3D-ΔPDF method for single crystal diffuse scattering data analysis

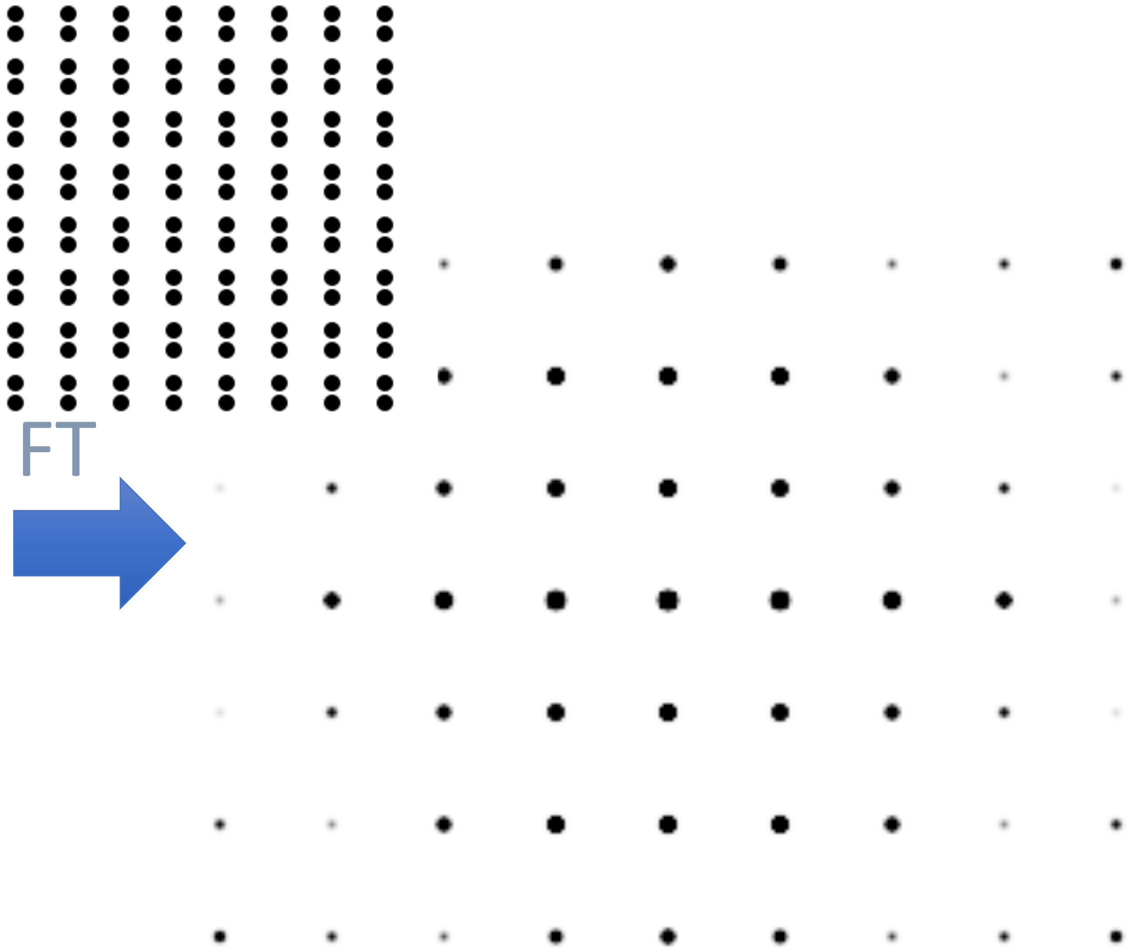
Arkadiy Simonov

ETH Zürich

Diffuse scattering analysis:

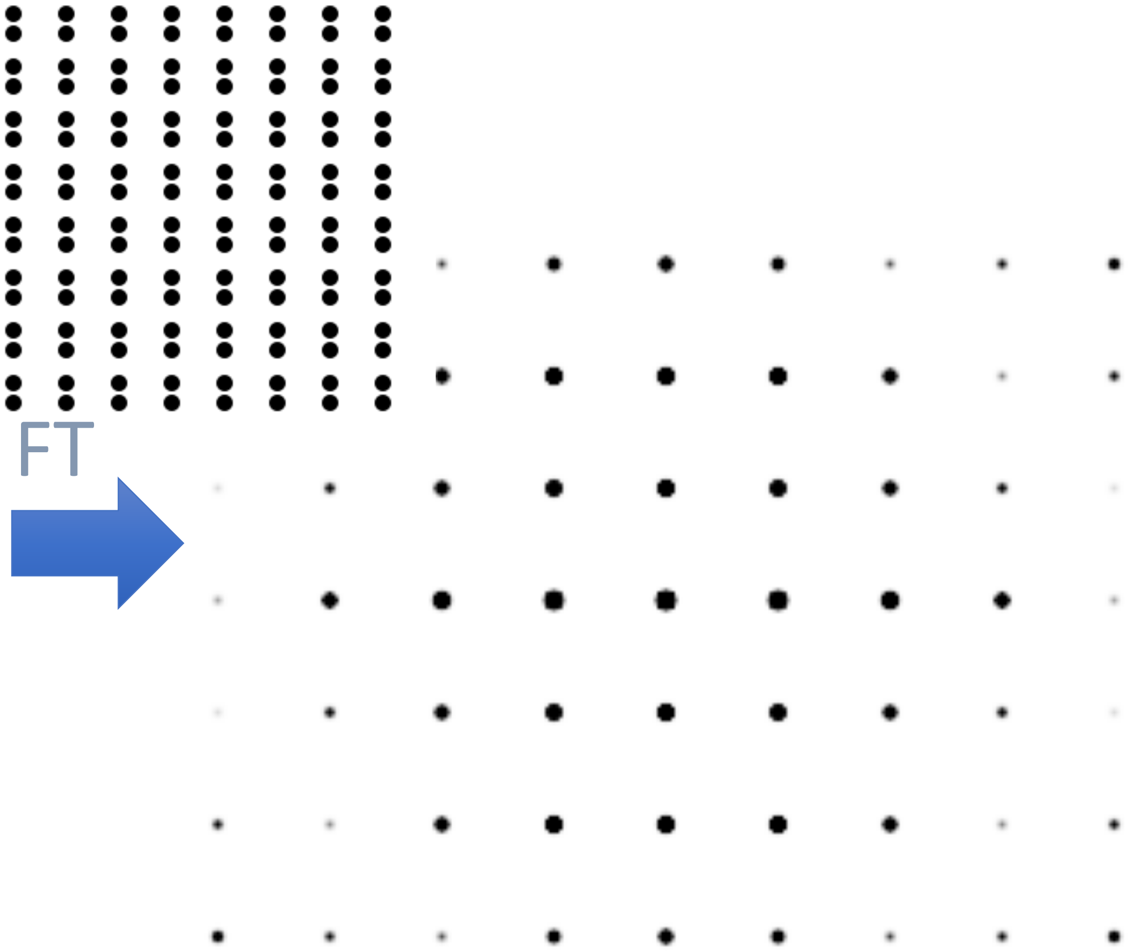
- Patterson function
- Pair distribution function (PDF)
- Difference PDF (ΔPDF)
- Software (Yell & Meerkat)

