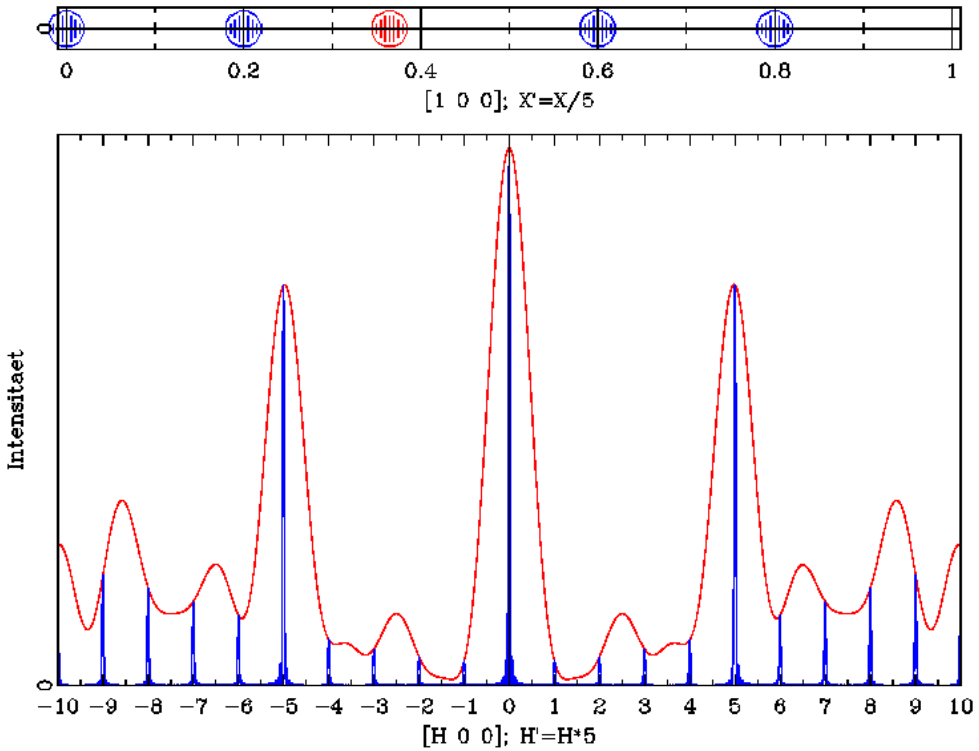
how to avoid finite size effects

solution A: **periodic boundary conditions**

crystal of 5 unit cells with disorder

→ zero points of finite size effects at h = j/5

additional diffuse scattering



calculation via
periodic boundary conditions
at positions: h = ℤ + j/M

corresponds to
Bragg reflections of a
periodic super structure
with M-fold unit cell

this restriction
allows to recognize the
effect of disorder
much better

make sure you have started DISCUS_SUITE

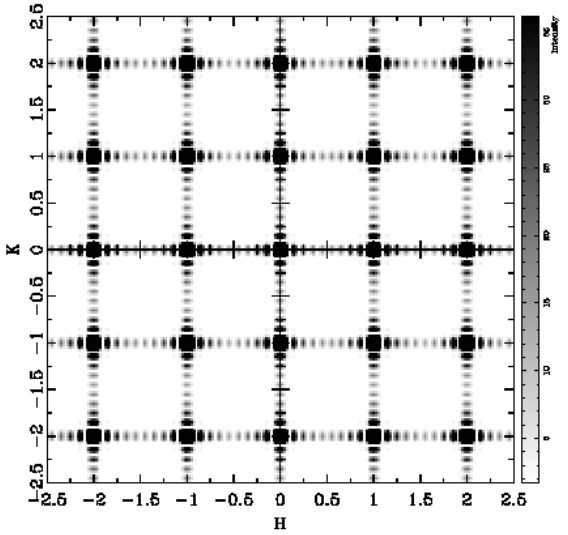
change to directory Lectures\02.Calculation_Scattering

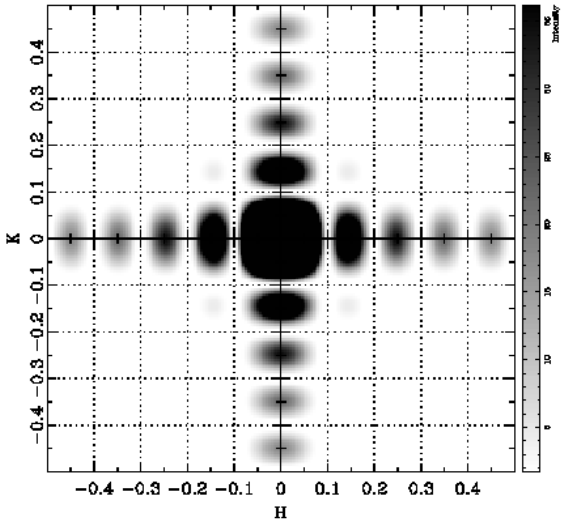
run macro 1d_periodic.mac with different numbers as input parameter:

suite> **@1d_periodic.mac 5**

2D crystal of 10*10 Si atoms

Calculated neutron diffraction pattern (intensity)