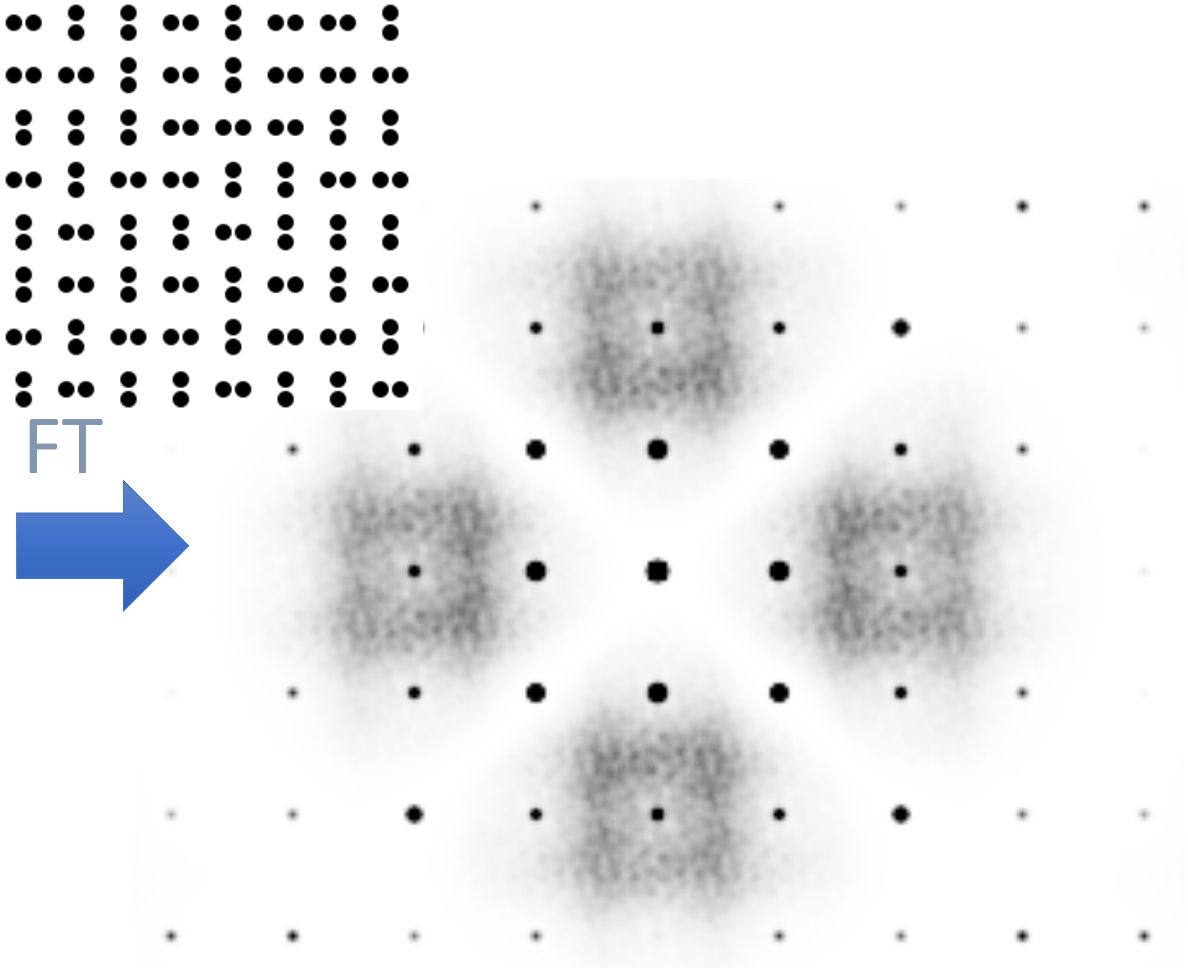
Bragg and diffuse scattering



Ordered structure = Bragg peaks

Bragg and diffuse scattering

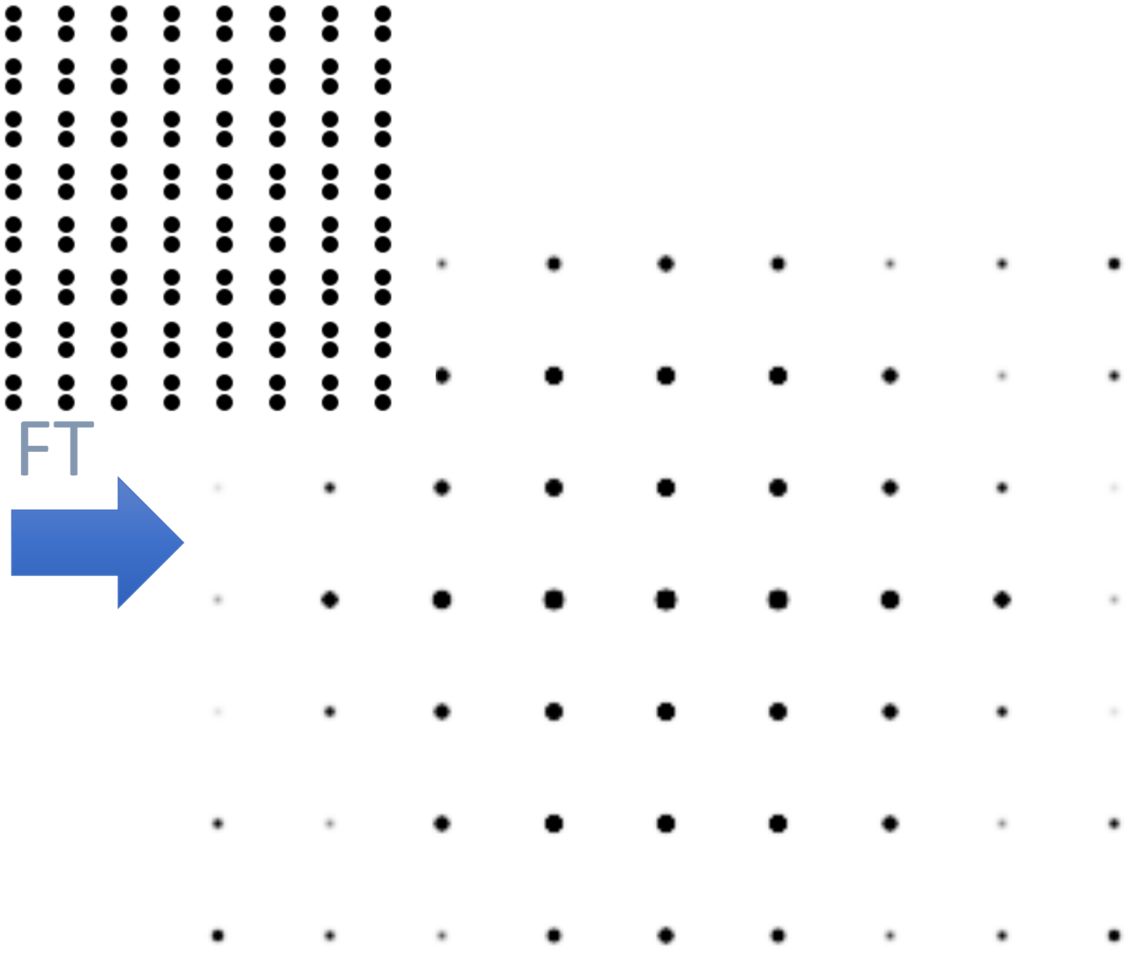




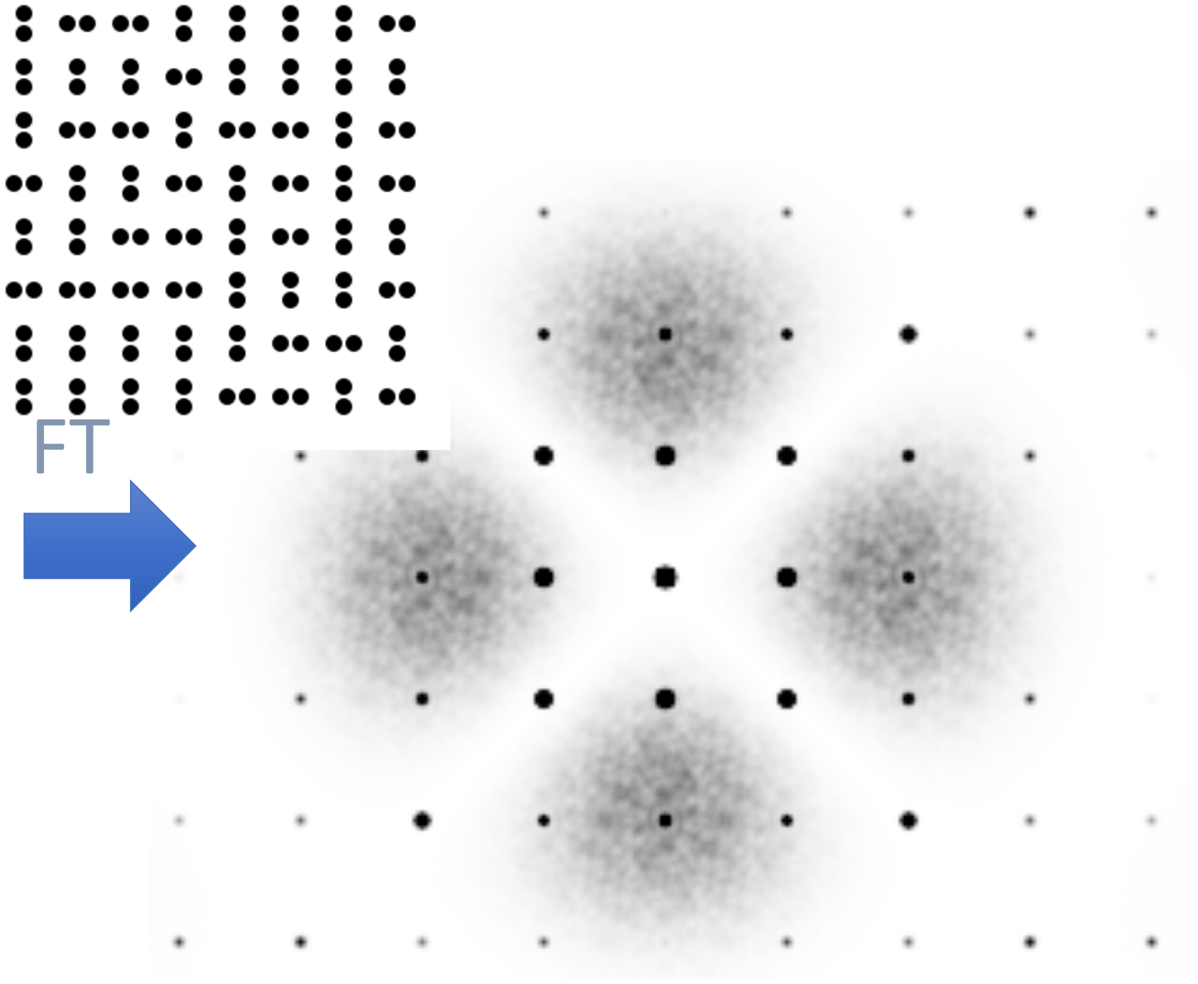
Ordered structure = Bragg peaks

Disordered = Bragg peaks + Diffuse scattering

Bragg and diffuse scattering

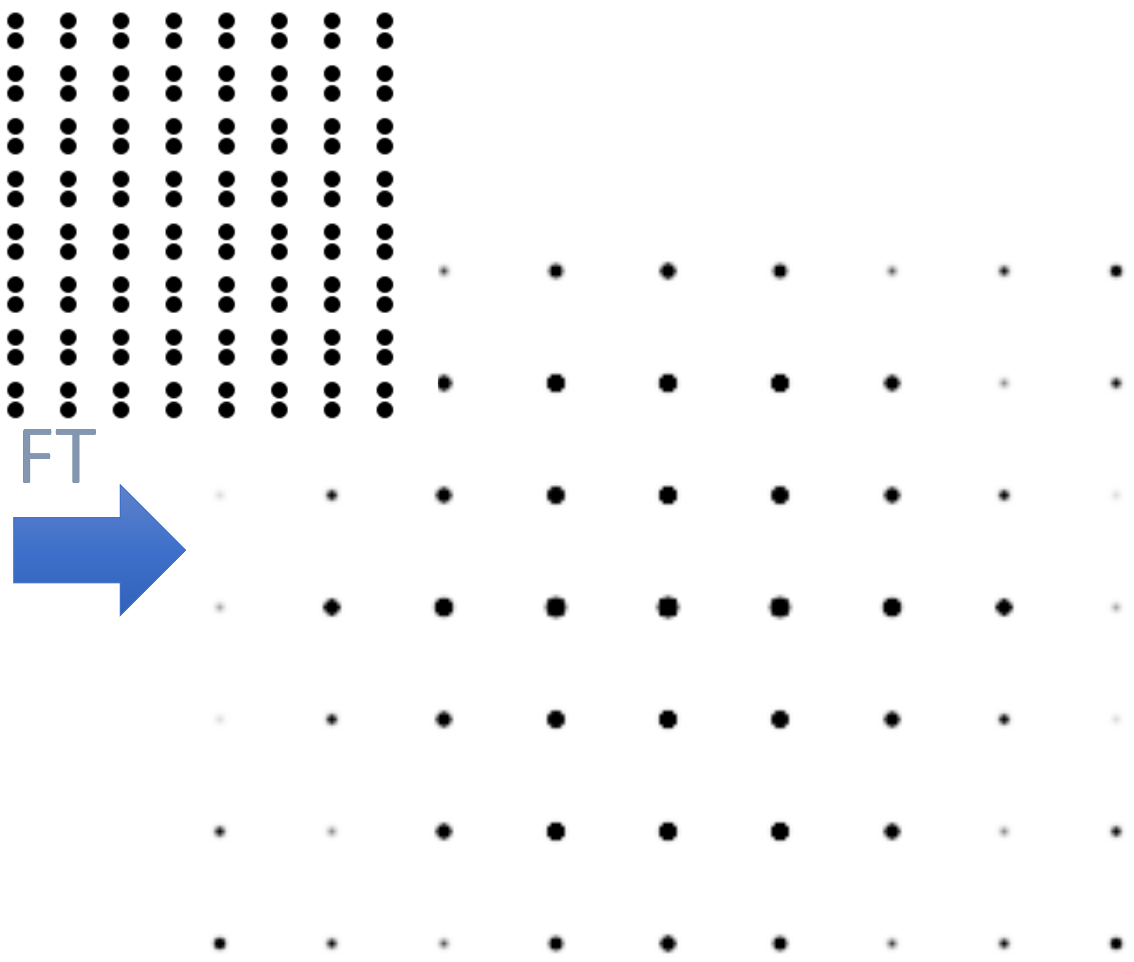


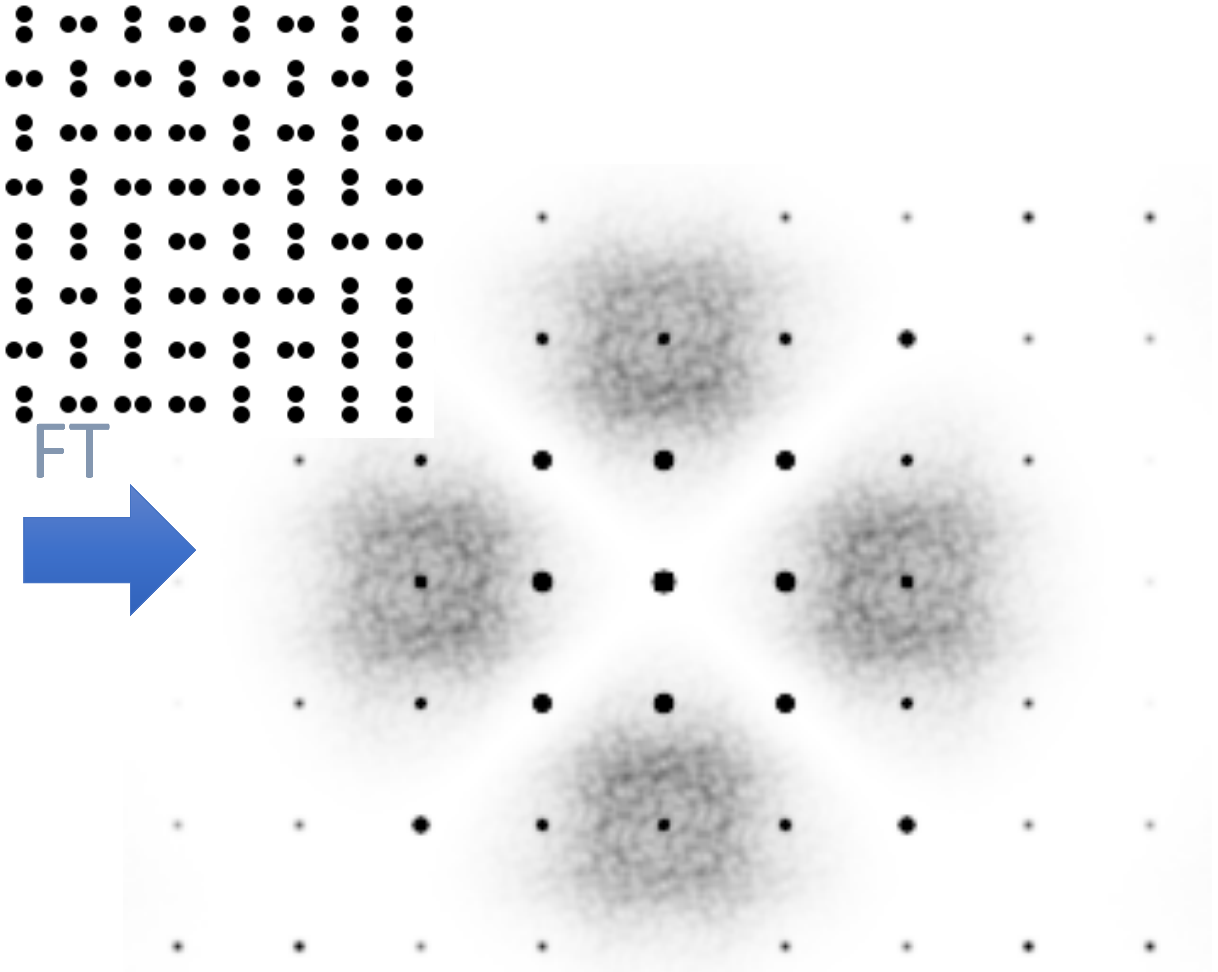
Ordered structure = Bragg peaks



Disordered = Bragg peaks + Diffuse scattering

Bragg and diffuse scattering

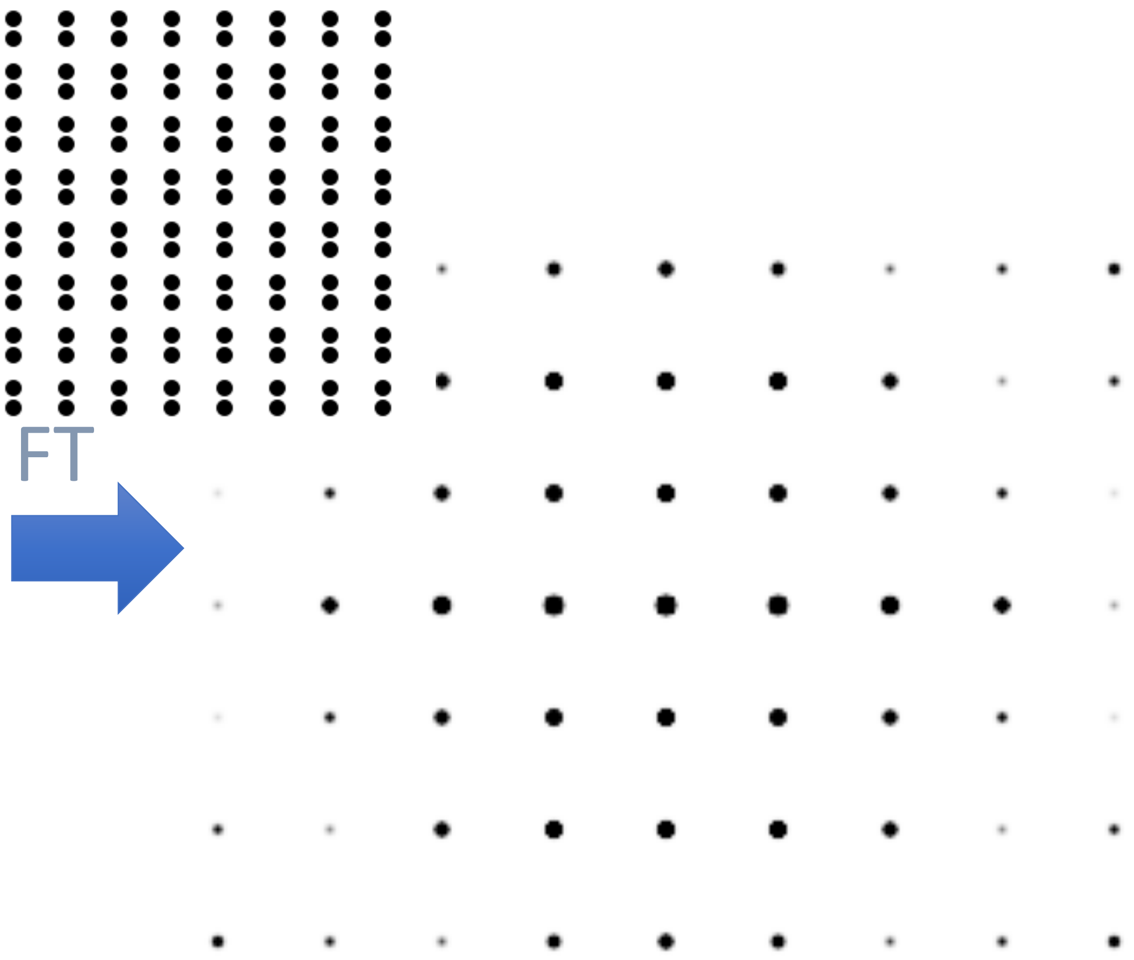




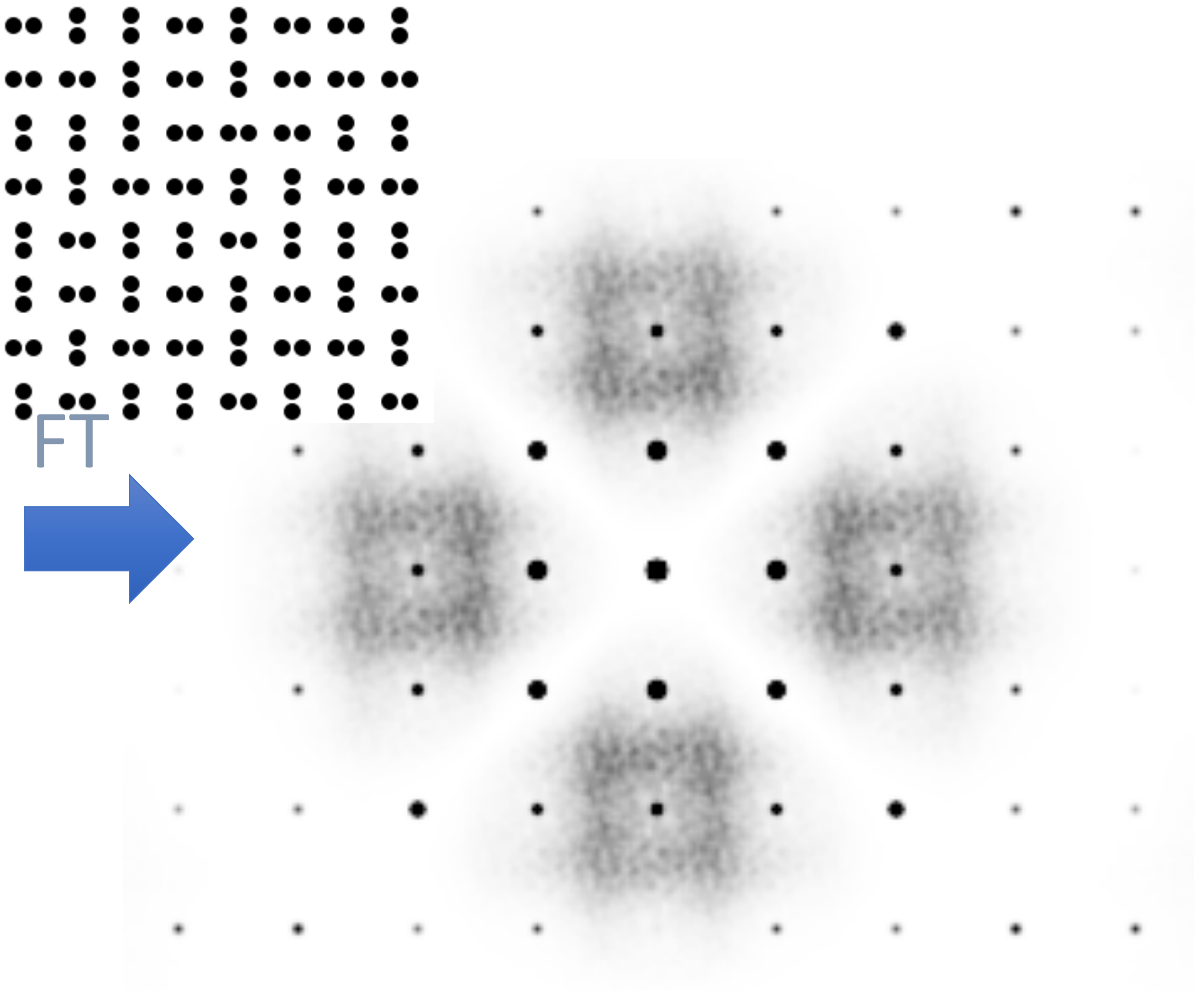
Ordered structure = Bragg peaks

Disordered = Bragg peaks + Diffuse scattering

Bragg and diffuse scattering

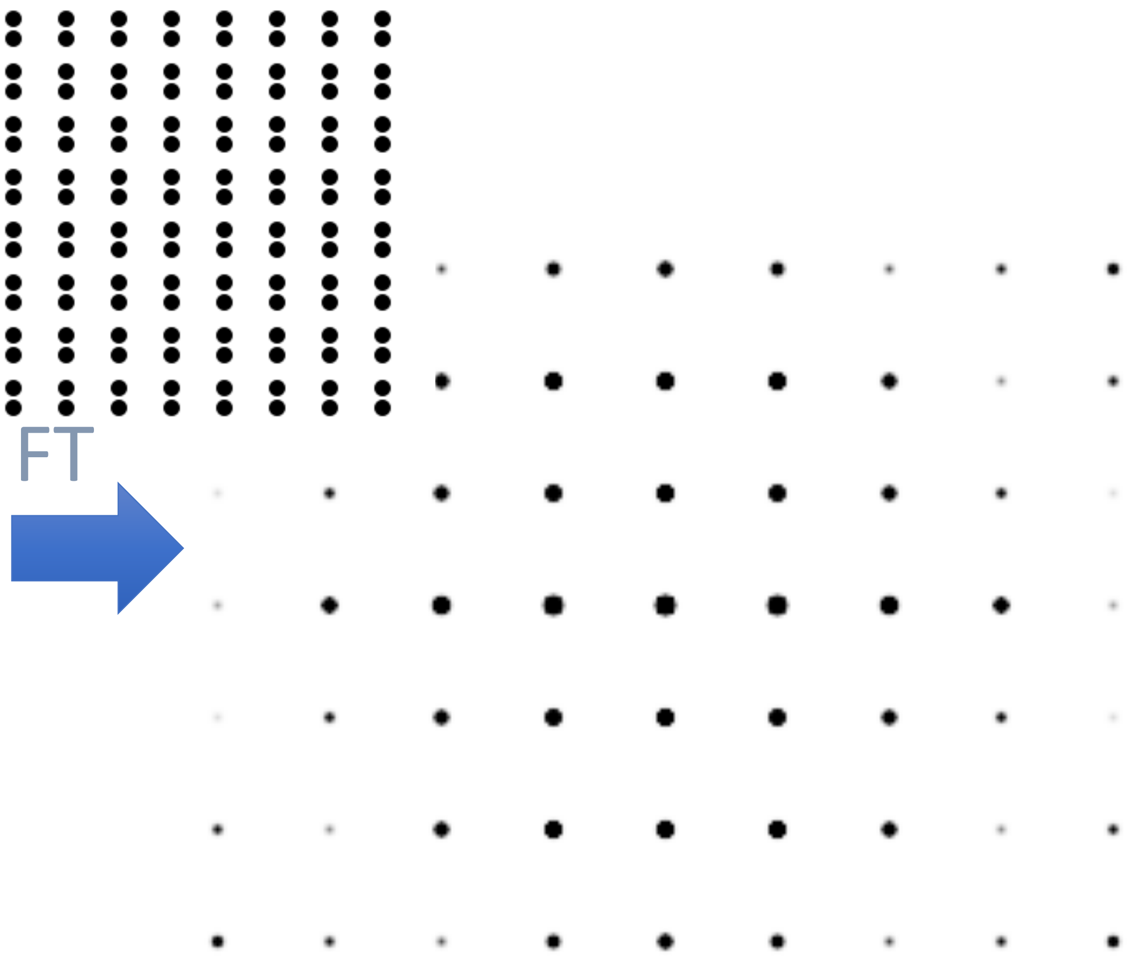


Ordered structure = Bragg peaks

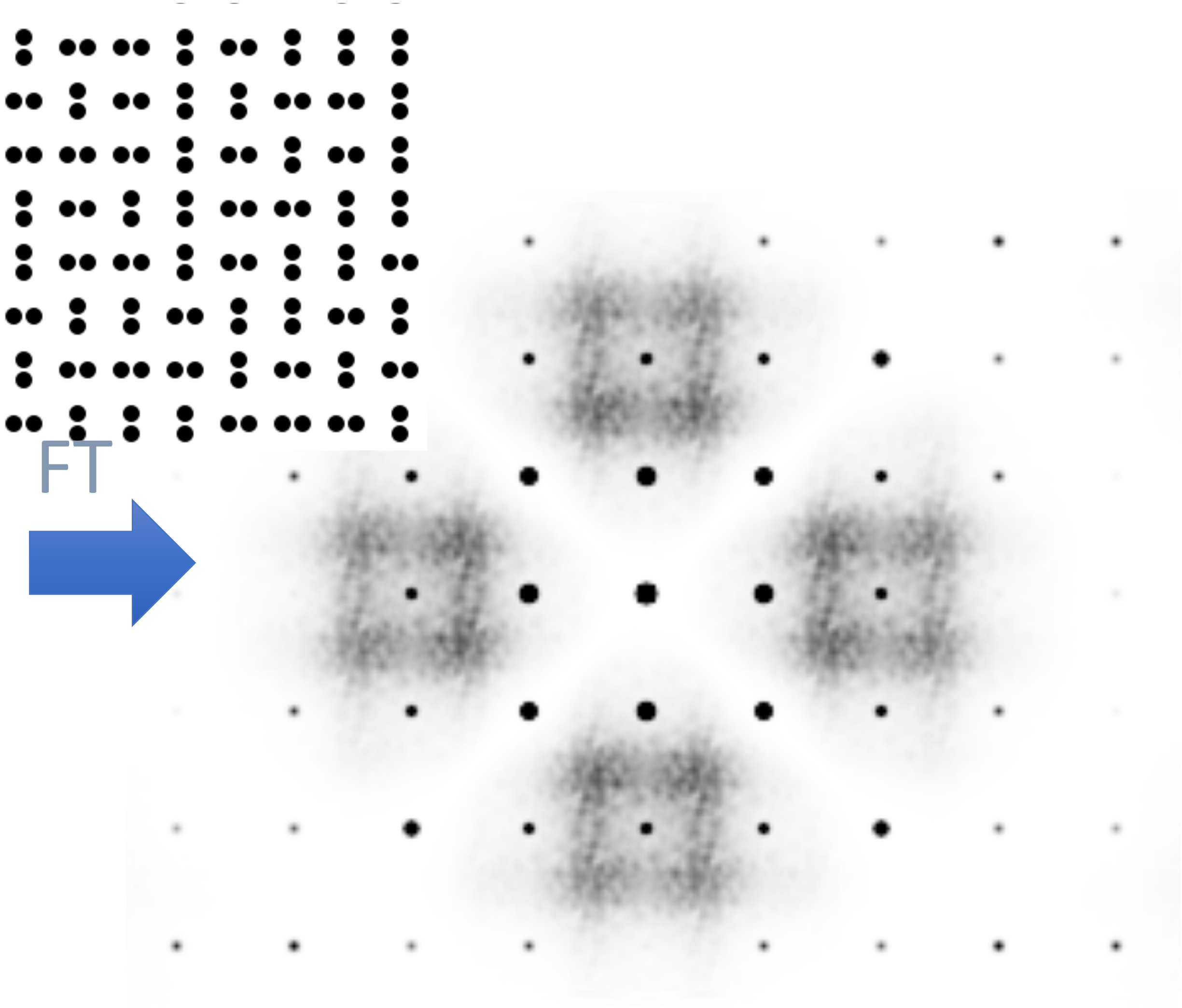


Disordered = Bragg peaks + Diffuse scattering

Bragg and diffuse scattering

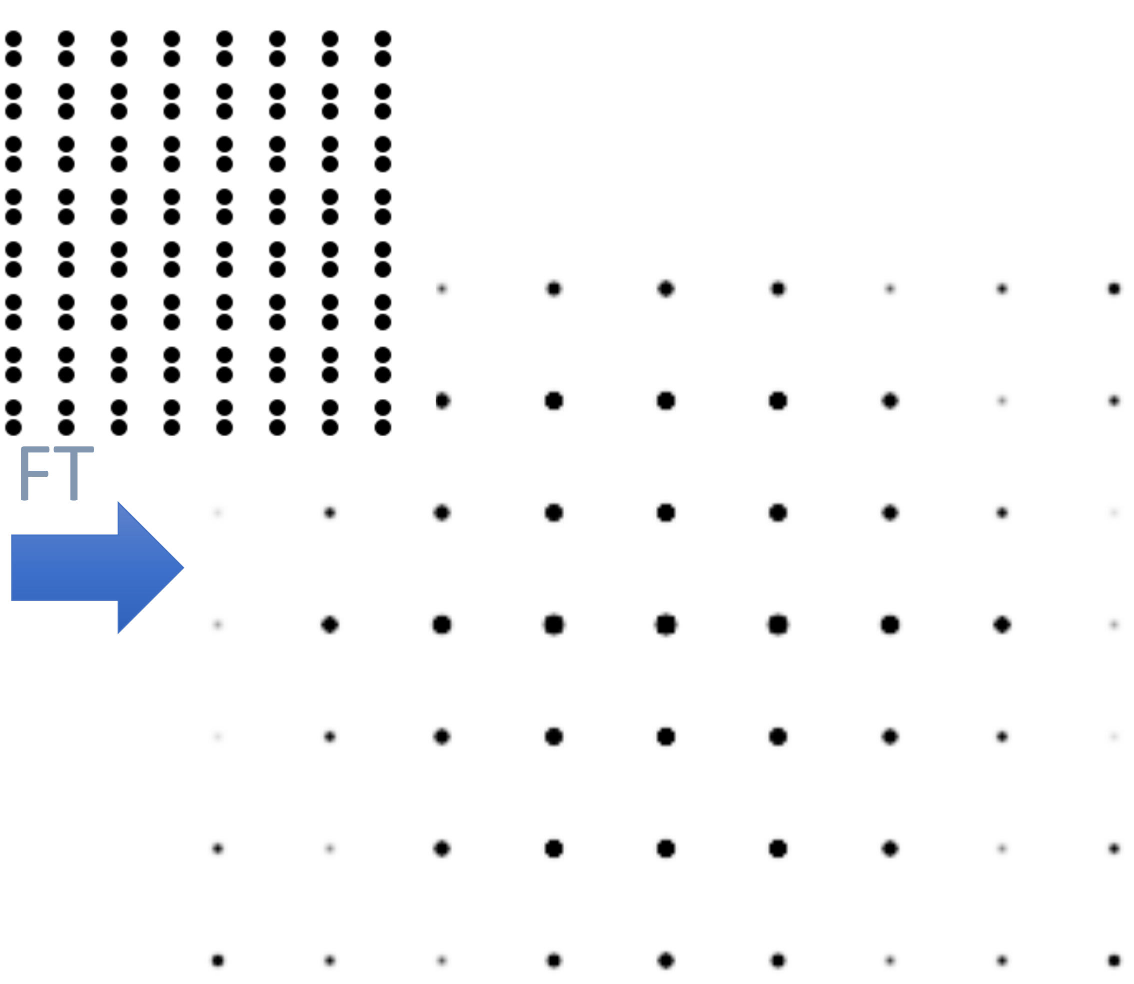


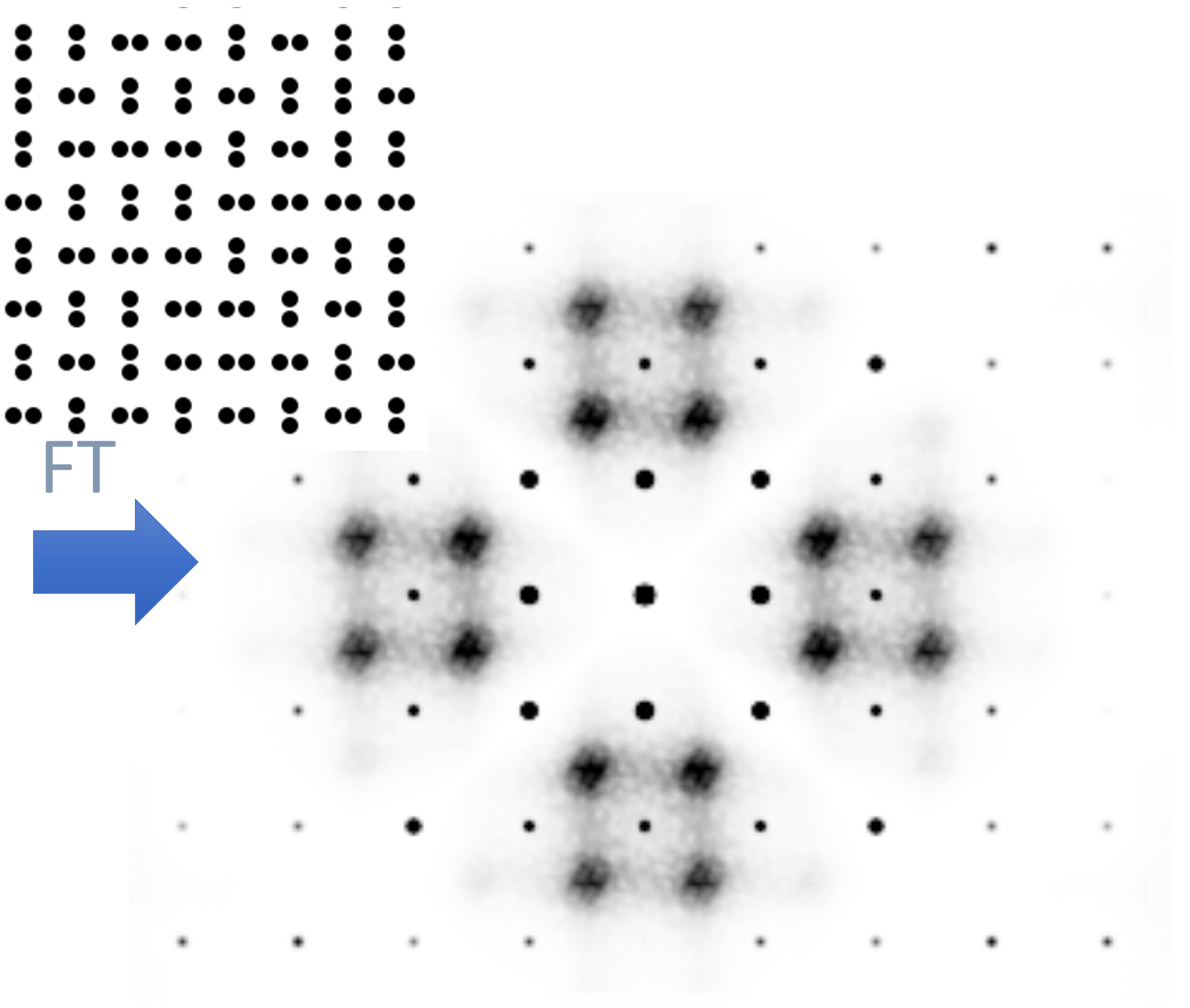
Ordered structure = Bragg peaks



Disordered = Bragg peaks + Diffuse scattering

Bragg and diffuse scattering

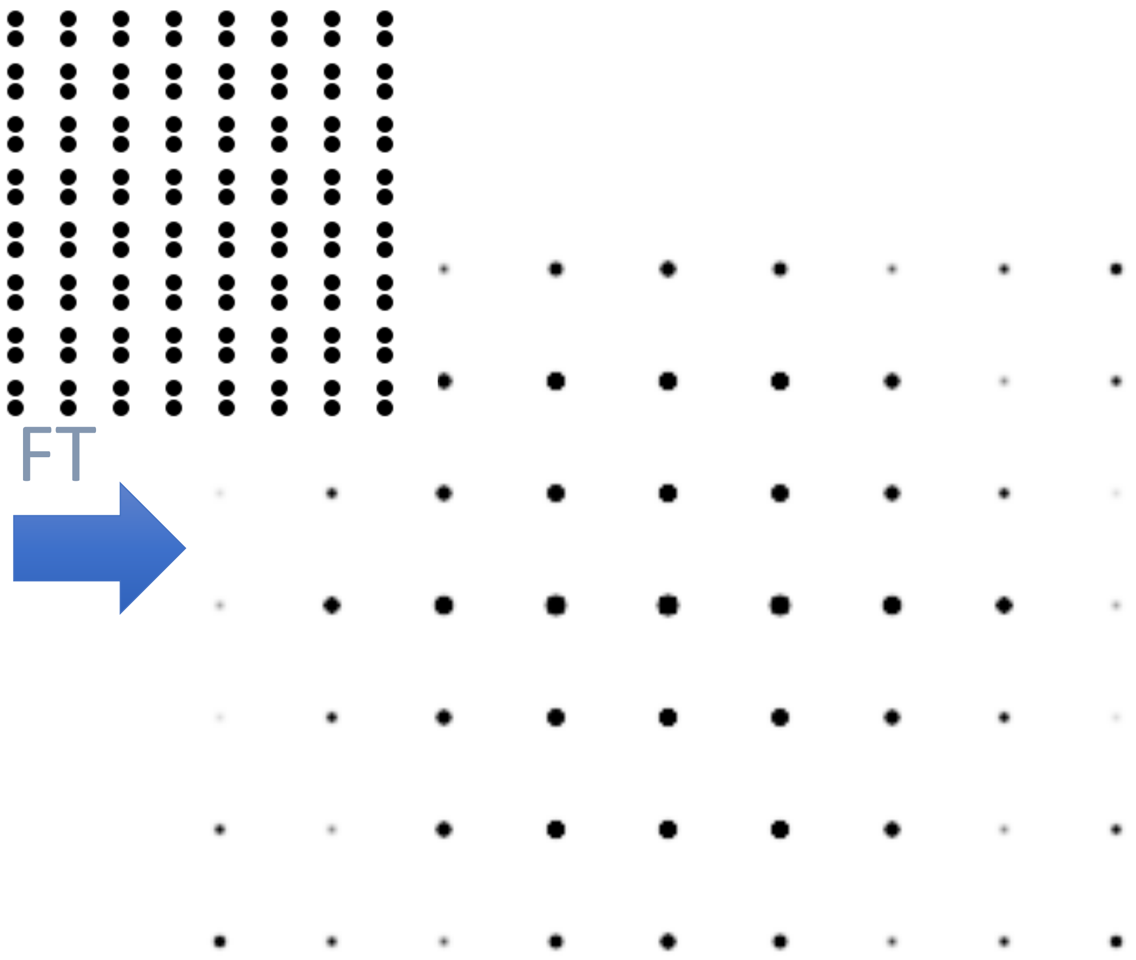




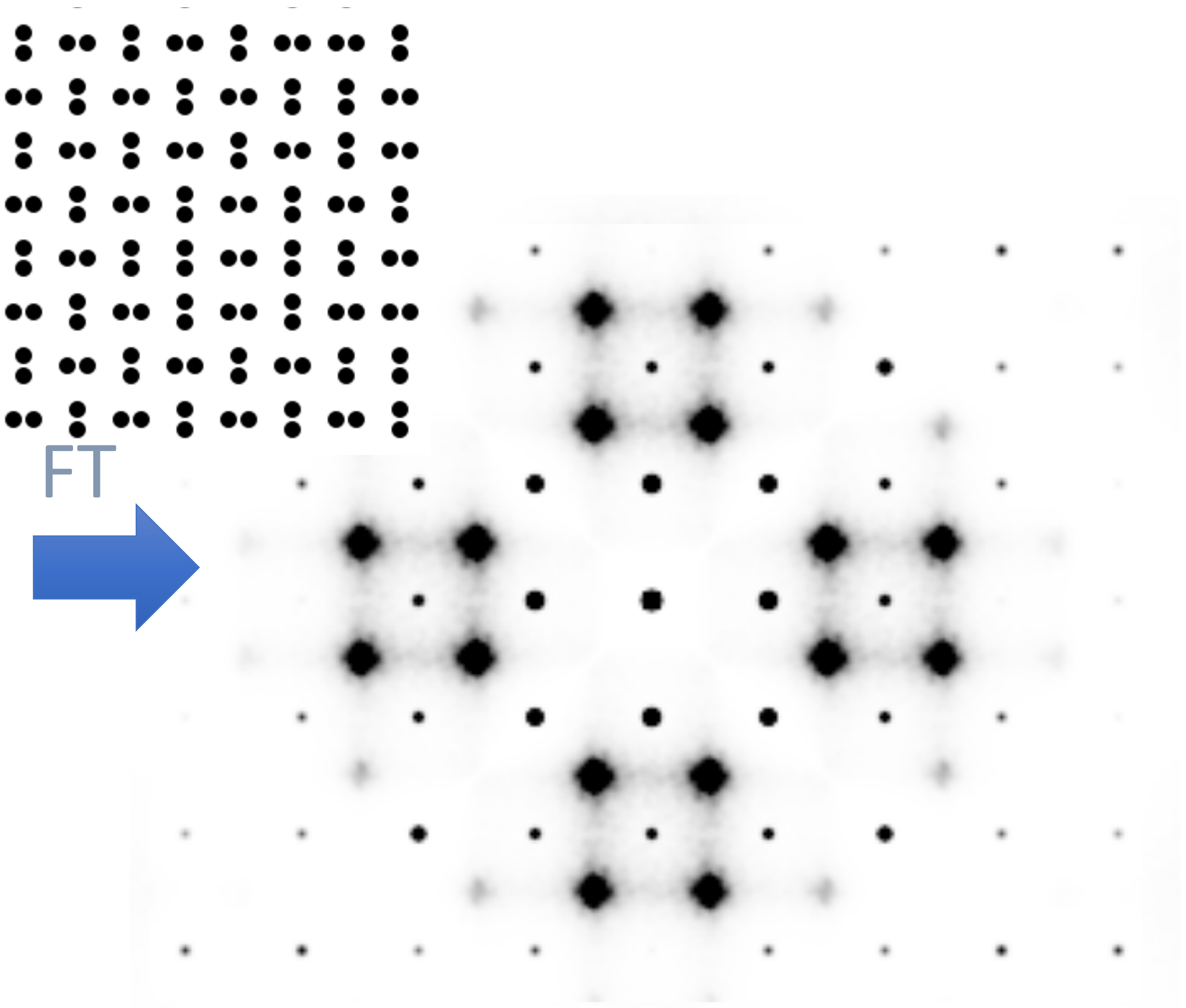
Ordered structure = Bragg peaks

Disordered = Bragg peaks + Diffuse scattering

Bragg and diffuse scattering



Ordered structure = Bragg peaks



Disordered = Bragg peaks + Diffuse scattering

Formalism

$$I_{\mathrm{Diffuse}} = I_{\mathrm{Total}} - I_{\mathrm{Bragg}}$$

Formalism

$$\mathrm{I}_{\mathrm{Diffuse}} = \mathrm{I}_{\mathrm{Total}} - \mathrm{I}_{\mathrm{Bragg}} =$$

$$= \mathrm{FT}\left[\langle \rho \star \rho \rangle - \langle \rho \rangle \star \langle \rho \rangle\right]$$

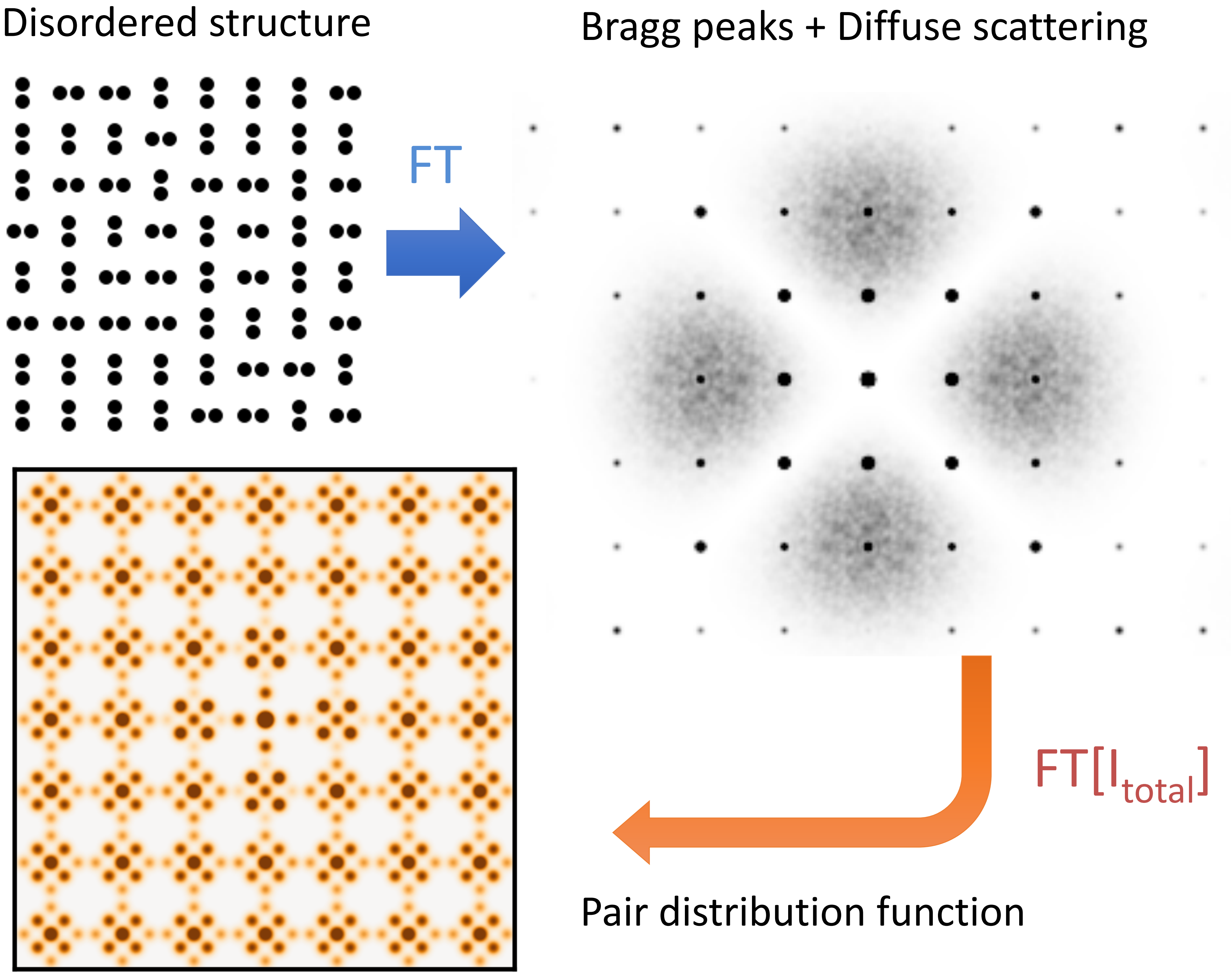
Formalism

$$\mathrm{I}_{\mathrm{Diffuse}} = \mathrm{I}_{\mathrm{Total}} - \mathrm{I}_{\mathrm{Bragg}} =$$

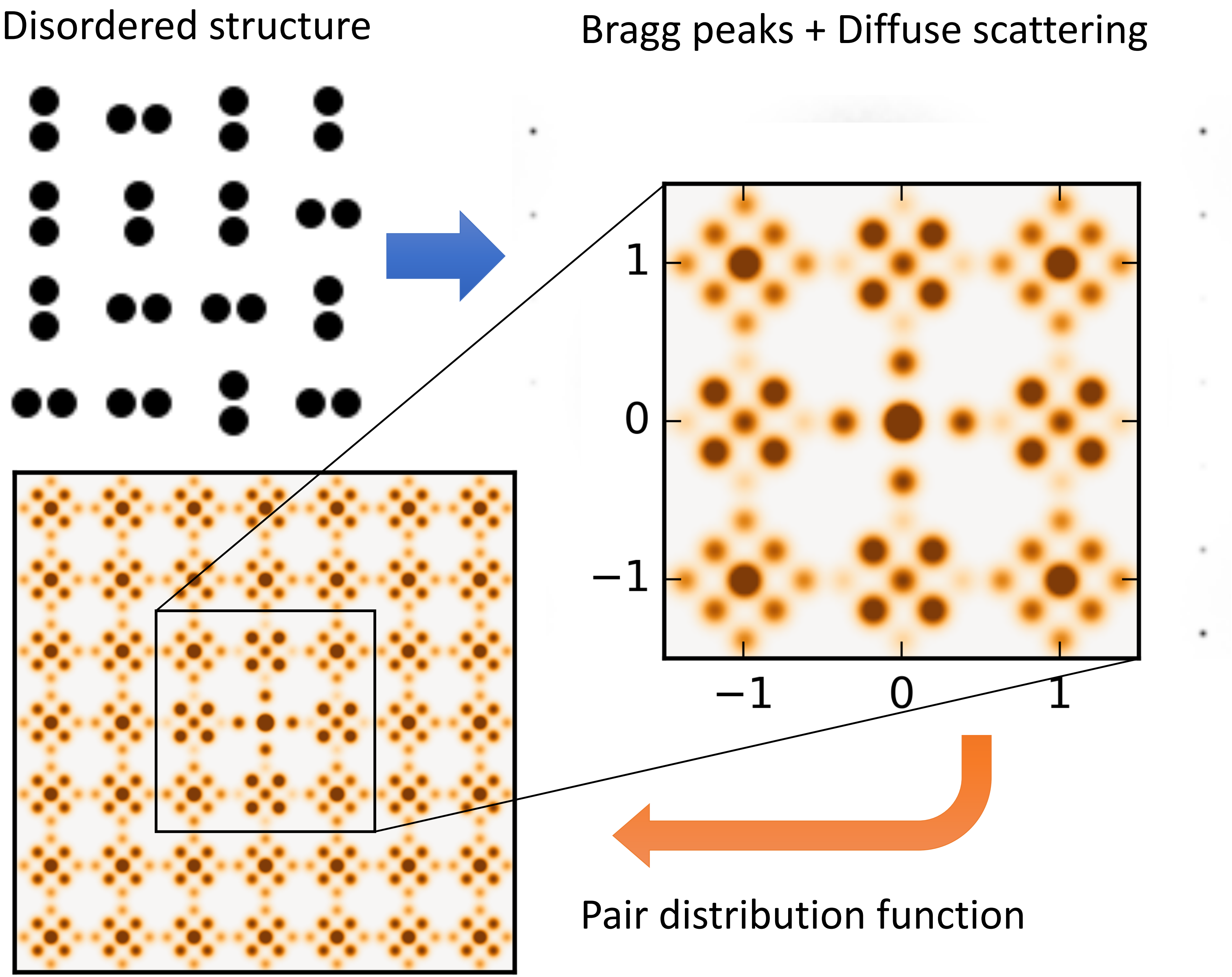
$$= \mathrm{FT}\left[\langle \rho \star \rho \rangle - \langle \rho \rangle \star \langle \rho \rangle\right]$$

Pair distribution function

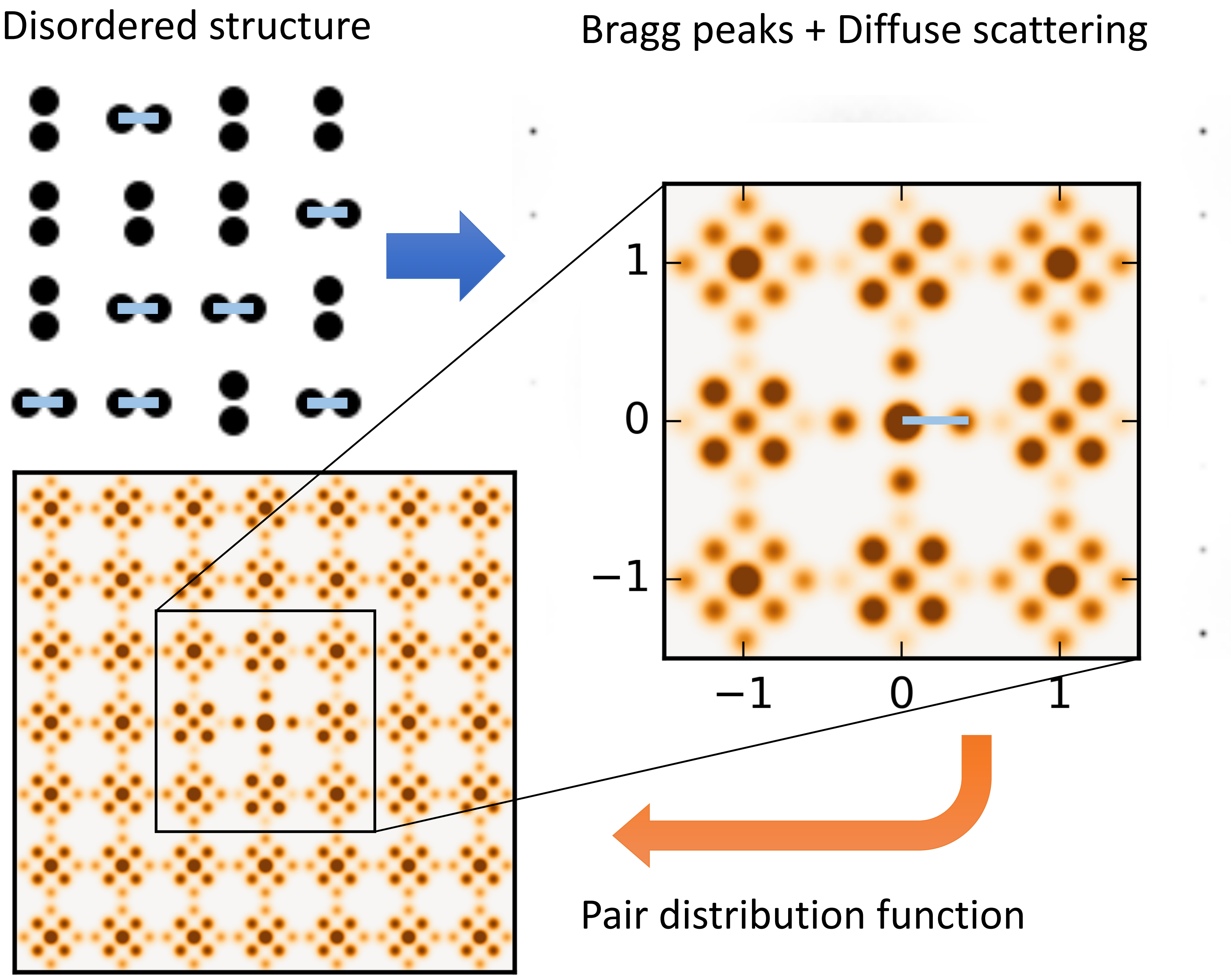
Patterson function



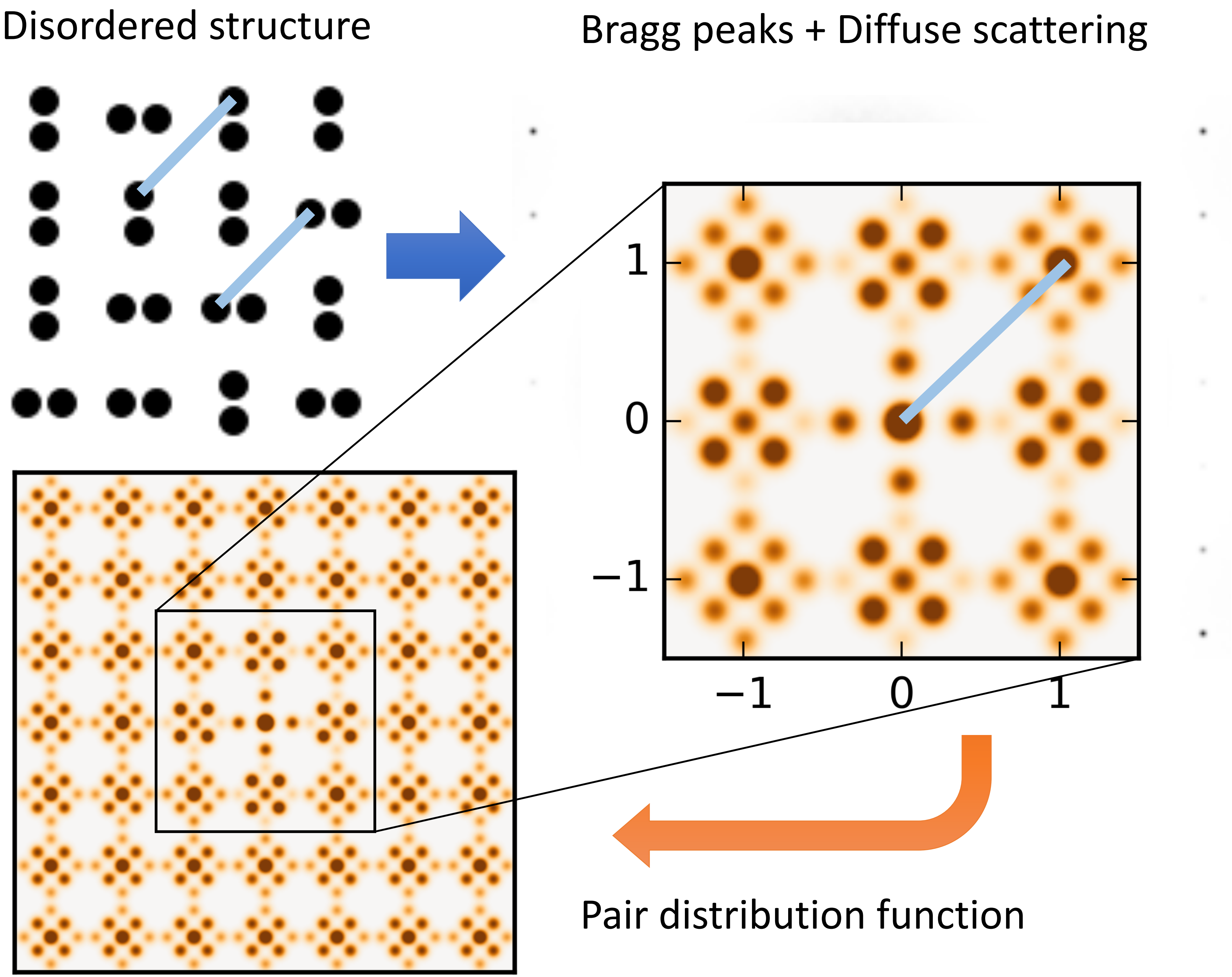
Disordered structure
Bragg peaks + Diffuse scattering
FT
FT[I_total]
Pair distribution function