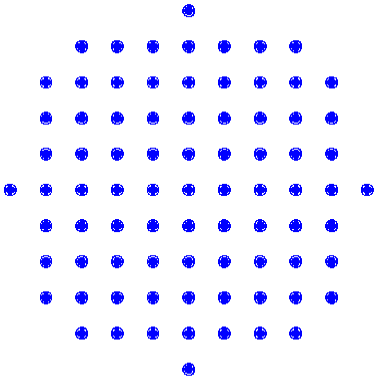


periodic reflections spaced at 1/(Si-Si)

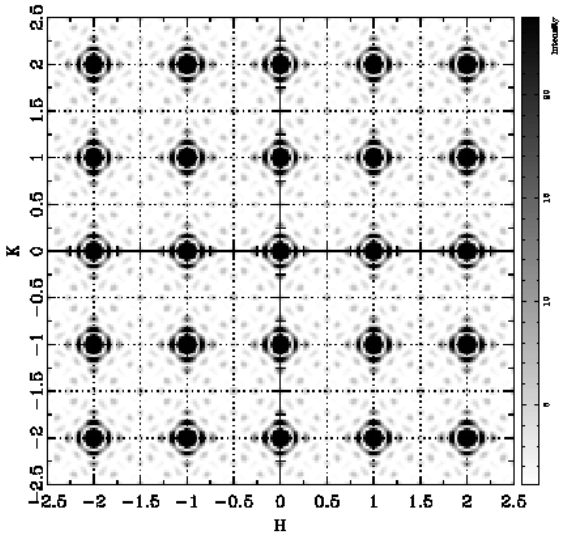
detail of a reflection

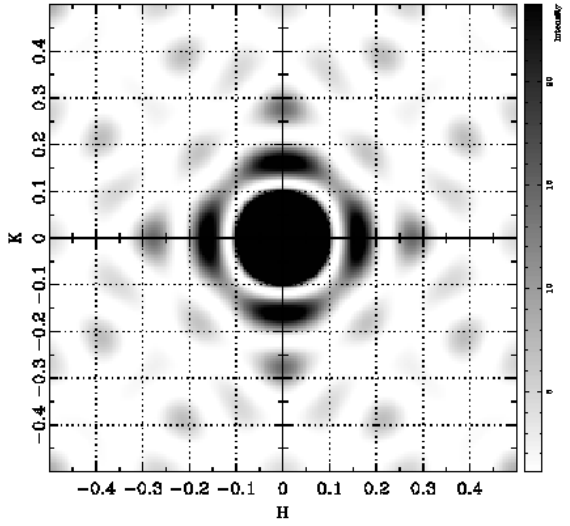
zero points at 1/10 reziprocal lattice constants

2D crystal ~ roughly circular in shape



Calculated neutron diffraction pattern (intensity)





Periodic reflections spaced at 1/(Si-Si) detail of a reflection

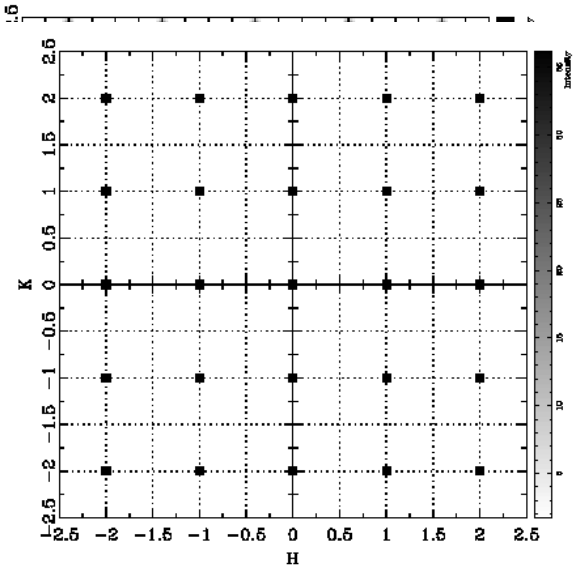
circular subsidiary maxima
zero points at 1/diameter