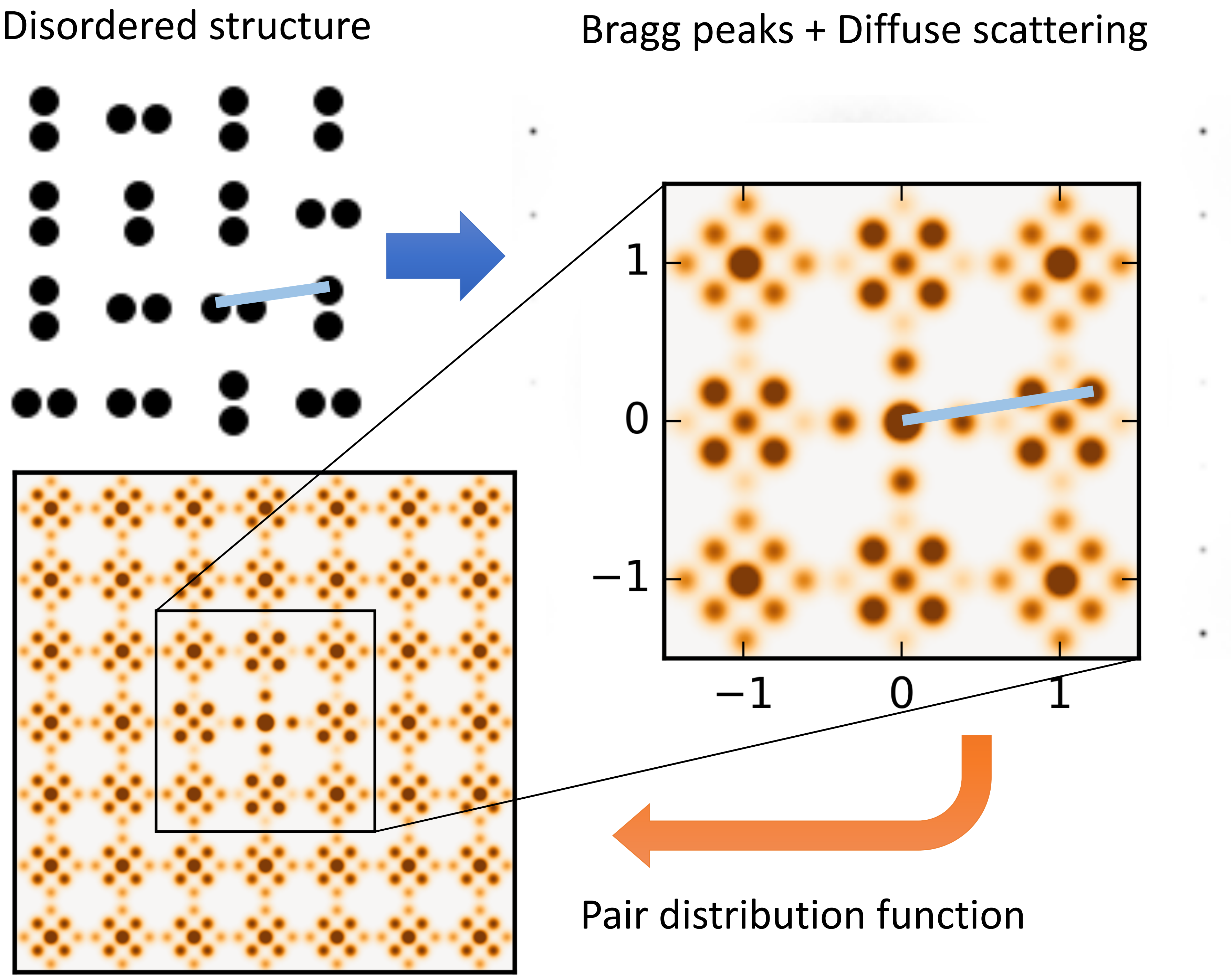


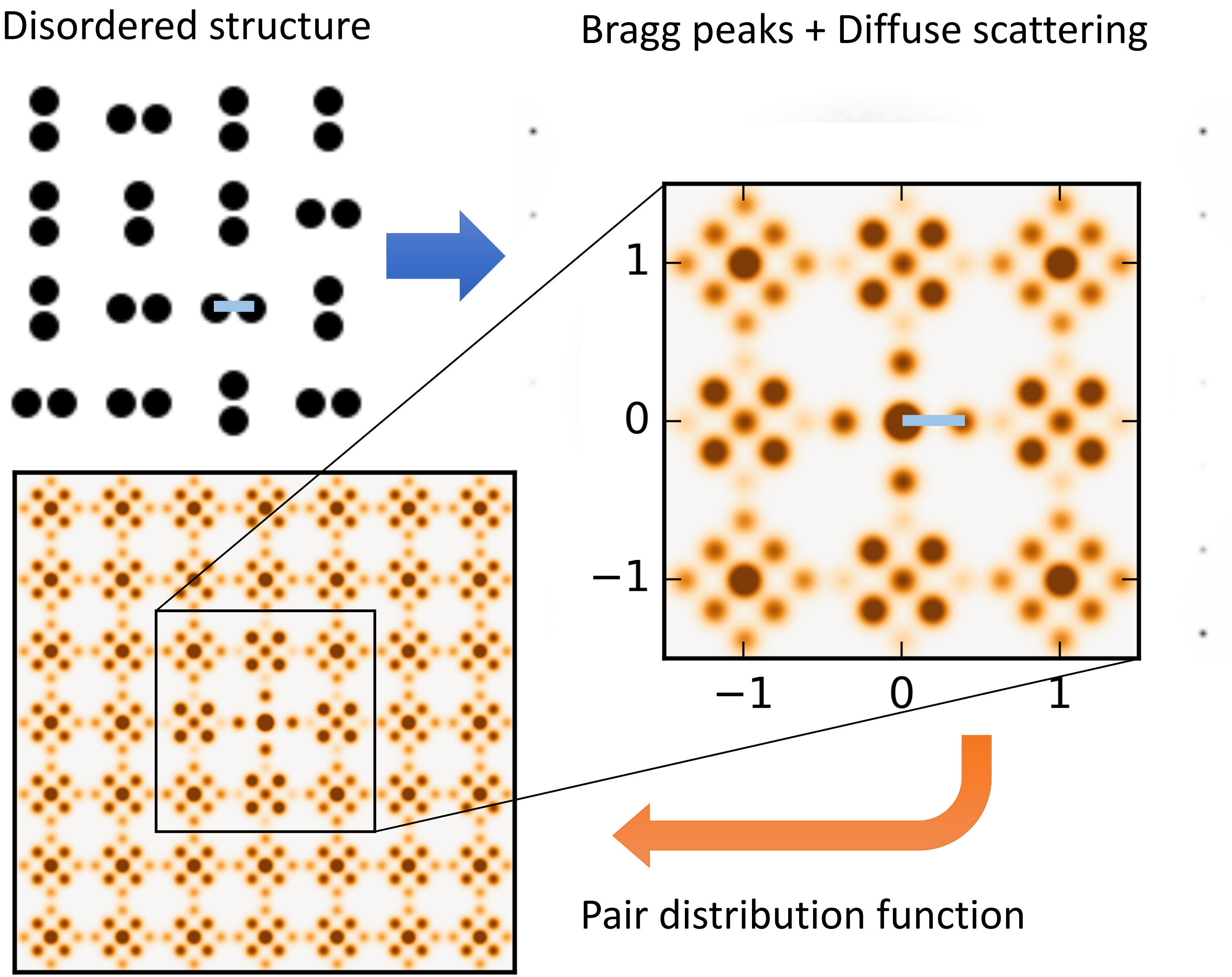
Disordered structure
Bragg peaks + Diffuse scattering
1
0
−1
−1
0
1
Pair distribution function



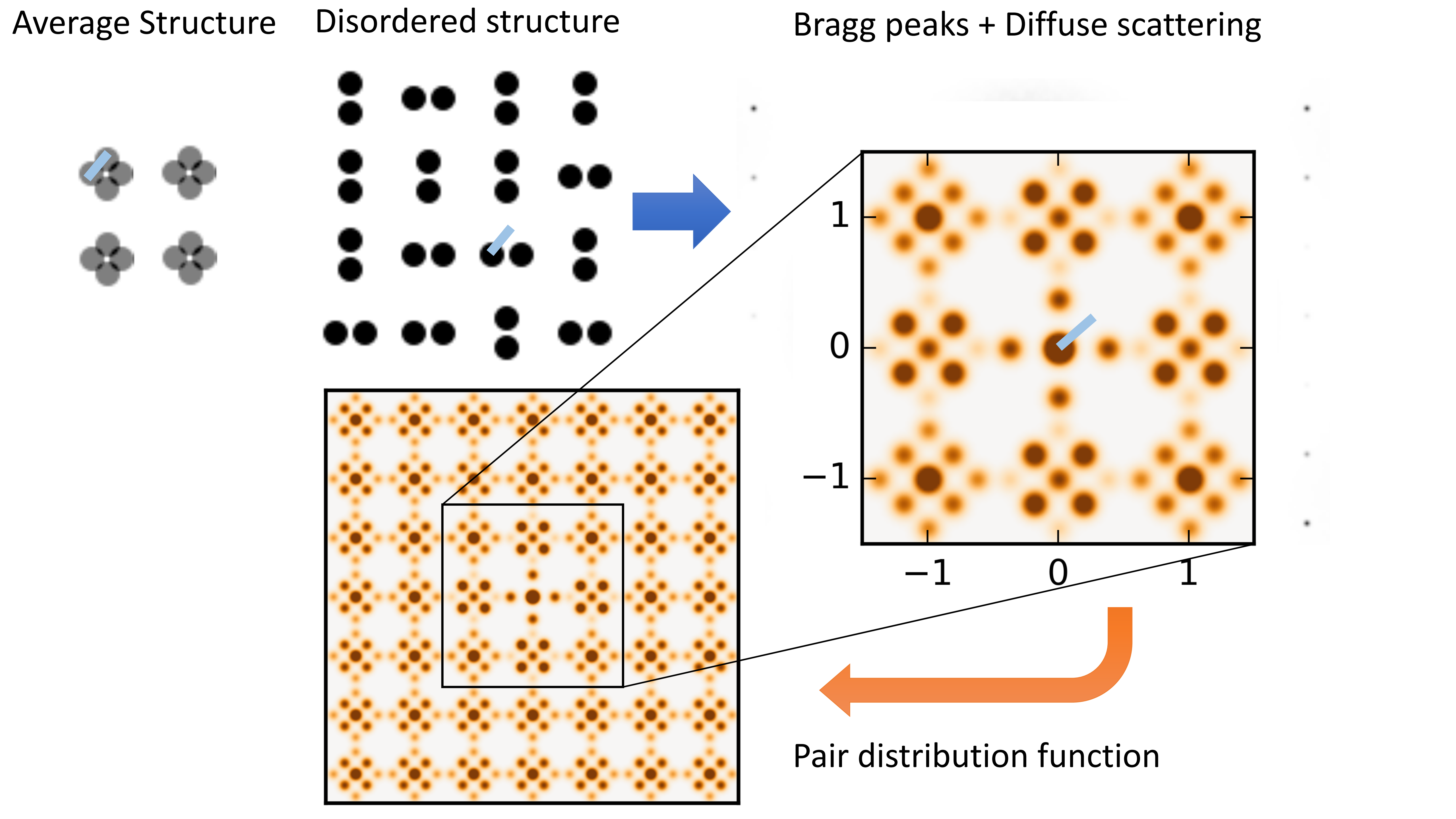
Disordered structure
Bragg peaks + Diffuse scattering
1
0
−1
−1
0
1
Pair distribution function


Disordered structure
Bragg peaks + Diffuse scattering
Pair distribution function
1
0
−1
−1
0
1

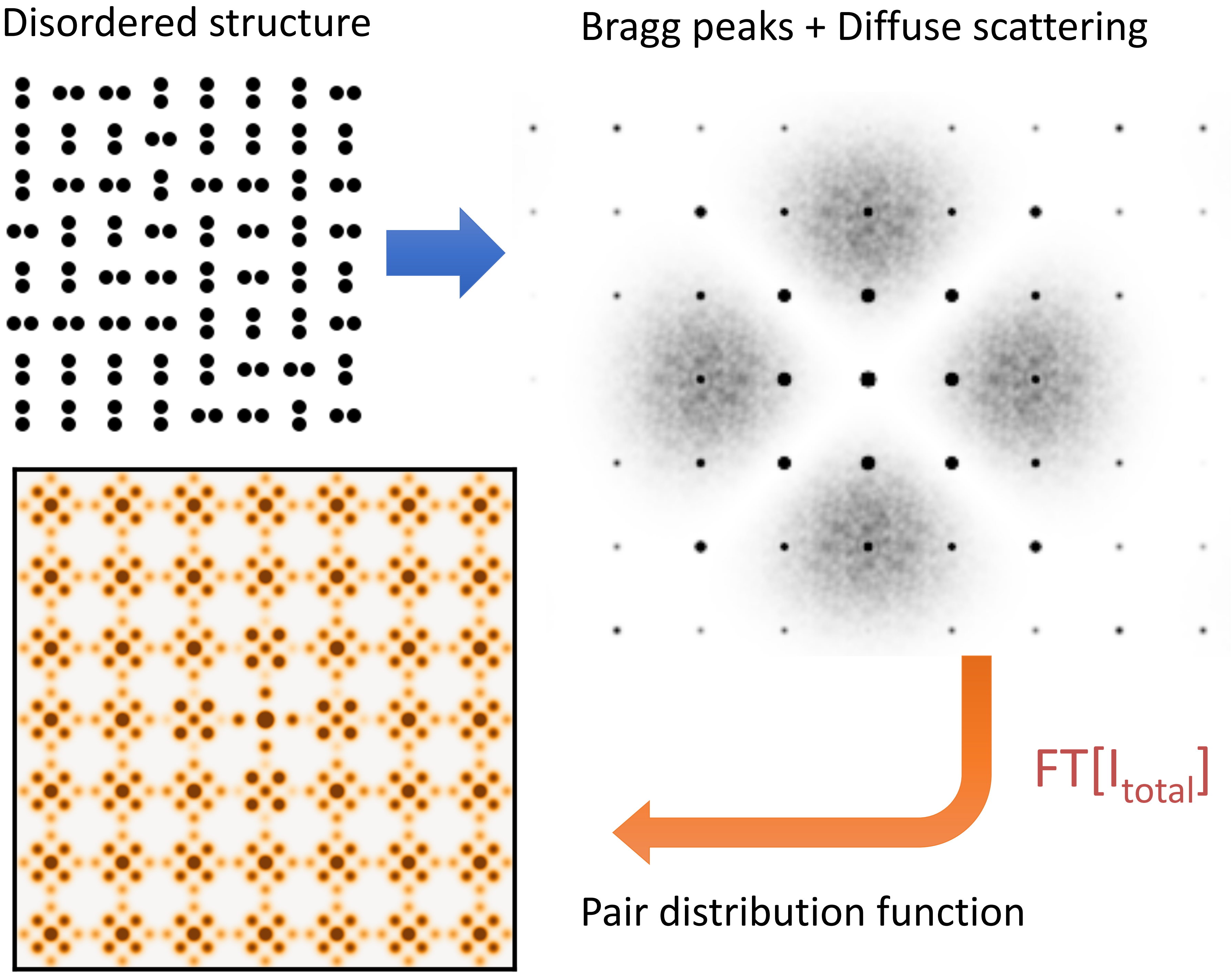

Disordered structure
Bragg peaks + Diffuse scattering
1
0
−1
−1
0
1
Pair distribution function



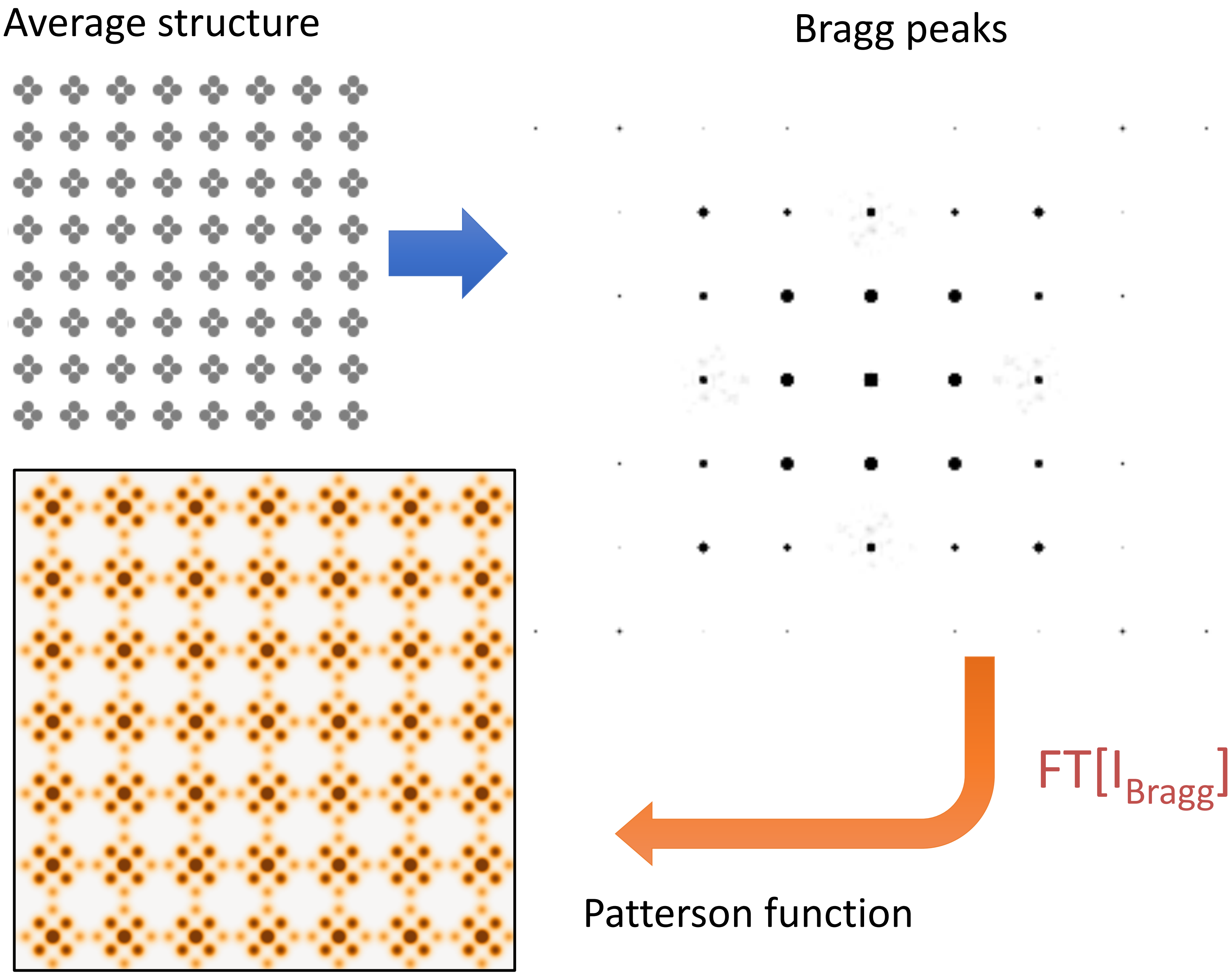
Disordered structure
Bragg peaks + Diffuse scattering
1
0
−1
−1
0
1
Pair distribution function

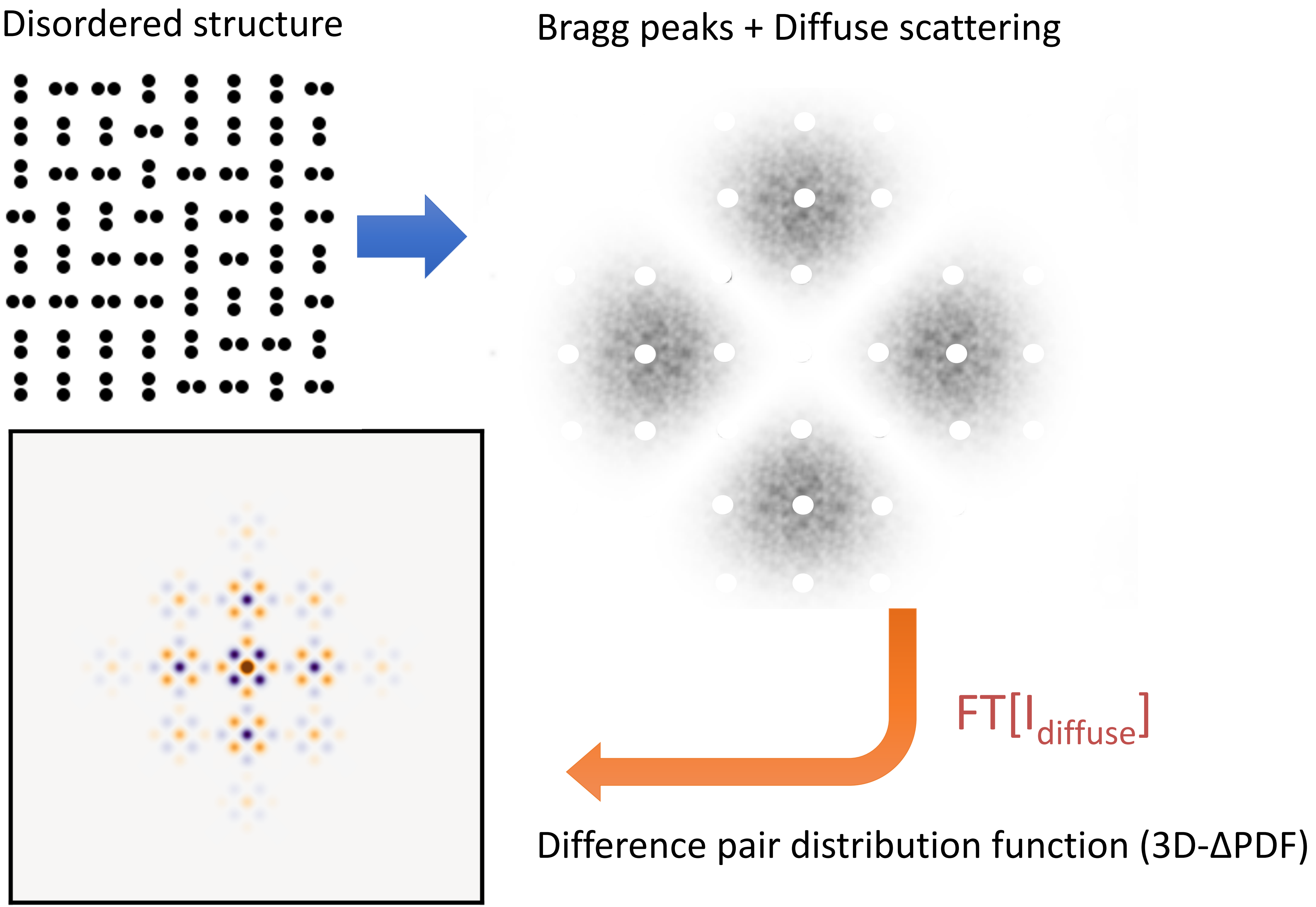


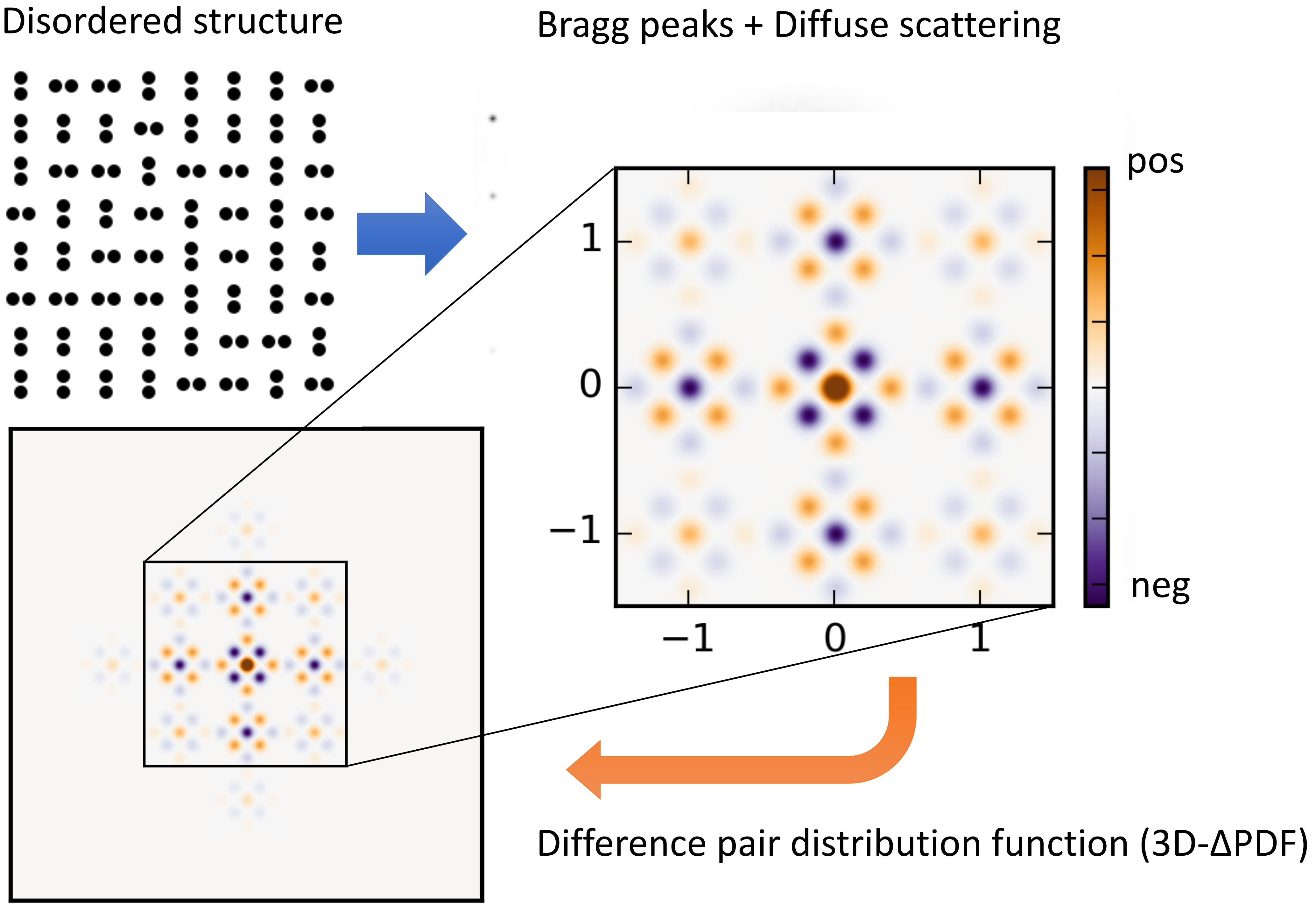
Average Structure
Disordered structure
Bragg peaks + Diffuse scattering
1
0
−1
−1
0
1
Pair distribution function



Disordered structure
Bragg peaks + Diffuse scattering
FT[I$_{total}$]
Pair distribution function


Average structure
Bragg peaks
$FT[I_{Bragg}]$
Patterson function


Disordered structure
Bragg peaks + Diffuse scattering
FT[I_diffuse]
Difference pair distribution function (3D-ΔPDF)



Disordered structure
Bragg peaks + Diffuse scattering
pos
neg
1
0
−1
−1
0
1
Difference pair distribution function (3D-ΔPDF)

Formalism

$$I_{Diffuse} = I_{Total} - I_{Bragg}$$

Formalism

$$\mathrm{I}_{\mathrm{Diffuse}} = \mathrm{I}_{\mathrm{Total}} - \mathrm{I}_{\mathrm{Bragg}} =$$

$$= \mathrm{FT}\left[\langle \rho \star \rho \rangle - \langle \rho \rangle \star \langle \rho \rangle\right]$$

Formalism

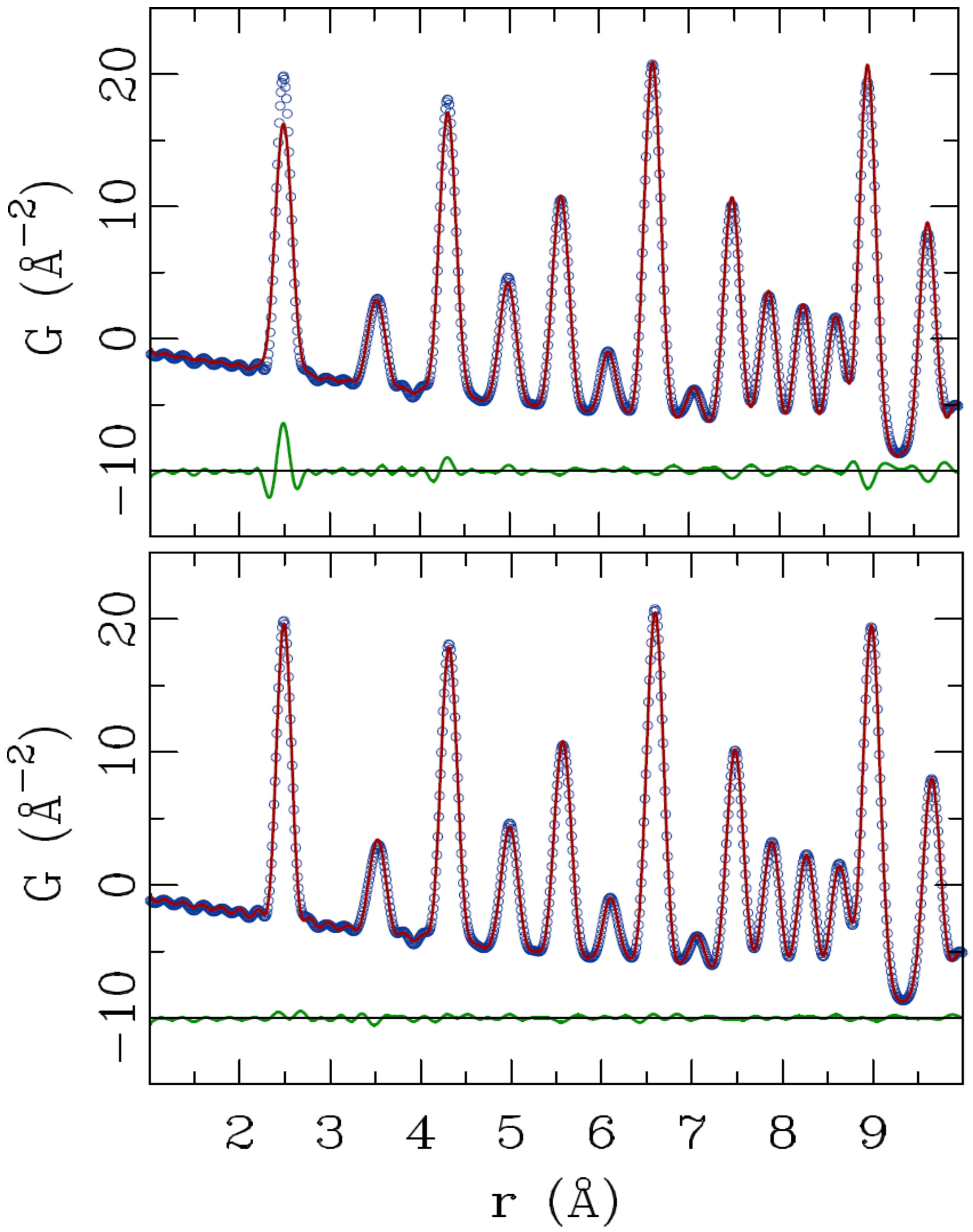
$$\mathrm{I}_{\mathrm{Diffuse}} = \mathrm{I}_{\mathrm{Total}} - \mathrm{I}_{\mathrm{Bragg}} =$$

$$= \mathrm{FT}\left[\langle \rho \star \rho \rangle - \langle \rho \rangle \star \langle \rho \rangle\right]$$

Pair distribution function

Patterson function

Why calculate delta PDF



Nickel PDF,
Emil Božin

3D-ΔPDF formalism and fingerprints of different correlation types

Formalism

$$I_{Diffuse} = FT\left[\langle \rho * \rho \rangle - \langle \rho \rangle * \langle \rho \rangle\right]$$

$$\mathrm{I}_{\mathrm{Diffuse}}(\vec{h}) = \sum_{uvw,pq} f_p f_q^* p_{uvw}^{pq} \exp(2\pi i \vec{h} \vec{r}_{uvw}^{pq}) \exp(4\pi^2 \vec{h} U_{uvw}^{pq} \vec{h}) - I_{av}$$

Joint probability

Distance between two atoms

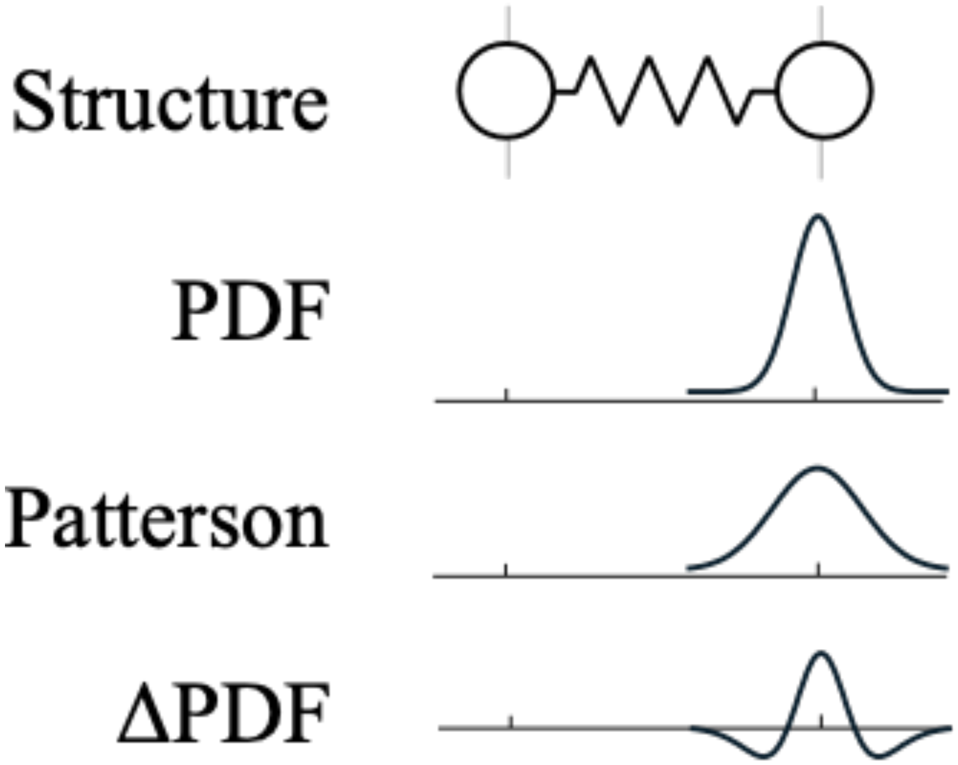
Joint ADP

$$F(\vec{h}) = \left| \sum_{uvw,p} f_p p_p \exp(2\pi i \vec{h}(\vec{r}_p + \vec{r}_{uvw})) \exp(4\pi^2 \vec{h} U_p \vec{h}) \right|^2$$

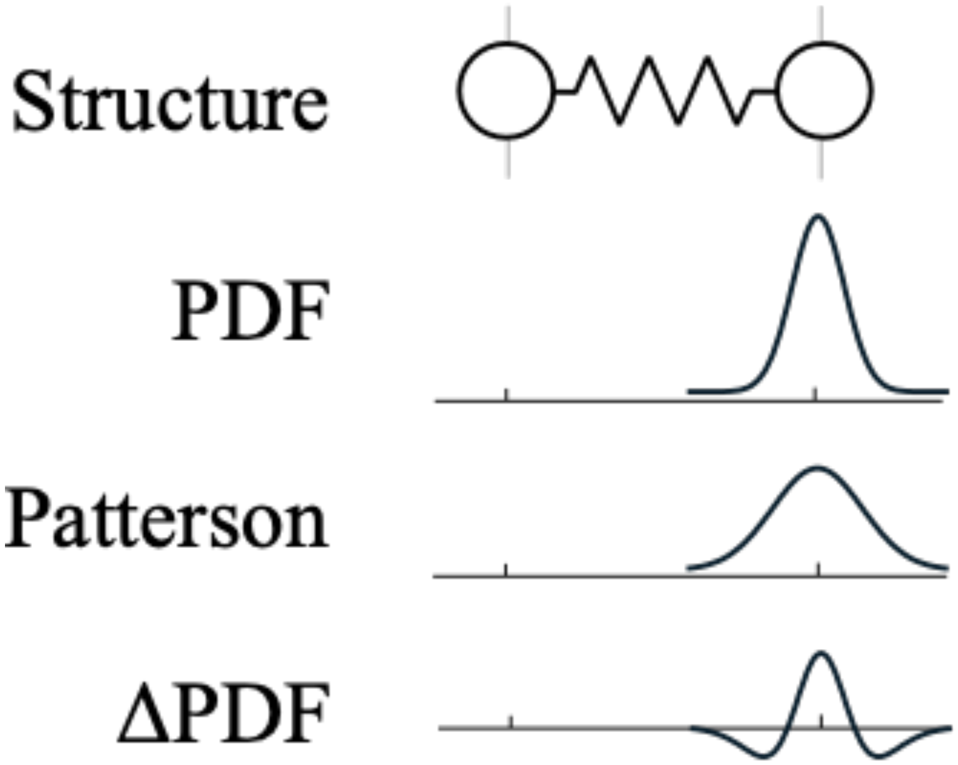
Possible correlations:

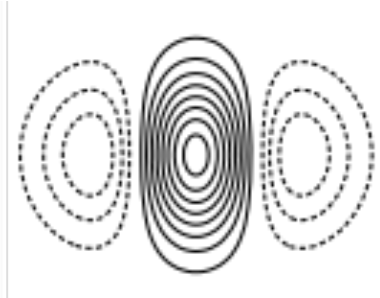
- $\Delta\, p_{ij} \neq 0$ - substitutional correlation
- $\Delta\, U_{ij} \neq 0$ - displacement correlation
- $\Delta\, \boldsymbol{r}ij \neq 0$ - size effect