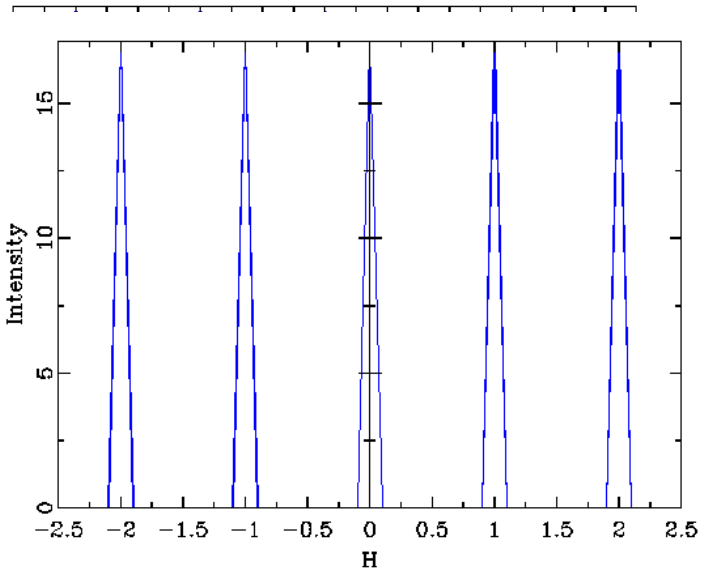
how to avoid finite size effects: solution A: **periodic boundary conditions**

crystal shaped as block of M*N*O unit cells

→ Zero points at h = j/M
k = j/N
l = j/O

Calculation **only** at these positions





h*r ==> (j/M)*r = j * (r/M) = h' * r'

restriction of h to j/M corresponds to the restriction of an h' to integer values
for a crystal with a unit cell M times in size! ==> periodic boundary conditions

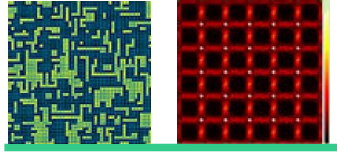
Write a macro that

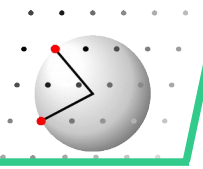
reads primitive.cell and creates a 2-D crystal of size N*N*1

Calculates the 2-D fourier	use:	fourier_2d.mac
Writes the output in standard format	use:	output.mac
Writes the structure for a plot with kuplot	use:	plot.mac

in kuplot check your results with macro k2d_generic.mac:

kuplot > @k2d_generic.mac <file_base>





make sure you are in Lectures\02.Calculation_Scattering

Write a macro that
reads primitive.cell and creates a 2-D crystal of size N*N*1

Calculates the 2-D fourier	use:	fourier_2d.mac
Writes the output in standard format	use:	output.mac
Writes the structure for a plot with kuplot	use:	plot.mac

```
discus
read
  cell primitive.cell, $1, $1, 1
#
@fourier_2d
#
@output_fourier primitive
#
@plot primitive
#
branch kuplot
@k2d_generic.mac primitive
exit
exit
```

in kuplot check your results with macro k2d_generic.mac:

kuplot > @k2d_generic <file_base>

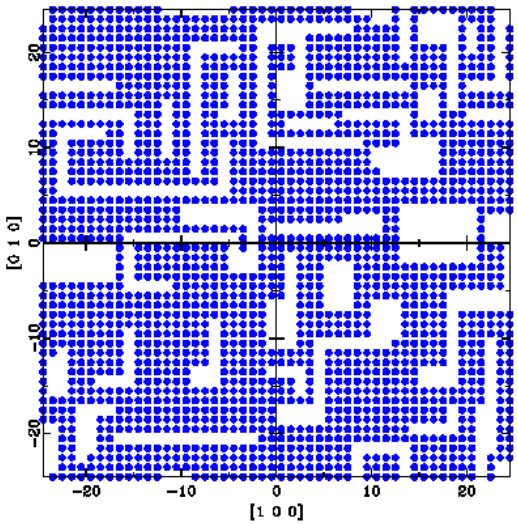
how to avoid finite size effects

solution A: **periodic boundary conditions**

example: crystal of 50*50*1 unit cells

zero points at h = j/50
k = j/50
l = j/1

Calculate reciprocal space **only** at these positions



crystal of two different atom types

Preference for equal neighbours along [100] and [010]

we expect diffuse scattering in linesnormal to [100]* and [010]*

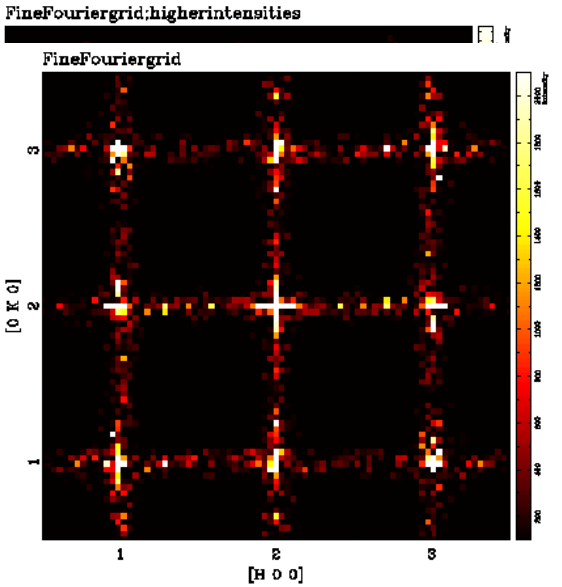
How to avoid finite size effects

solution A: **periodic boundary conditions**

example: crystal as block of 50*50*1 unit cells

zero points at h = j/50
k = j/50
l = j/1

Calculate scattering **only** at these points



Fourier with grid 0.0375*a*

Finite size effect or diffuse scattering?

Expect diffuse scattering in rods normal to [100]*

sharp lines of finite size effects are superimposed on diffuse scattering!

How to avoid finite size effects

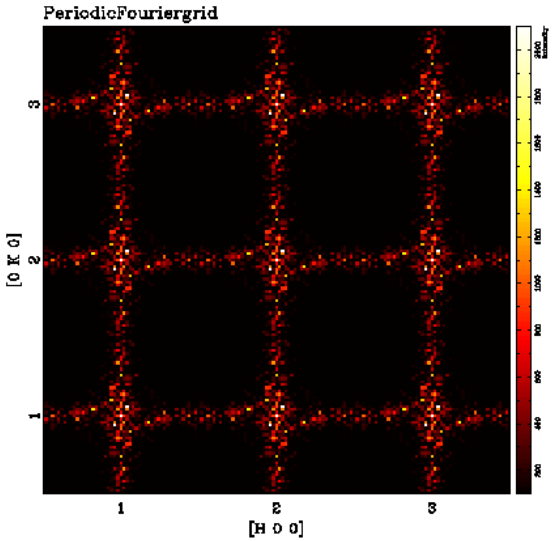
solution A: **periodic boundary conditions**

example: crystal as block of 50*50*1 unit cells

zero points at

h = j/50
k = j/50
l = j/1

Calculate scattering **only** at these points



Fourier with grid 0.02*a*

Finite size effect or diffuse scattering?

Expect diffuse scattering in rods normal to [100]*

Just the diffuse scattering remains

How to avoid finite size effects solution B: **Subtract the diffraction by the average structure**

Only applicable to disordered structures, otherwise I - <I> = 0

Works with crystals of any shape

1. average the structure project all atoms into a single unit cell
2. calculate diffraction at the same grid as required for diffuse scattering
3. subtract the two intensities

→ only diffuse scattering remains

I(average structure) = zero
except at: Bragg reflections + subsidiary maxima

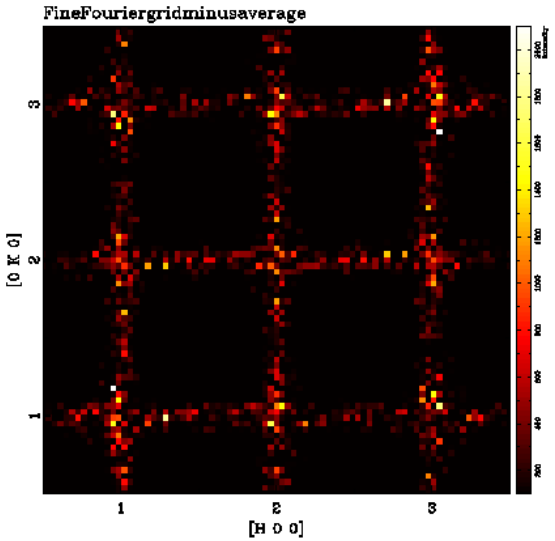
Works only if: Intensity of Bragg reflections is not too different from that of perfect/average structure
scattering by disodered structure is very diffuse