Displacement correlation

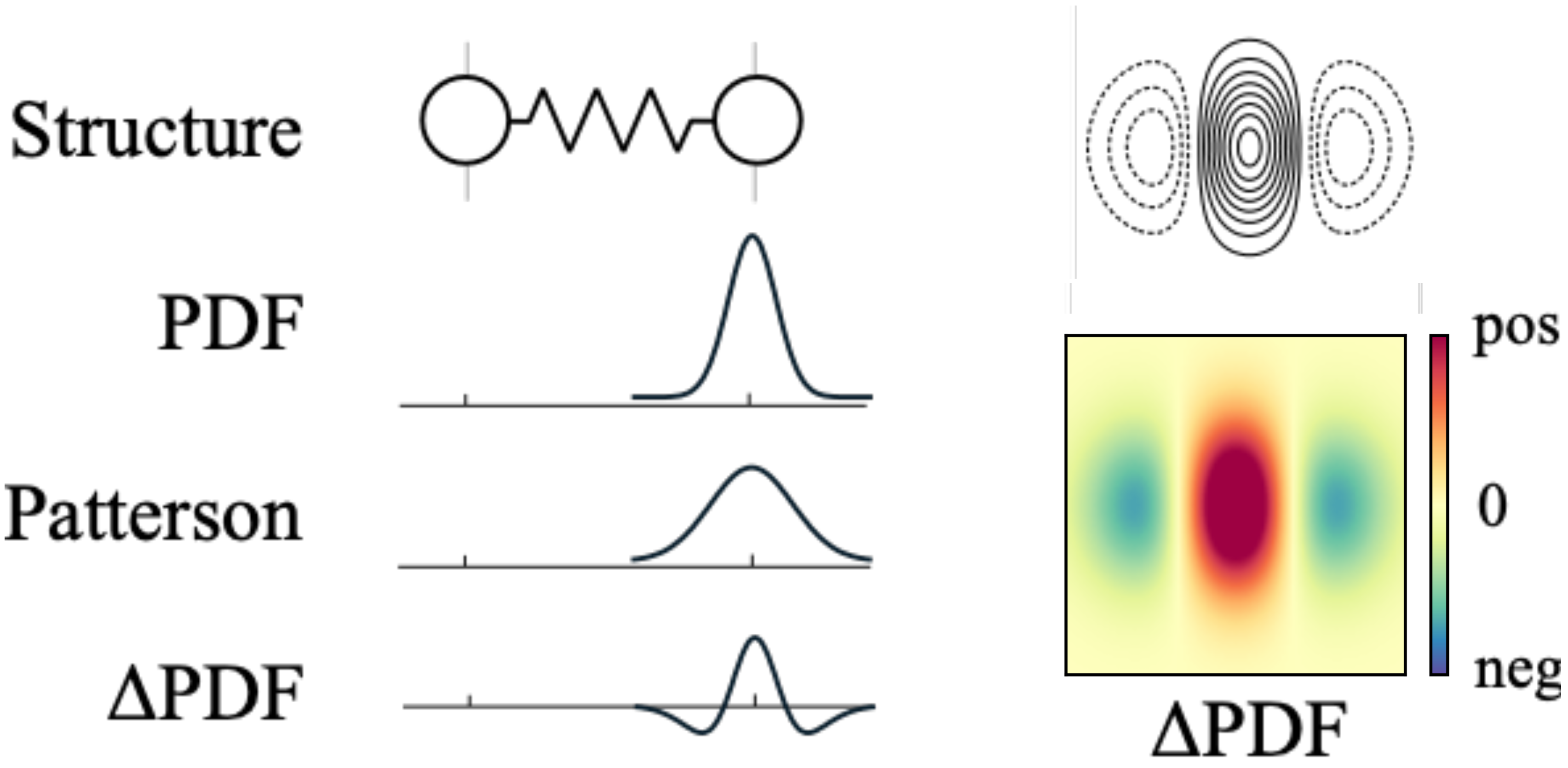


Displacement correlation

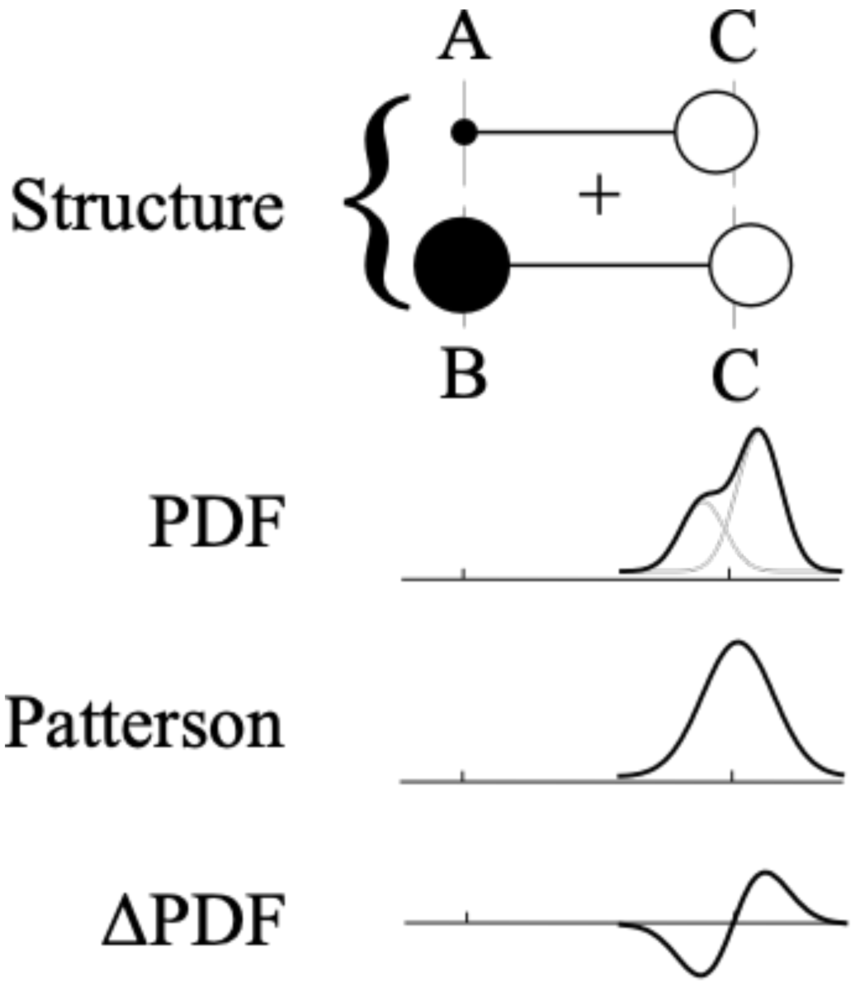




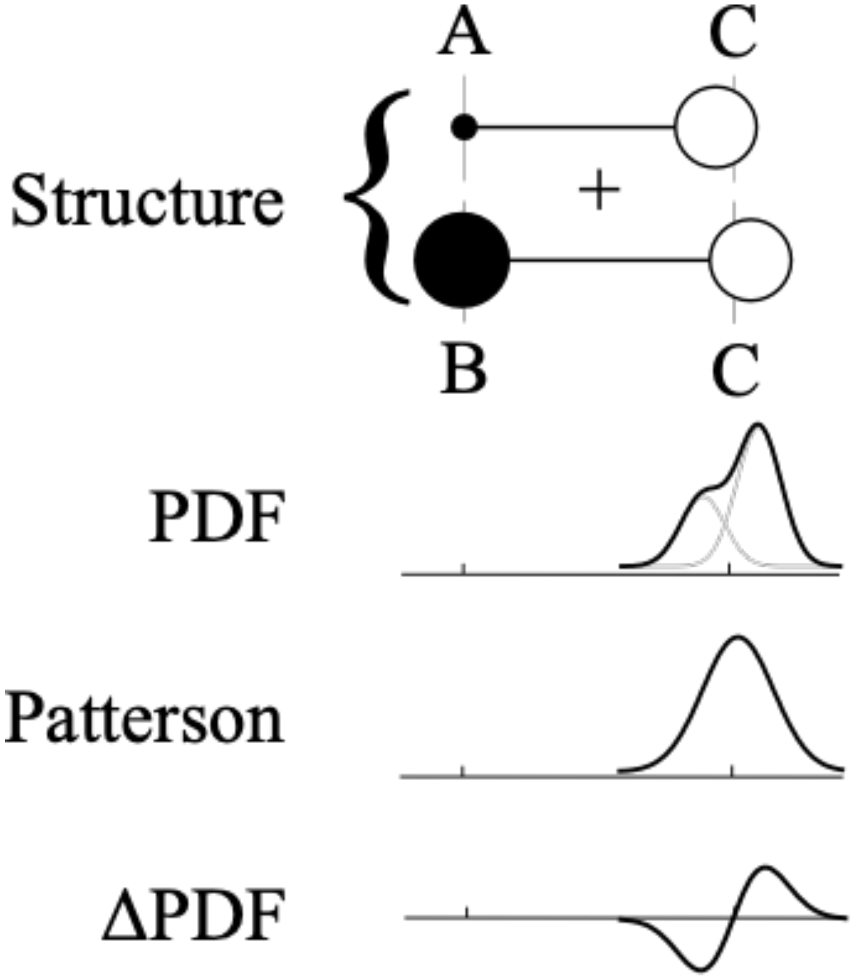
Displacement correlation

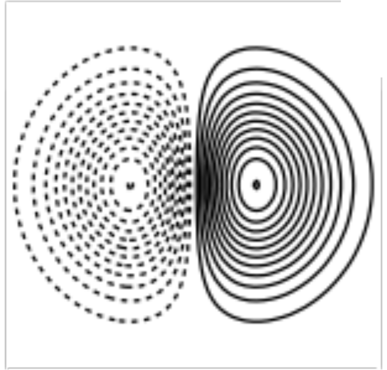


Size Effect

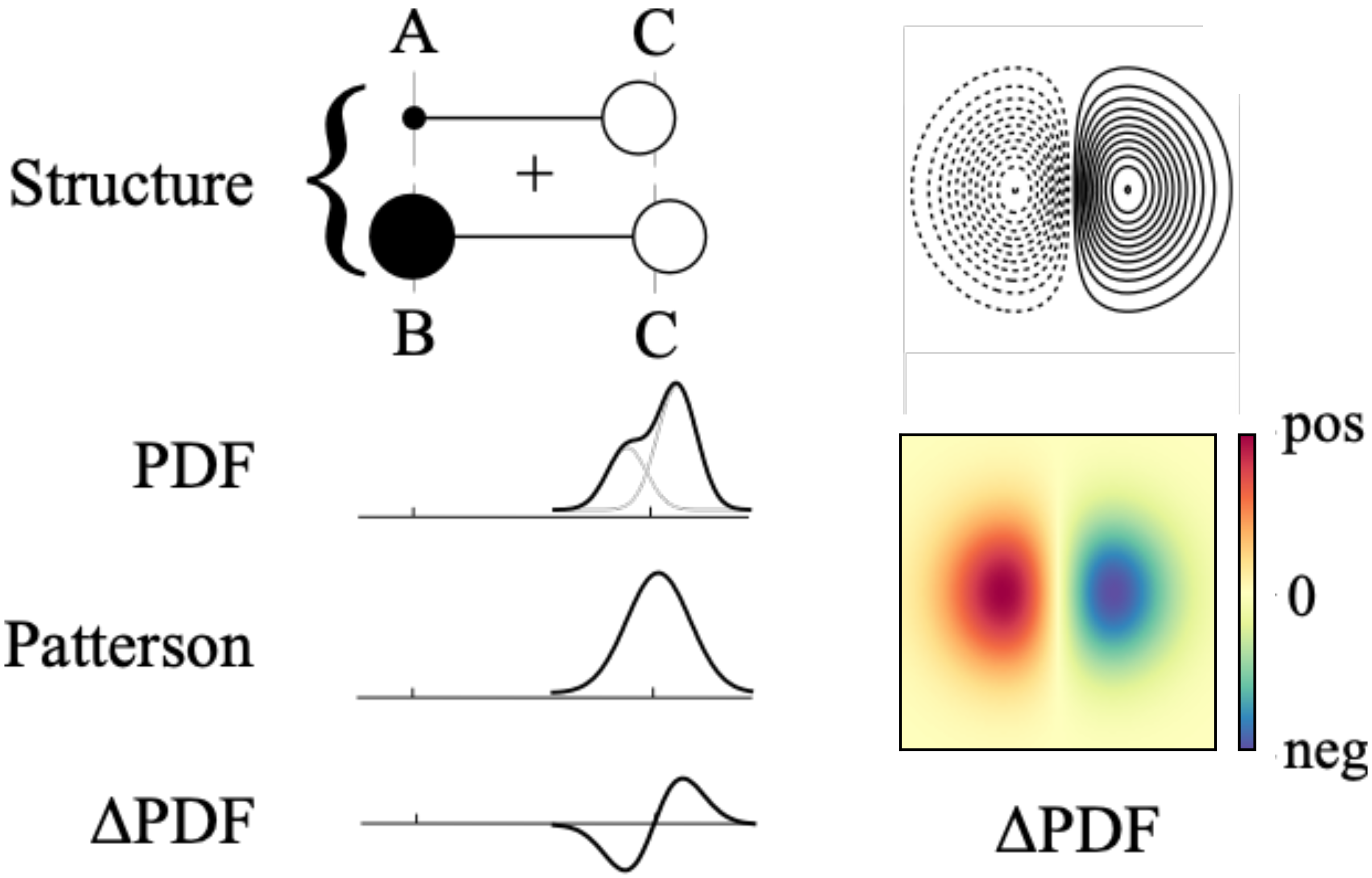


Size Effect

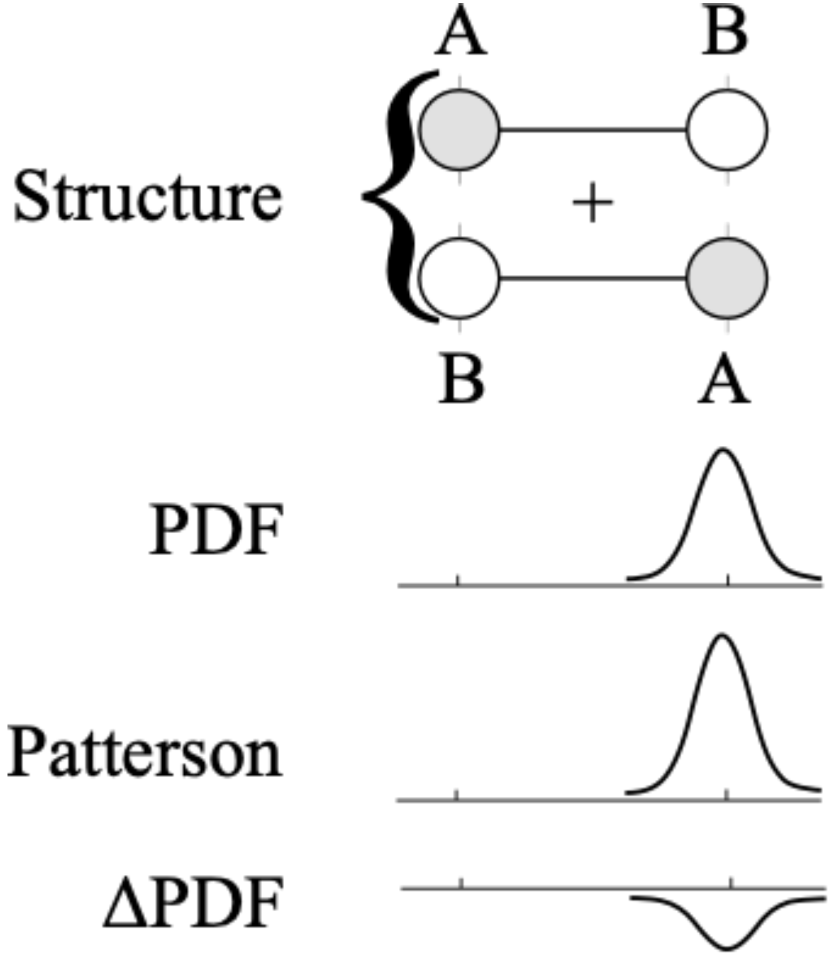




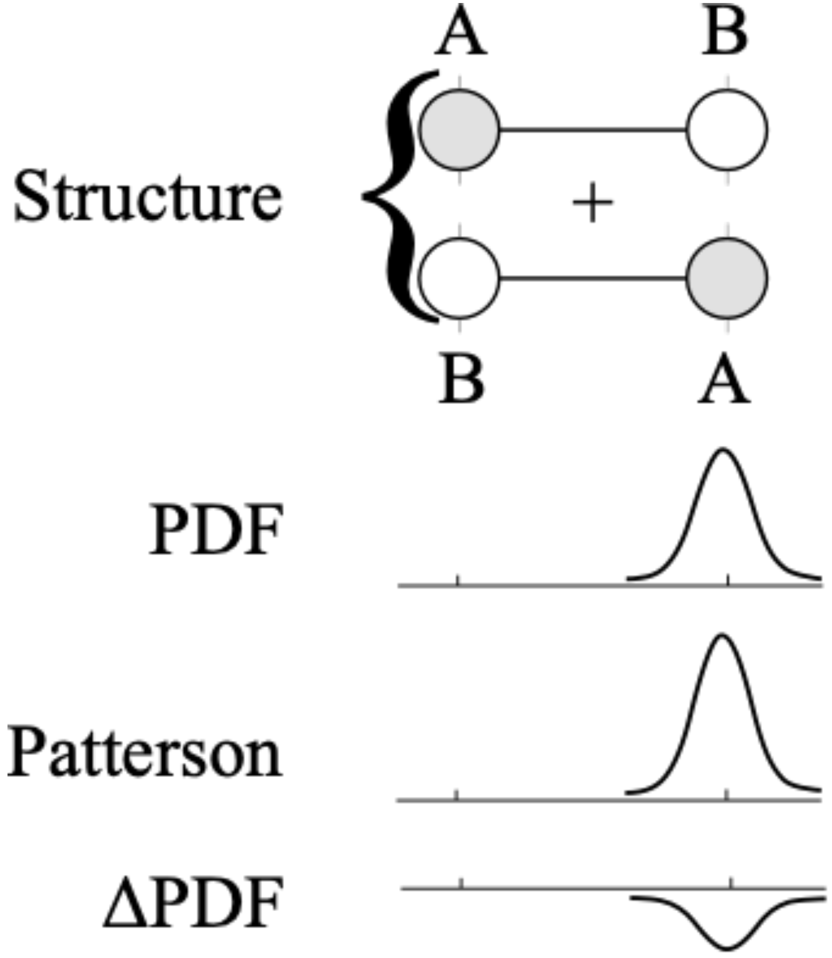
Size Effect

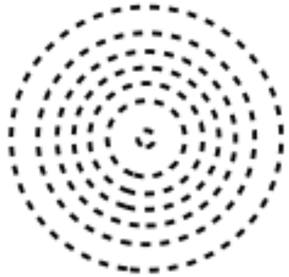


Substitutional correlation

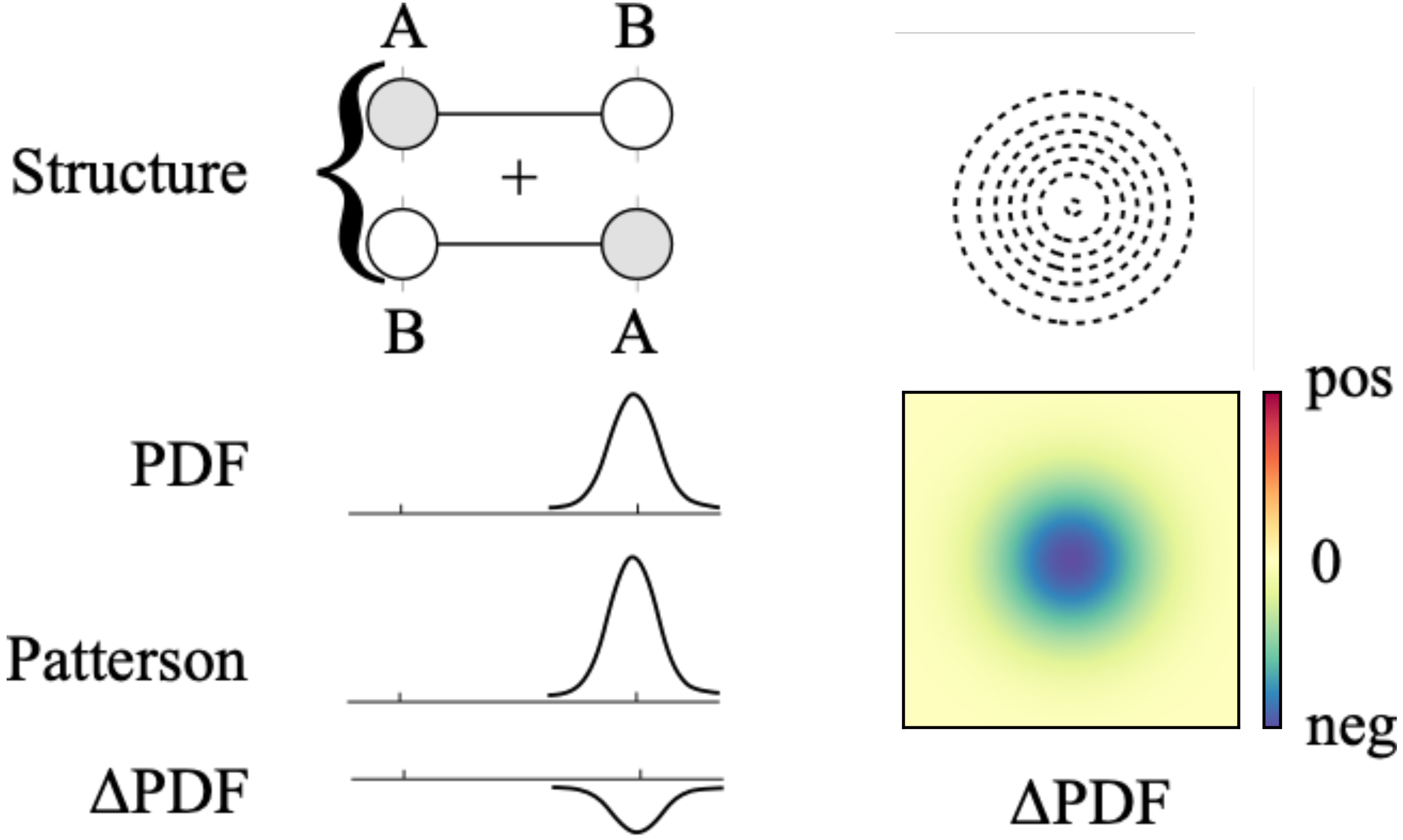


Substitutional correlation



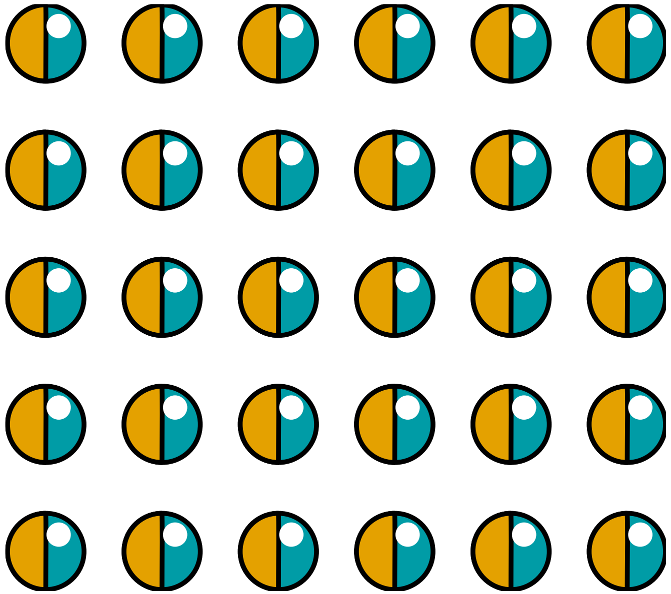


Substitutional correlation

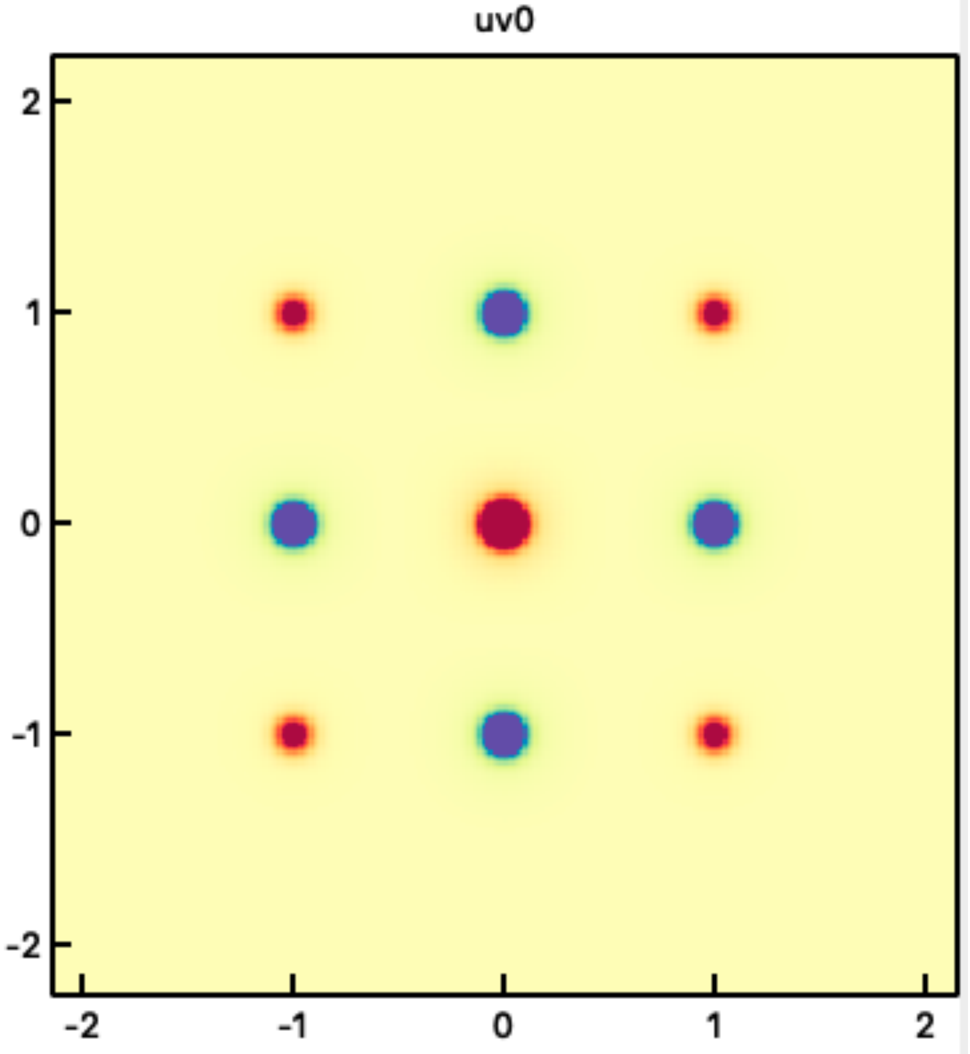


3D-ΔPDF DIDACTIC EXAMPLES

Guess disorder

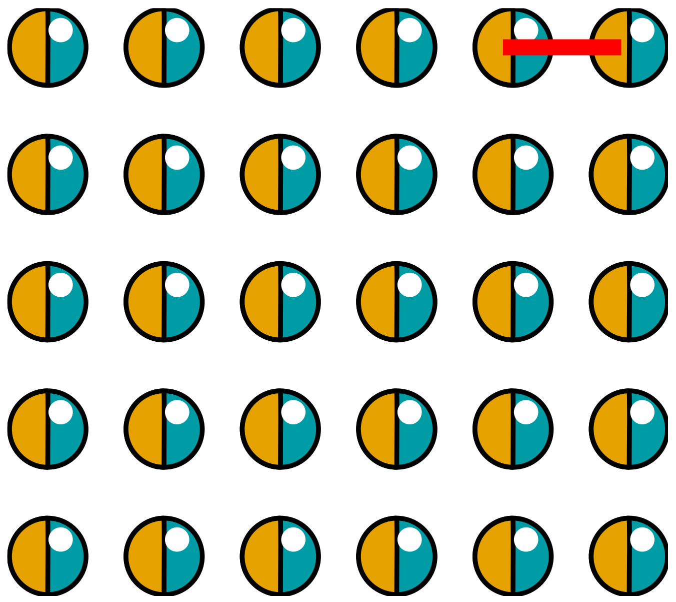


Average structure

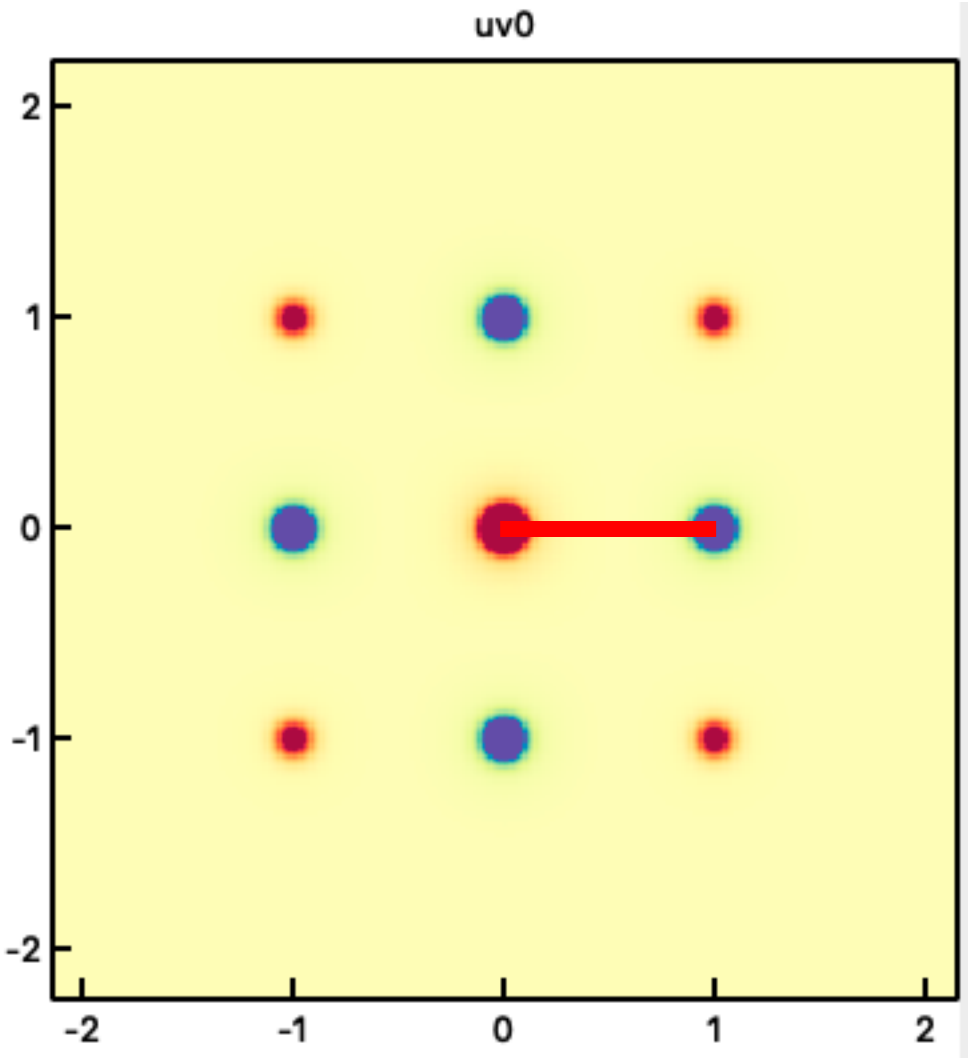


2D-ΔPDF

Guess disorder