how to avoid finite size effects

solution B: **Subtract the diffraction by the average structure**

example: crystal as block of M*N unit cells

I - <I>



Fourier with grid 0.0375*a*

grid does not match crystal size

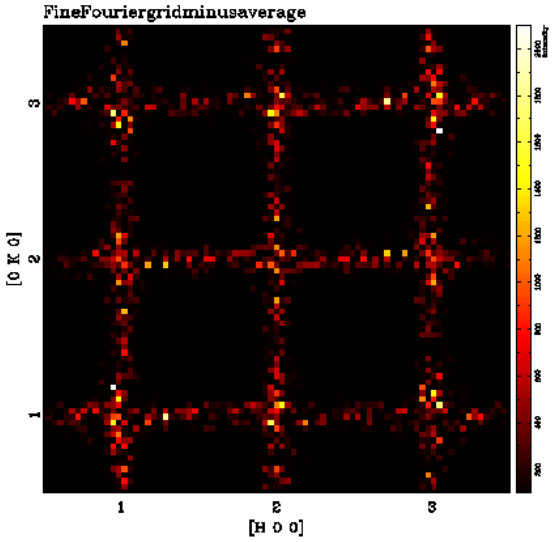
only diffuse scattering remains!

coherence

With larger crystals you might observe
high frequency oszillations

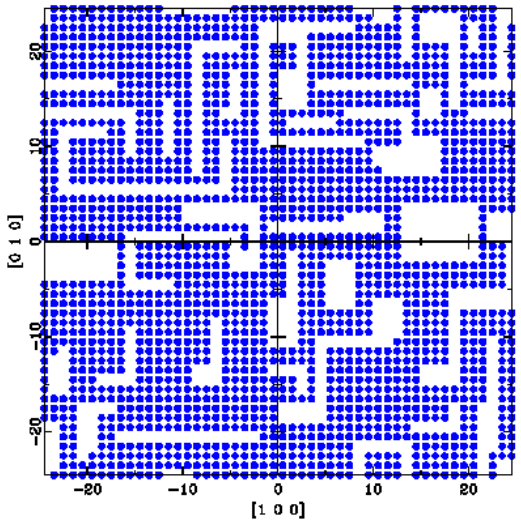
Also, often the crystal will be too small for a good average of the disorder

I - < I >



diffuse scattering is
very noisy

Pattern calculated for 50*50 unit cells
way too small



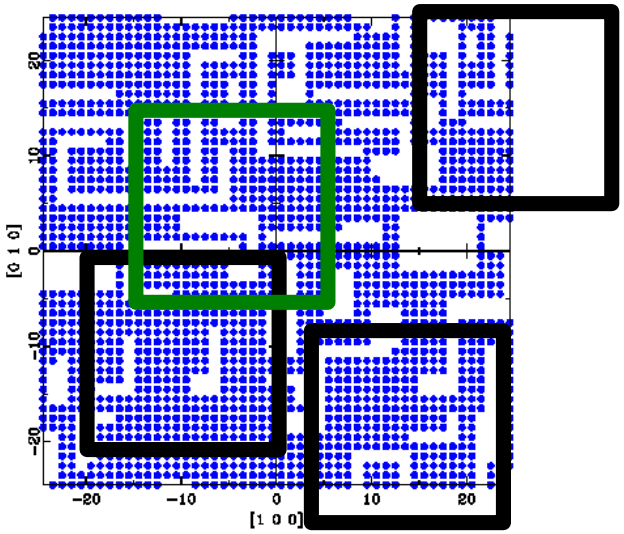
There are many more configurations
than realized in this small crystal

coherence

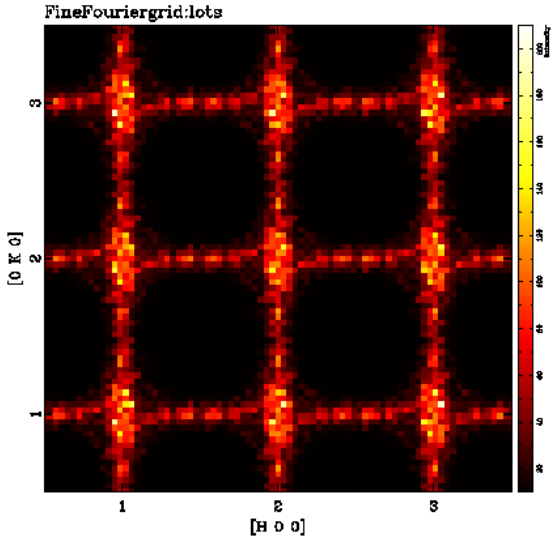
With larger crystals you might observe
high frequency oszillations