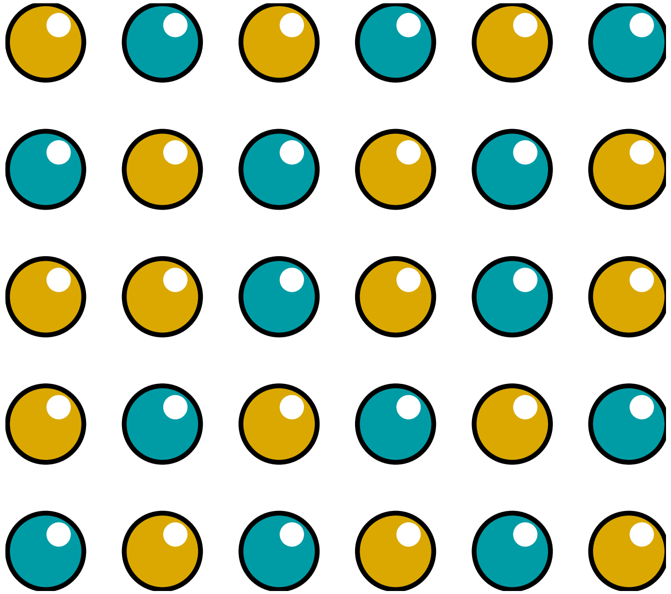


Average structure

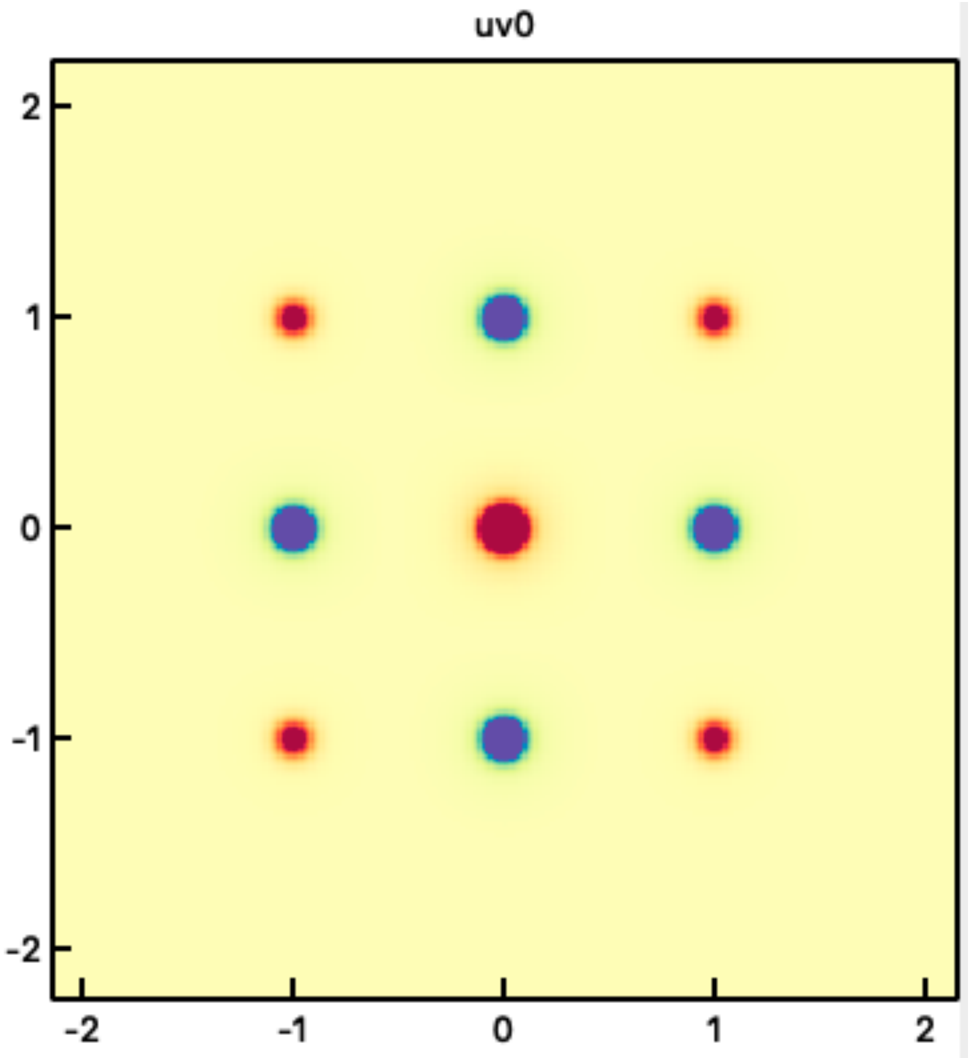


2D-ΔPDF

Guess disorder: occupancy disorder with correlations

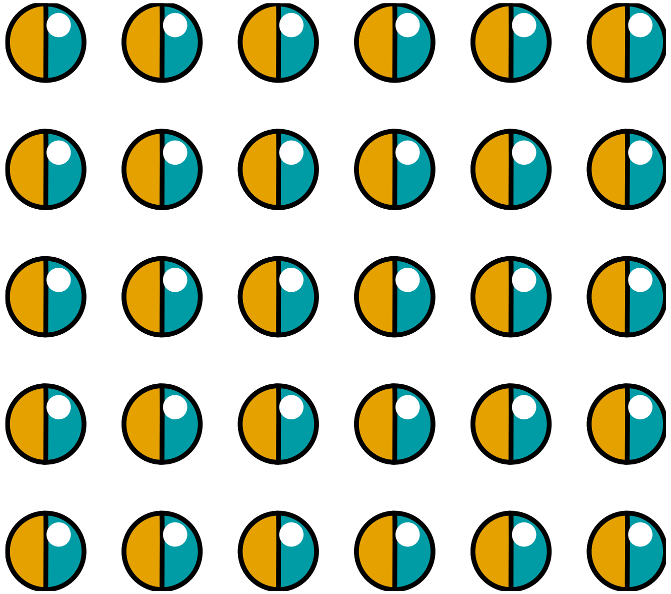


Average structure

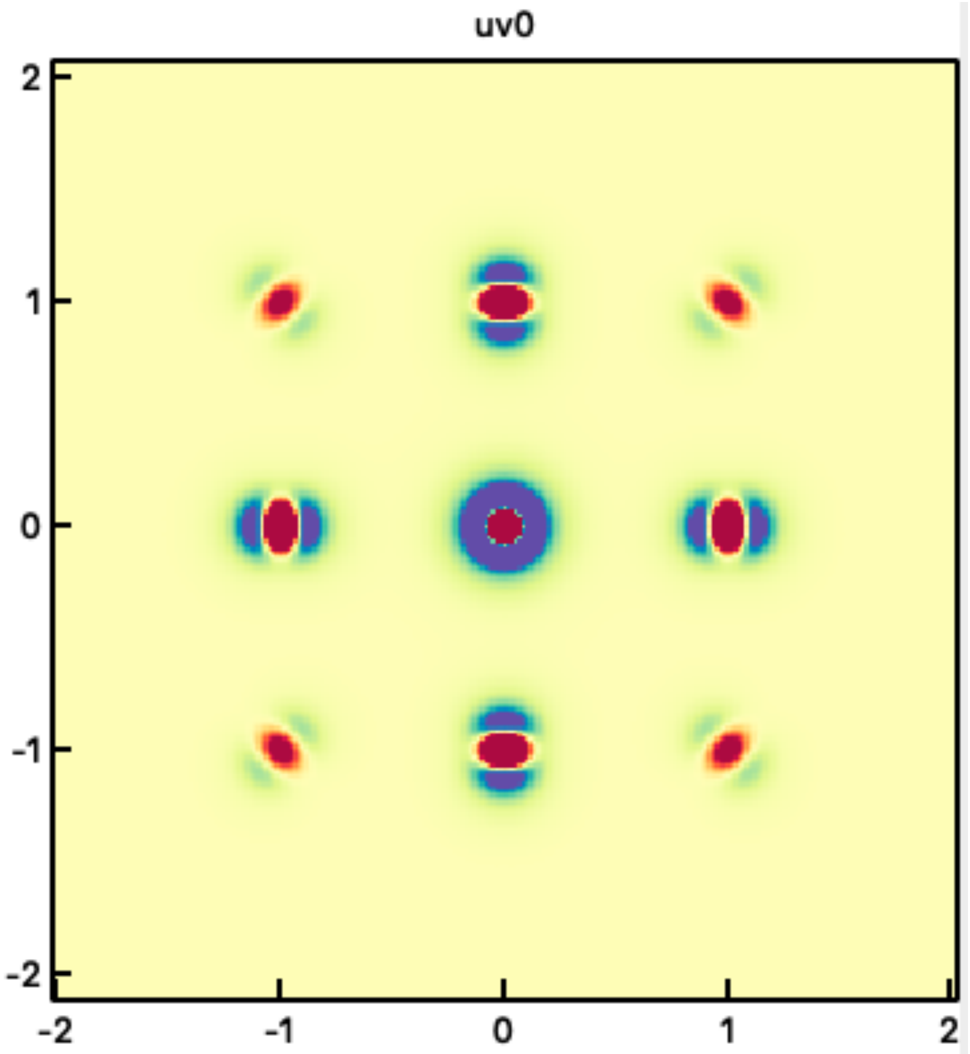


2D-ΔPDF

Guess disorder

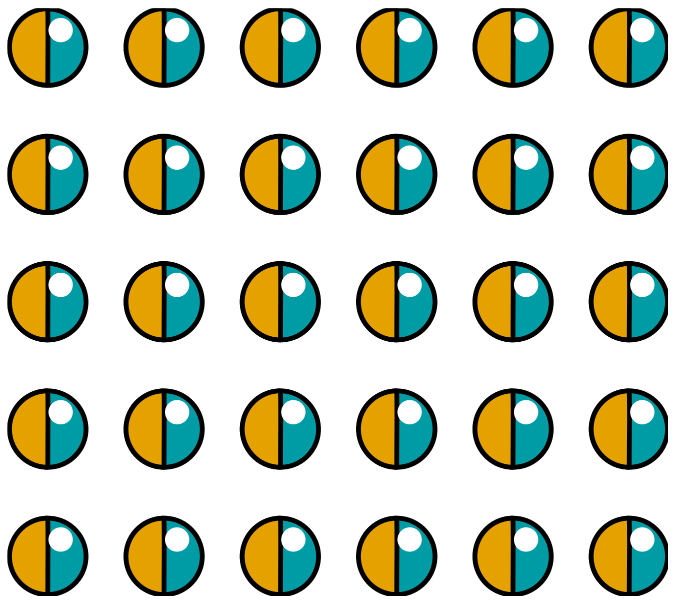


Average structure

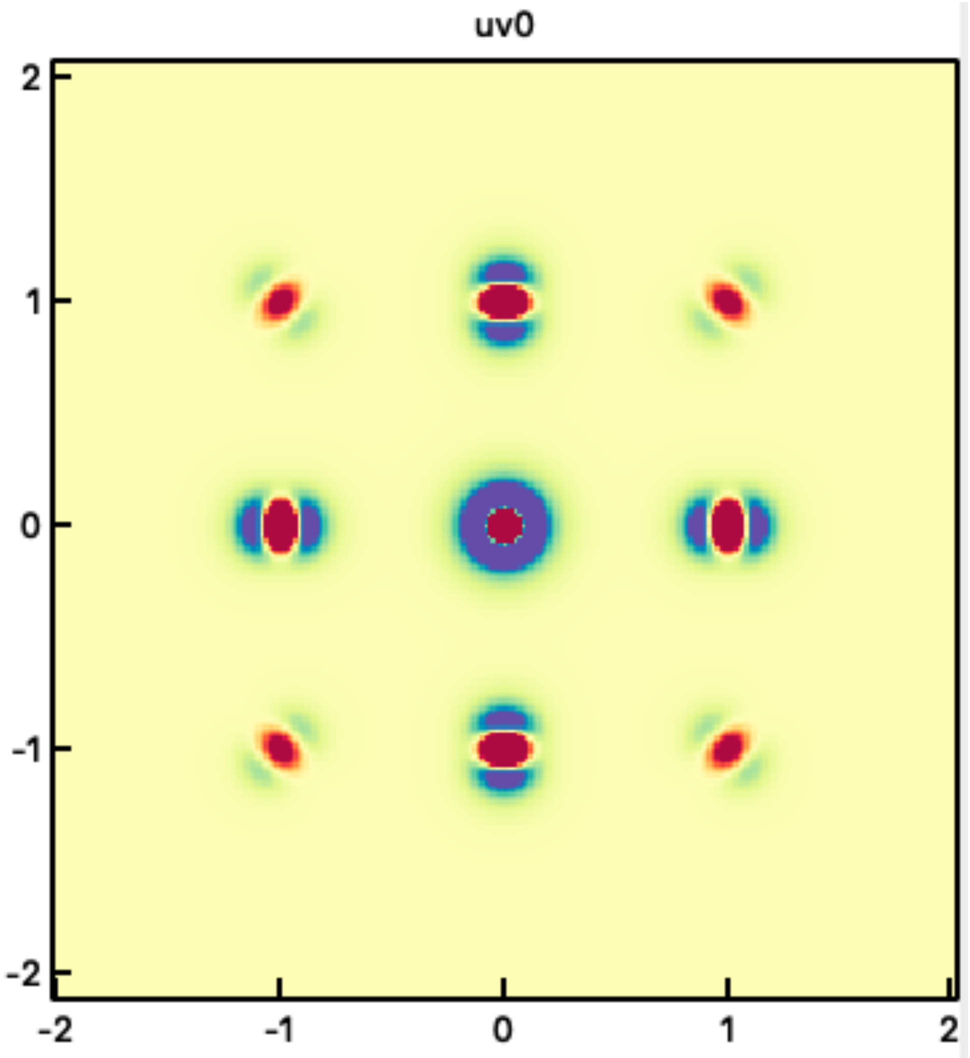


2D-ΔPDF

Guess disorder: correlated displacements



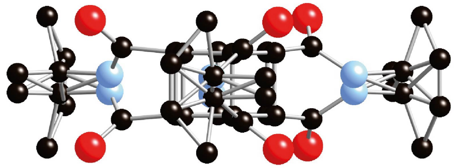
Average structure



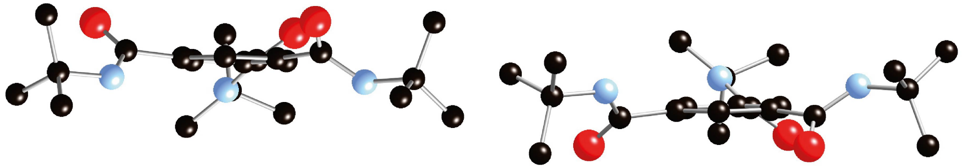
2D-ΔPDF

Real world example:
Tris-t-butyl-benzene-tricarboxamide

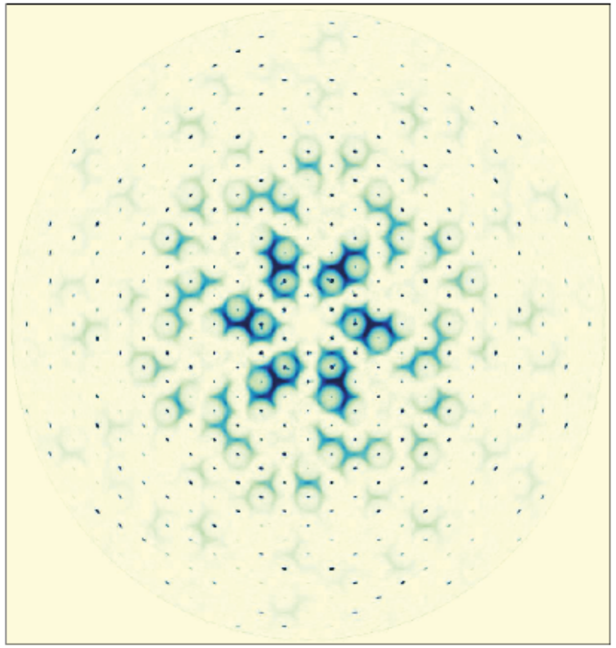
Tris-t-butyl-benzene-tricarboxamide



Average



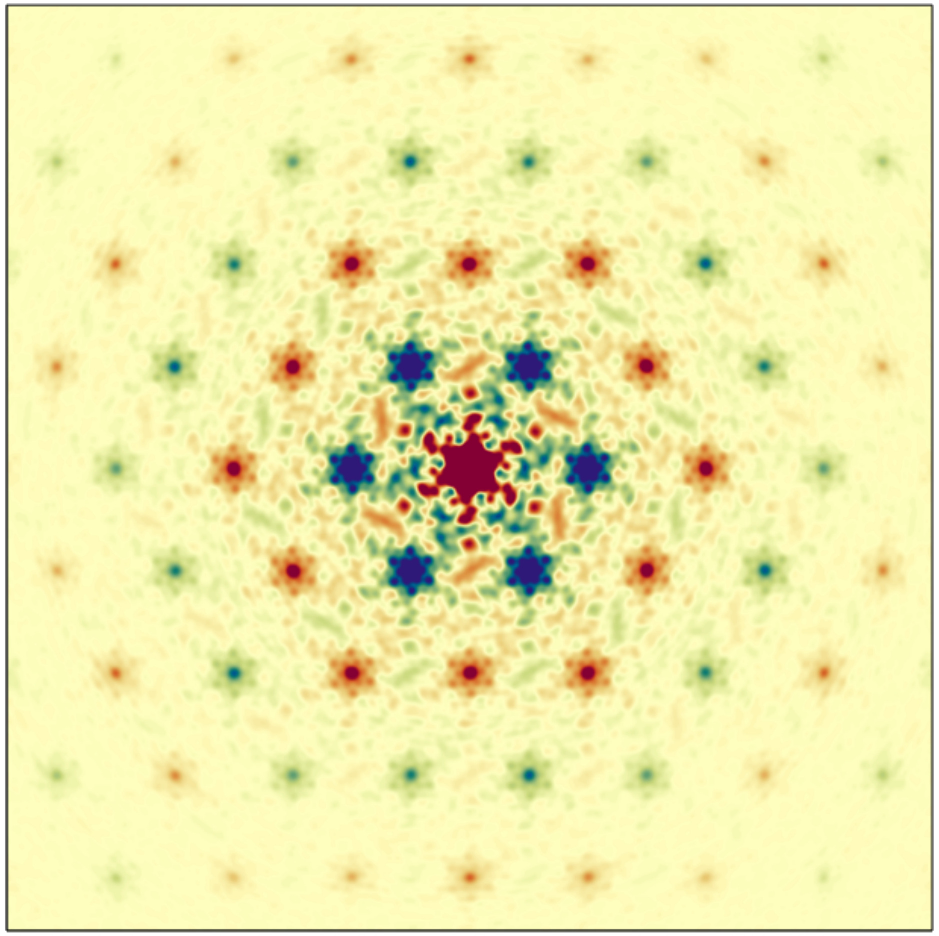
Real



X-ray scattering, hk1 layer

Simonov, A., Weber, T., & Steurer, W. (2014). J. Appl. Cryst., 47(6), 2011-2018.