Also, often the crystal will be too small for a good average of the disorder

I - < I >



I - < I > calculated for many small
lots randomly located in crystal



randomly located lots
finite size corrected
intensities averaged

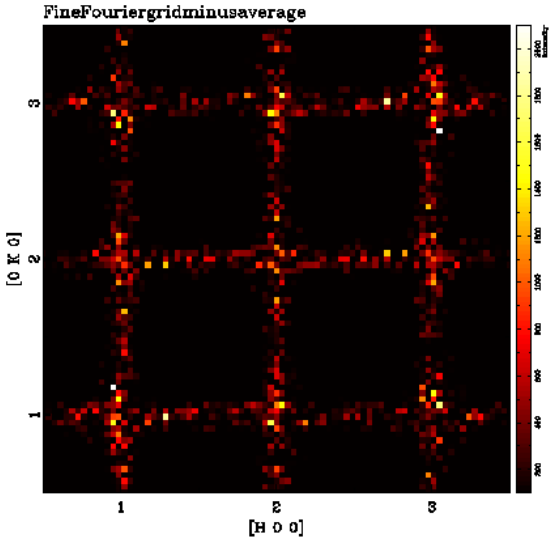
diffuse scattering
is less noisy

coherence

With larger crystals you might observe high frequency oscillations

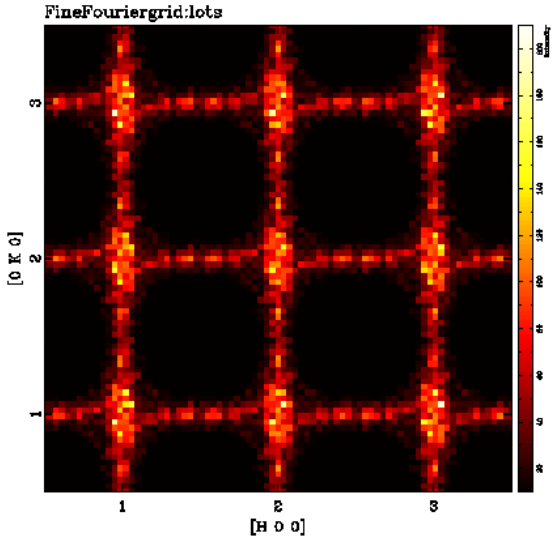
Crystal size too small to yield a good average

I - < I >



diffuse scattering is quite noisy

I - < I > calculated for many small lots, randomly placed within crystal



diffuse scattering is much less noisy

```
fourier
  neutron
  ll -2.5, 0.00, 0.00
  lr  2.5, 0.00, 0.00
  ul -2.5, 0.00, 0.00
  na  1001
  no     1
  abs    h
  ord    k
  temp  ignore
  disp  off

  set   aver, 50
  lots  box, 14, 14, 1, 50, yes

  show
  run
exit
#
output
  outf 1d.inte
  value intensity
  run
exit
```

Switch to fourier menu

- **calculate neutron diffraction pattern**
- **Lower Left corner in reciprocal space**
- **Lower Right corner**
- **Upper Left corner**
- **number of grid points along abscissa**
- **number of grid points along ordinate**
- **write H coordinate as abscissa**
- **write K coordinate as abscissa**
- **ignore thermal parameters**
- **switch anomalous dispersion off**

calculate the average intensity with 50% of the crystal

Use 50 box shaped lots sized 14 * 14 * 1

- **run the calculation**

switch to the output menu

- **write output to file „1d.inte“**
- **write intensities**
- **run the actual write process**

change to directory Lectures\02.Calculation_Scattering

start discus_suite

run macro **2d.mac** and then **2d_lots.mac**

suite> **@2d.mac**
suite>
suite> **@2d_lots.mac**

calculate: powder pattern Debye equation :

PDF

properties ...

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

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

each individual atom

atom pairs

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

r_{ij} vector 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.

```
read
cell silicon.cell,$1,$1,$1
#
powder
  xray
  set axis,q
  set calc,debye
  set disp,off
  set delta,0.0
  set qmin,0.5500
  set qmax,7.1000
  set dq,  0.0005
  set temp,use
  set wvle,1.54056
  set four,four
  set lpcor,bragg,26.58
  run
exit
output
  outf  powder.inte
  value inte
  form  powder,q
run
exit
```

Read a small crystal

switch to powder menu
- **radiation xray**
- **calculate on equally space q scale**
- **use Debye equation**
- **switch anomalous dispersion off**
- **switch convolution with resolution function off**
- **minimum Q value**
- **maximum Q value**
- **Q increment**
- **use the thermal parameters**
- **define the wavlelength**
- **(relevant for stacking faults only)**
- **define Lorentz and Polarisation calculation**
- **run the actual calculation**

switch to the output menu
- **define output file name**
- **write intensity values to the output file**
- **pattern will be written as powder pattern,**
  - **with x-axis in steps of Q**

```
read
cell silicon.cell,$1,$1,$1
#
powder
  xray
  set axis,q
  set calc,debye
  set disp,off
  set delta,0.0
  set qmin,0.5500
  set qmax,7.1000
  set dq,  0.0005
  set profile, pseudo
  set profile, uvw, 0,0,0.001
  set profile, eta, 0.5
  set profile, asym, 0,0,0,0
  set temp,use
  set wvle,1.54056
  set four,four
  set lpcor,bragg,26.58
  run
exit
```

Read a small crystal

switch to powder menu

- **radiation xray**
- **calculate on equally space q scale**
- **use Debye equation**
- **switch anomalous dispersion off**
- **switch convolution with resolution function off**
- **minimum Q value**
- **maximum Q value**
- **Q increment**
- **convolute with Pseudo-Voigt**
- **set u,v,w, parameters for Cagliotti**
- **set mixing parameter Eta=0 Lor; 1=Gauss**
- **set asymmetry parameters**
- **use the thermal parameters**
- **define the wavlelength**
- **(relevant for stacking faults only)**
- **define Lorentz and Polarisation calculation**
- **run the actual calculation**

make sure you have started DISCUS and KUPLOT

change to directory Lectures\02.Calculation_Scattering

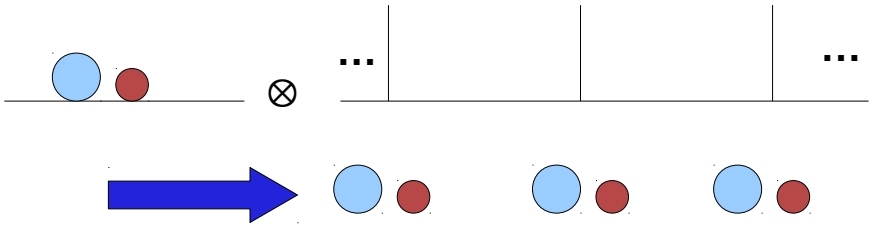
run macro **powder.mac** with different numbers as input parameter:

suite> **@powder.mac 6**

ideal crystal structure

all atoms as correct atom type on ideal site

structure factor $F(\vec{h}) = \sum_{j=1}^{N_{crystal}} f_j(|\vec{h}|) e^{2\pi i \vec{h} \vec{r}_j}$



if strictly periodic and infinite:

convolution of a unit cell and an infinite lattice:

in one dimension

Fourier transform: $F(crystal) = F\left[\left(\sum_{j=1}^{N_{cell}} (Atom\ at\ r)\right) \circ \sum_{k=-\infty}^{\infty} \delta(x - ka)\right]$

convolution theorem: $\mathcal{F}(g \otimes h) = \mathcal{F}(g) \bullet \mathcal{F}(h) = G \bullet H$

Fourier transform of a convolution is:
product of individual Fourier transforms

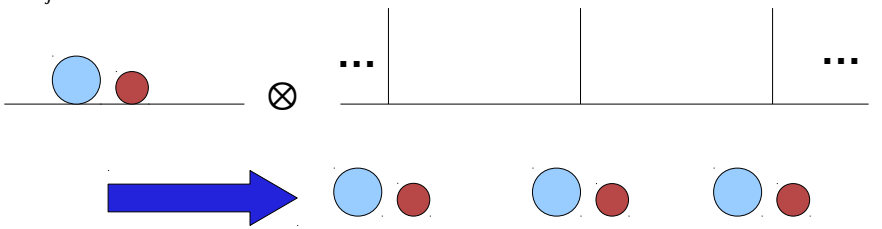
Multiplication theorem: $\mathcal{F}(g \bullet h) = \mathcal{F}(g) \otimes \mathcal{F}(h) = G \otimes H$

Fourier transform of a product is
convolution of individual Fourier transforms

ideal crystal structure

all atoms as correct atom type on ideal site

structure factor $F(\vec{h}) = \sum_{j=1}^{N_{Kristall}} f_j(|\vec{h}|)\, e^{2\pi i \vec{h}\vec{r}_j}$



if strictly periodic and infinite:

convolution of a unit cell with an infinite lattice:

in one dimension

Fourier transform:

$$F(crystal) = F\left[\left(\sum_{j=1}^{N_{cell}} (atom\,at\,r)\right) \circ \sum_{k=-\infty}^{\infty} \delta(x-ka)\right]$$

$$= F\left[\left(\sum_{j=1}^{N_{cell}} (atom\,at\,r)\right)\right] \cdot F\left[\sum_{k=-\infty}^{\infty} \delta(x-ka)\right]$$

$$= \left[\sum_{j=1}^{N_{cell}} f_j(|\vec{h}|)\, e^{2\pi i \vec{h}\vec{r}_j}\right] \cdot \left[\frac{1}{a}\sum_{h=-\infty}^{\infty} \delta\left(u-\frac{h}{a}\right)\right]$$

structure factor • **reciprocal lattice**

→ sum of infinitely sharp Bragg reflections, wheighted by structure factor

Ideal, yet finite crystal structure

= infinitely sized crystal multiplied by a box shaped function

electron density: $\rho(x)\cdot box$

in one dimension

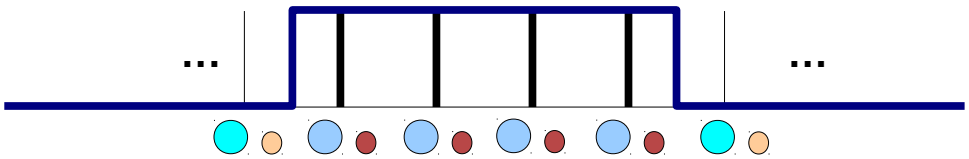
Fourier transform: $F(\rho(x)\cdot box)=F(\rho(x))\circ F(box)$

Fourier transform of box with full width A: $F(box)=\frac{\sin(\pi A u)}{\pi u}$

$$=\left[\sum_{j=1}^{N} f_j(|\vec{h}|)e^{2\pi i\vec{h}\vec{r}_j}\right]\cdot\left[\frac{1}{a}\sum_{h=-\infty}^{\infty}\delta\left(u-\frac{h}{a}\right)\right]\circ\frac{\sin(\pi A u)}{\pi u}$$

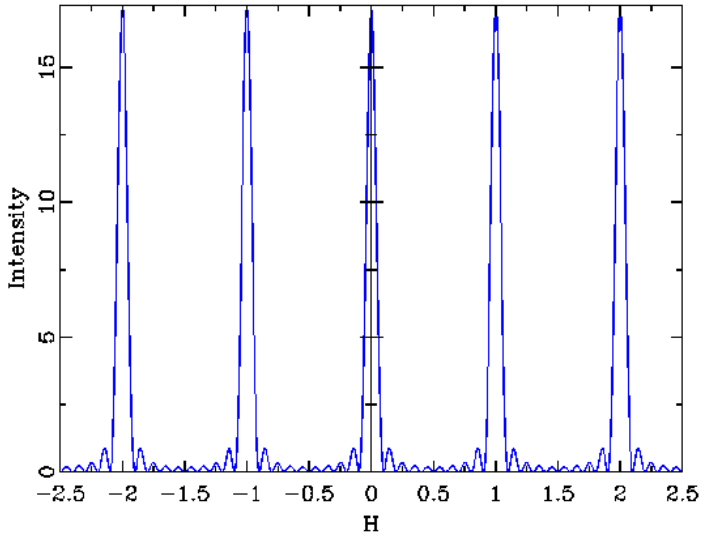
→ Sum of widened Bragg reflections with subsidiary maxima

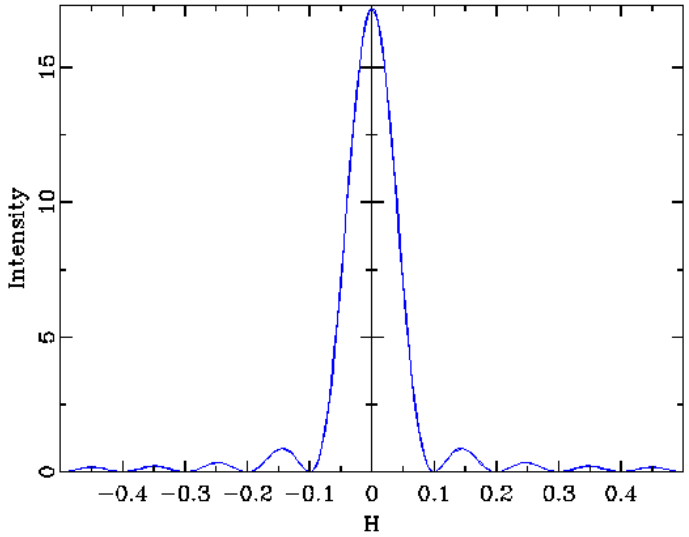
Zero points at u = j/A



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