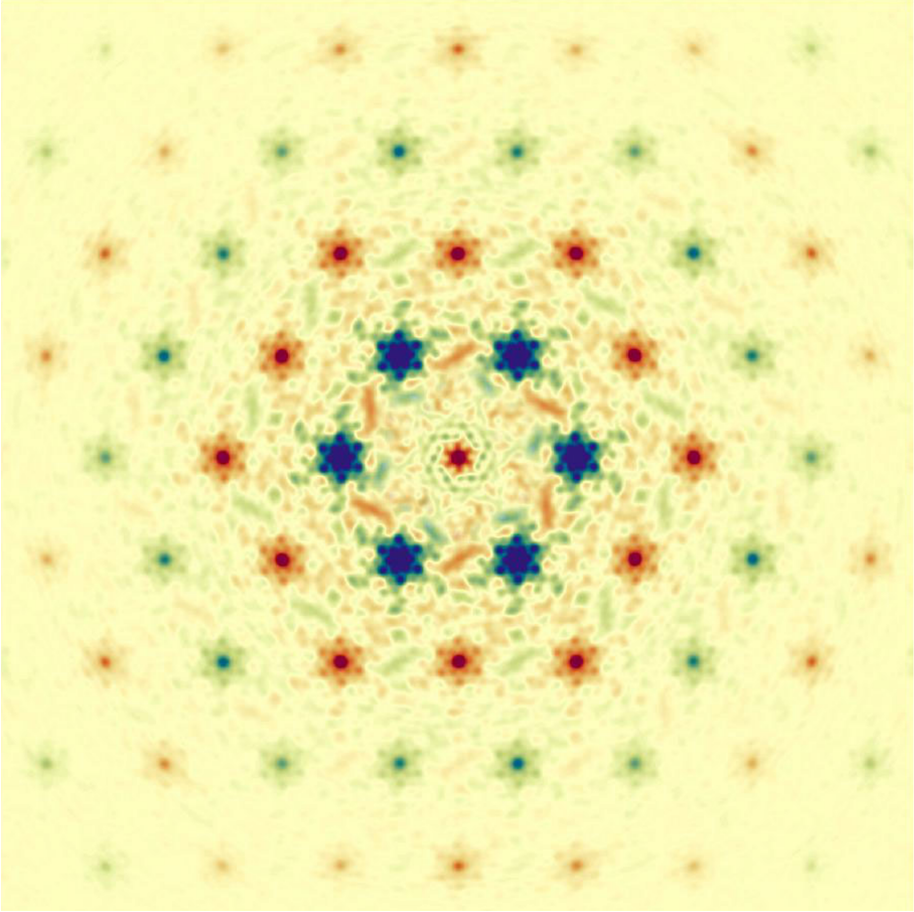
Experimental ΔPDF



ΔPDF, UV0 cut

tris-t-butyl-benzene-tricarboxamide

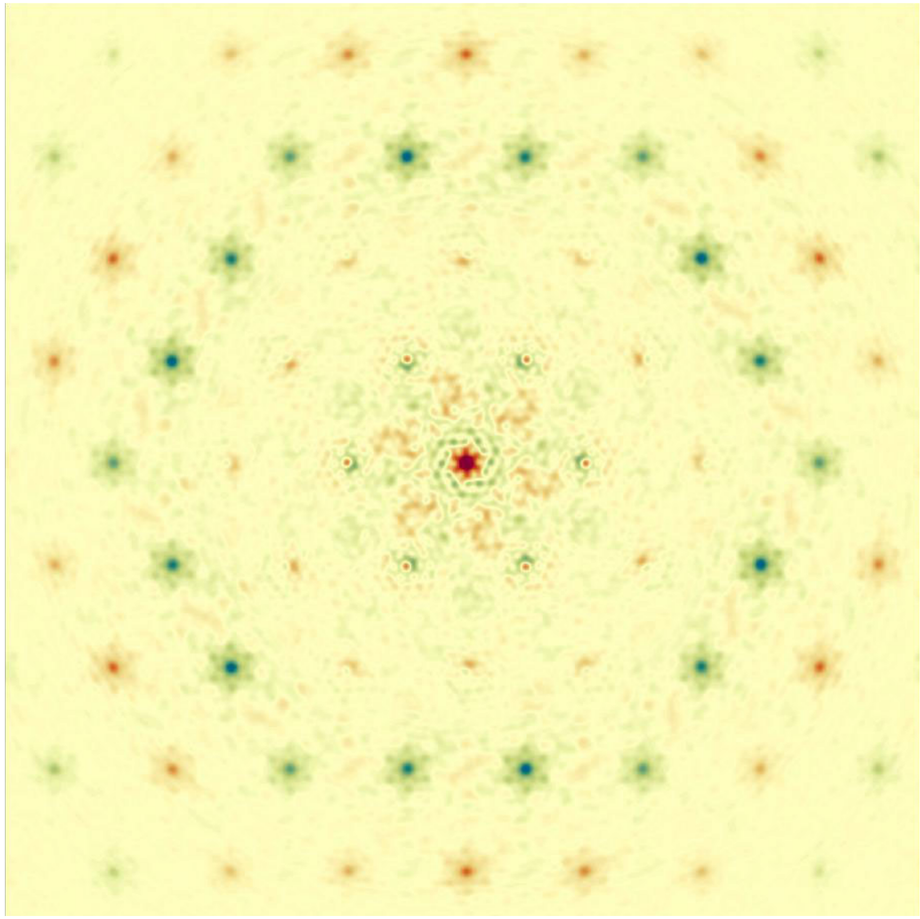
Refinement



Δ^2PDF, UV0 cut

tris-t-butyl-benzene-tricarboxamide

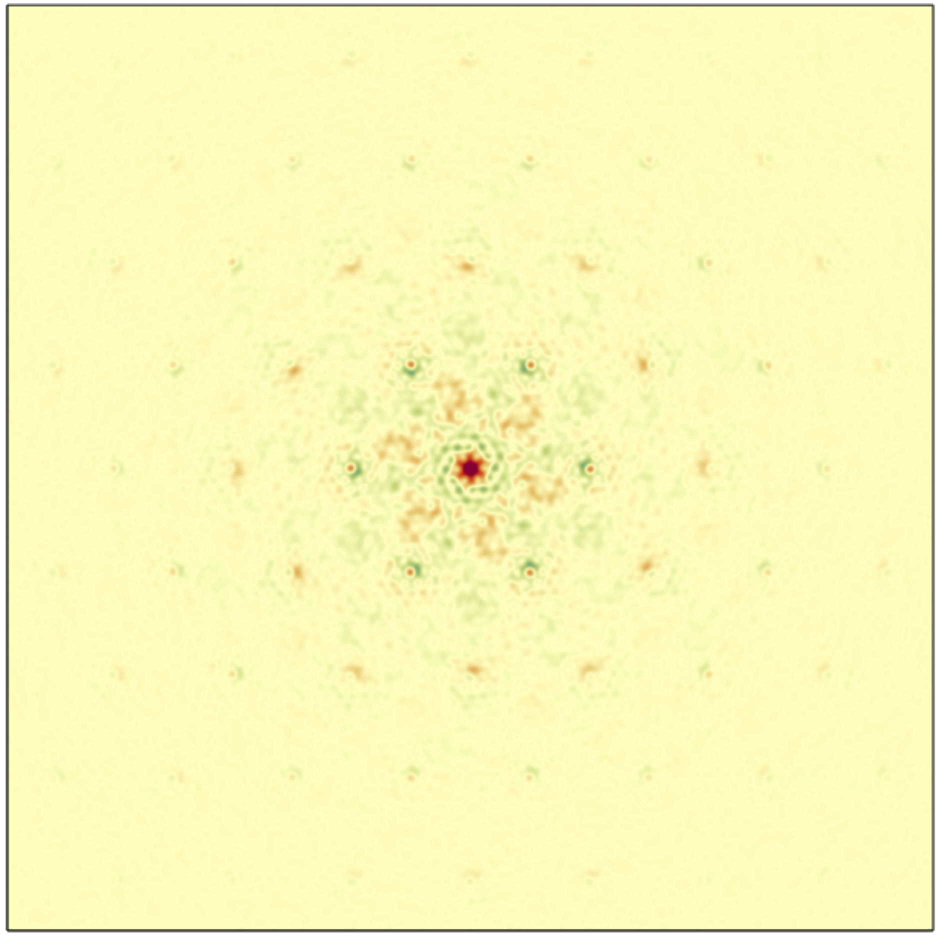
Refinement



Δ^2PDF, UV0 cut

tris-t-butyl-benzene-tricarboxamide

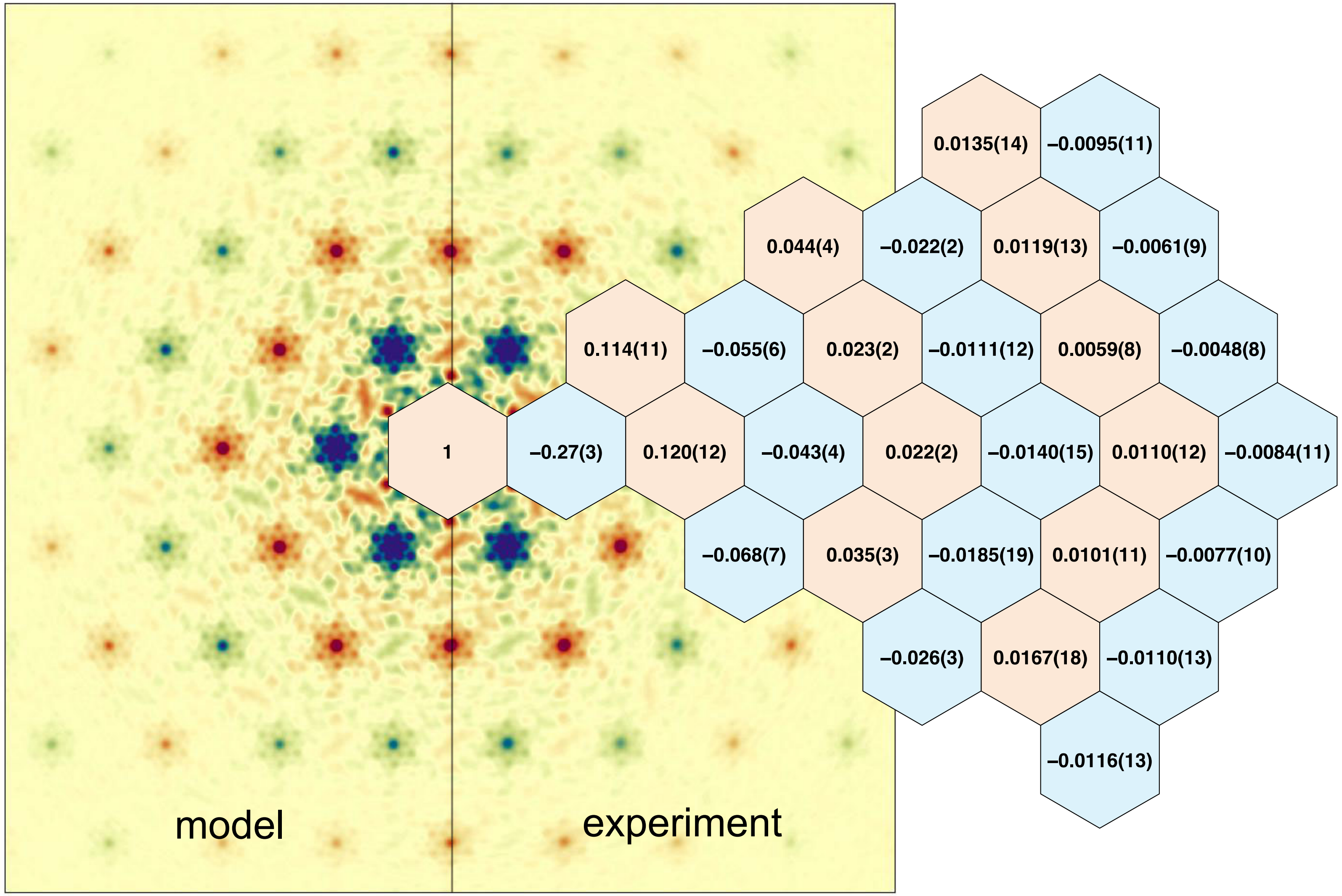
Refinement



Δ^2PDF, UV0 cut

tris-t-butyl-benzene-tricarboxamide

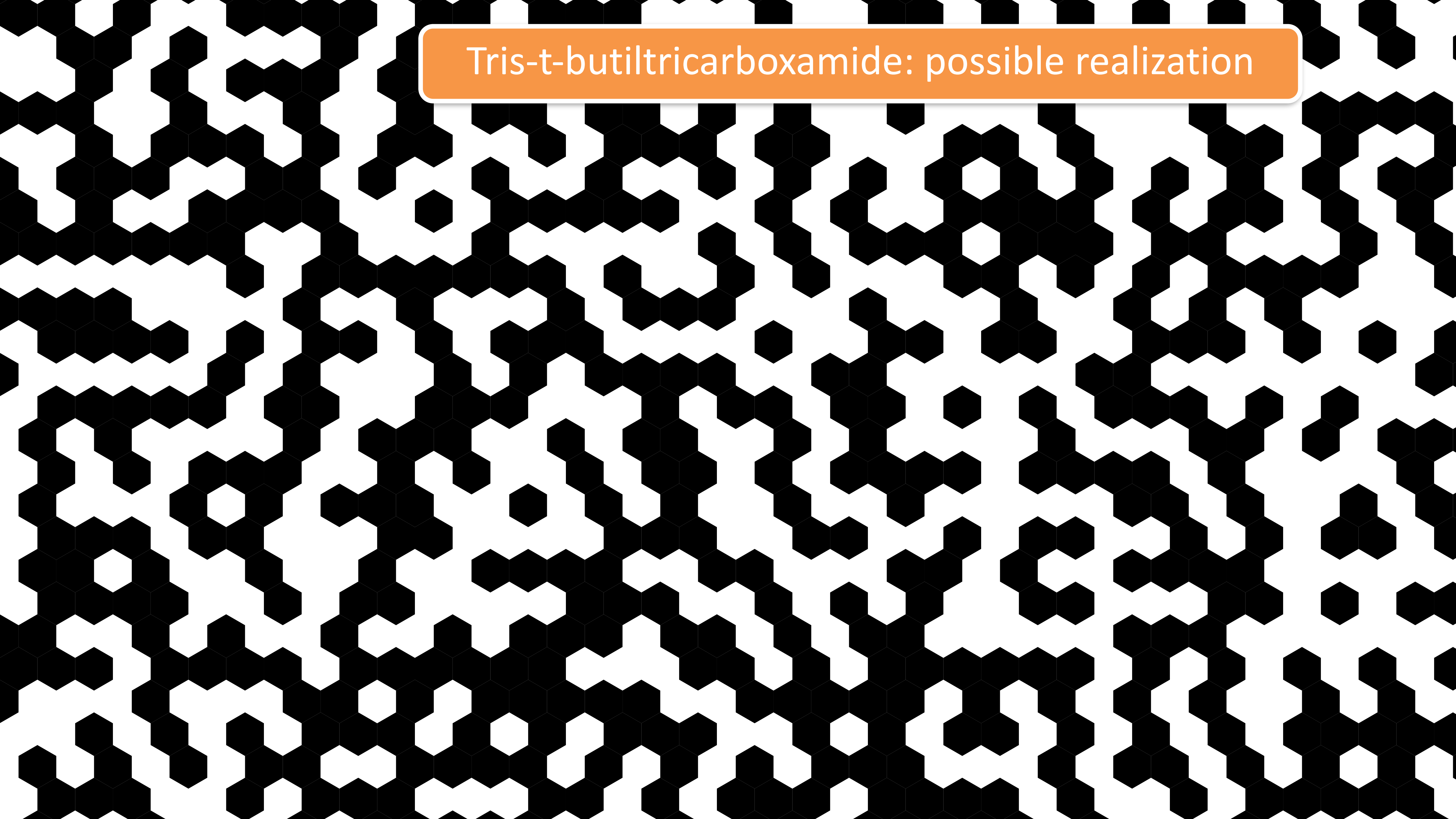
Results



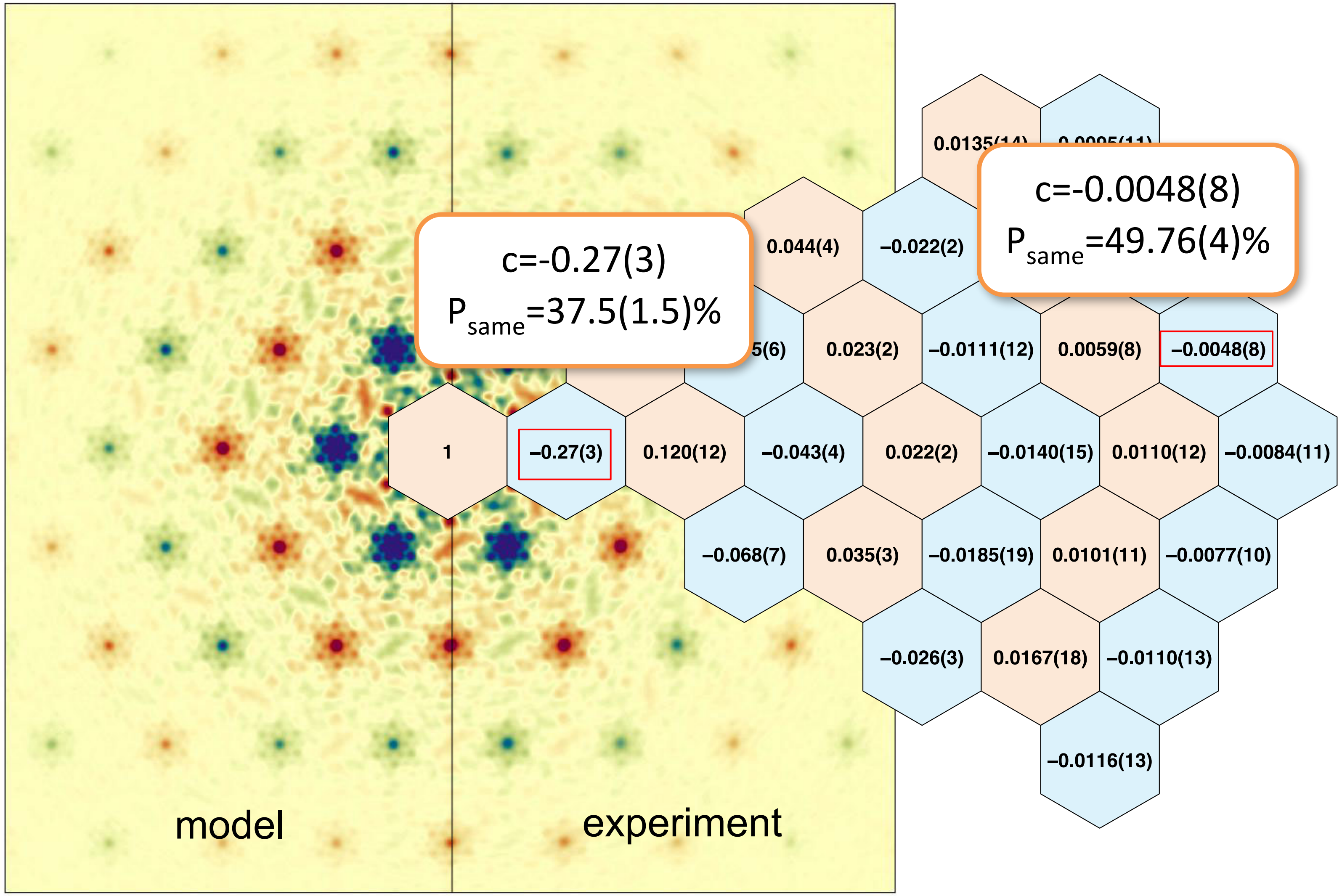
Refined correlation coefficients

Simonov, A., Weber, T., & Steurer, W. (2014).
J. Appl. Cryst., 47(6), 2011-2018.

Tris-t-butiltricarboxamide: possible realization



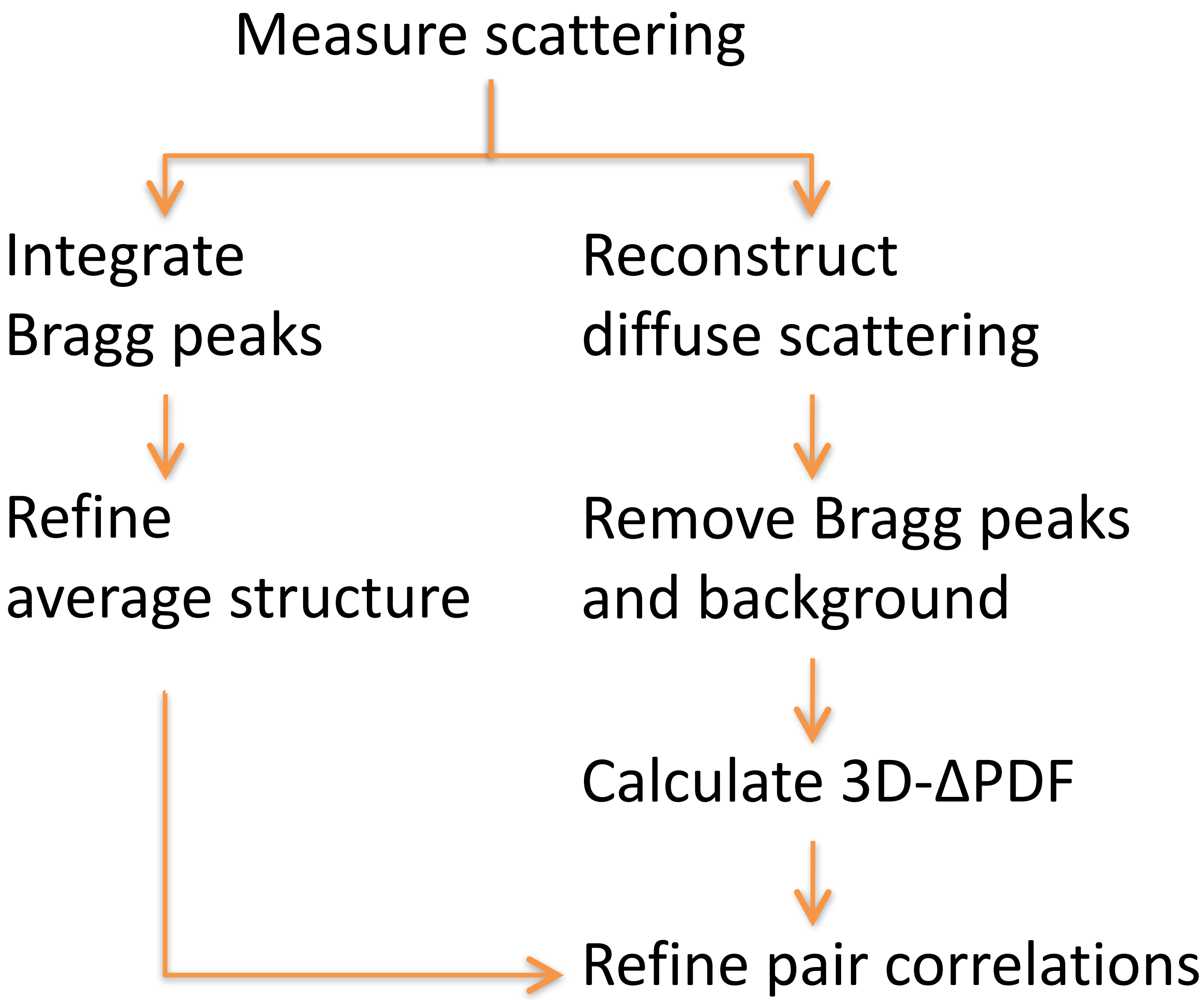
Results

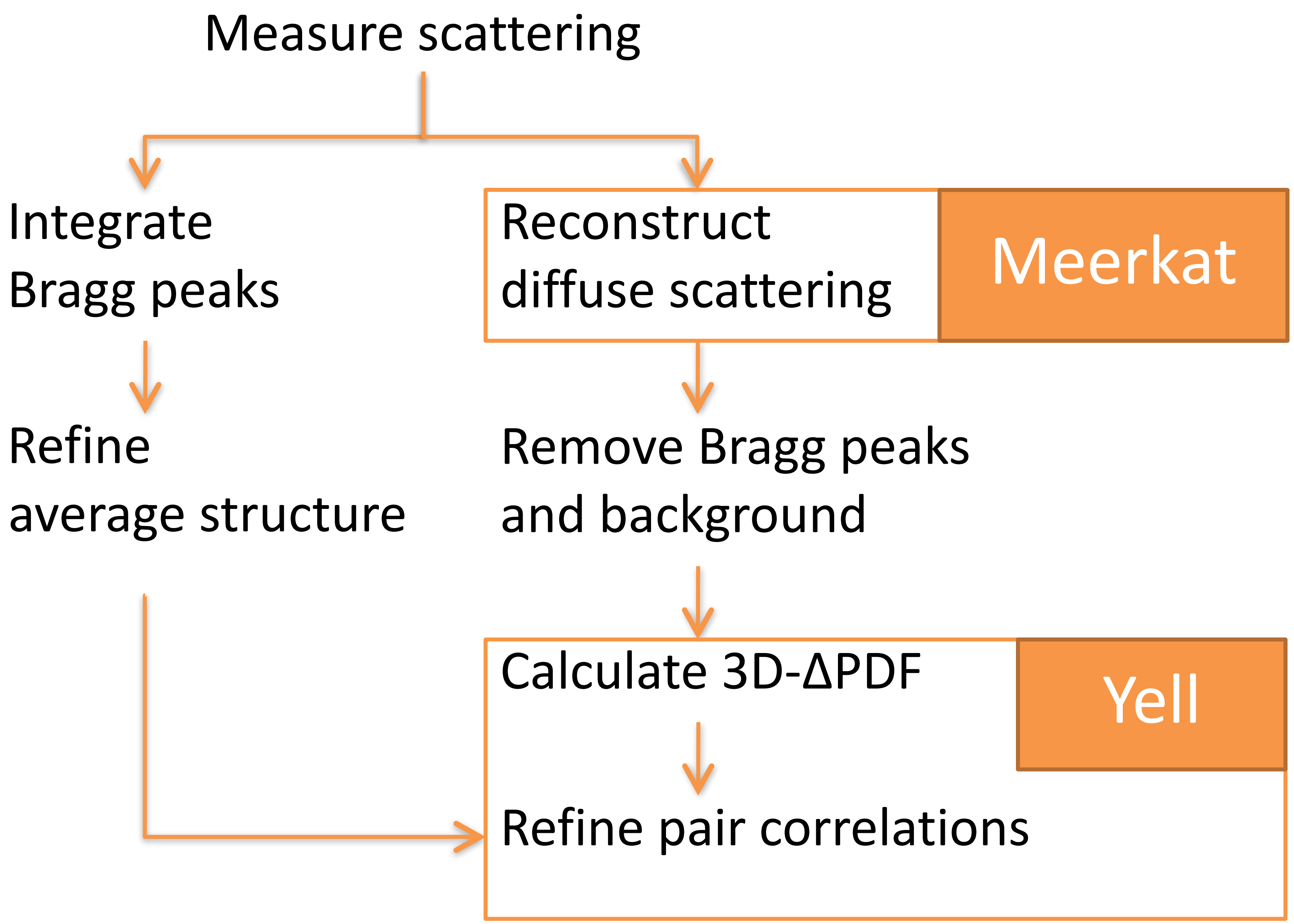


Refined correlation coefficients

Simonov, A., Weber, T., & Steurer, W. (2014).
J. Appl. Cryst., 47(6), 2011-2018.

SOFTWARE AND PROCEDURE

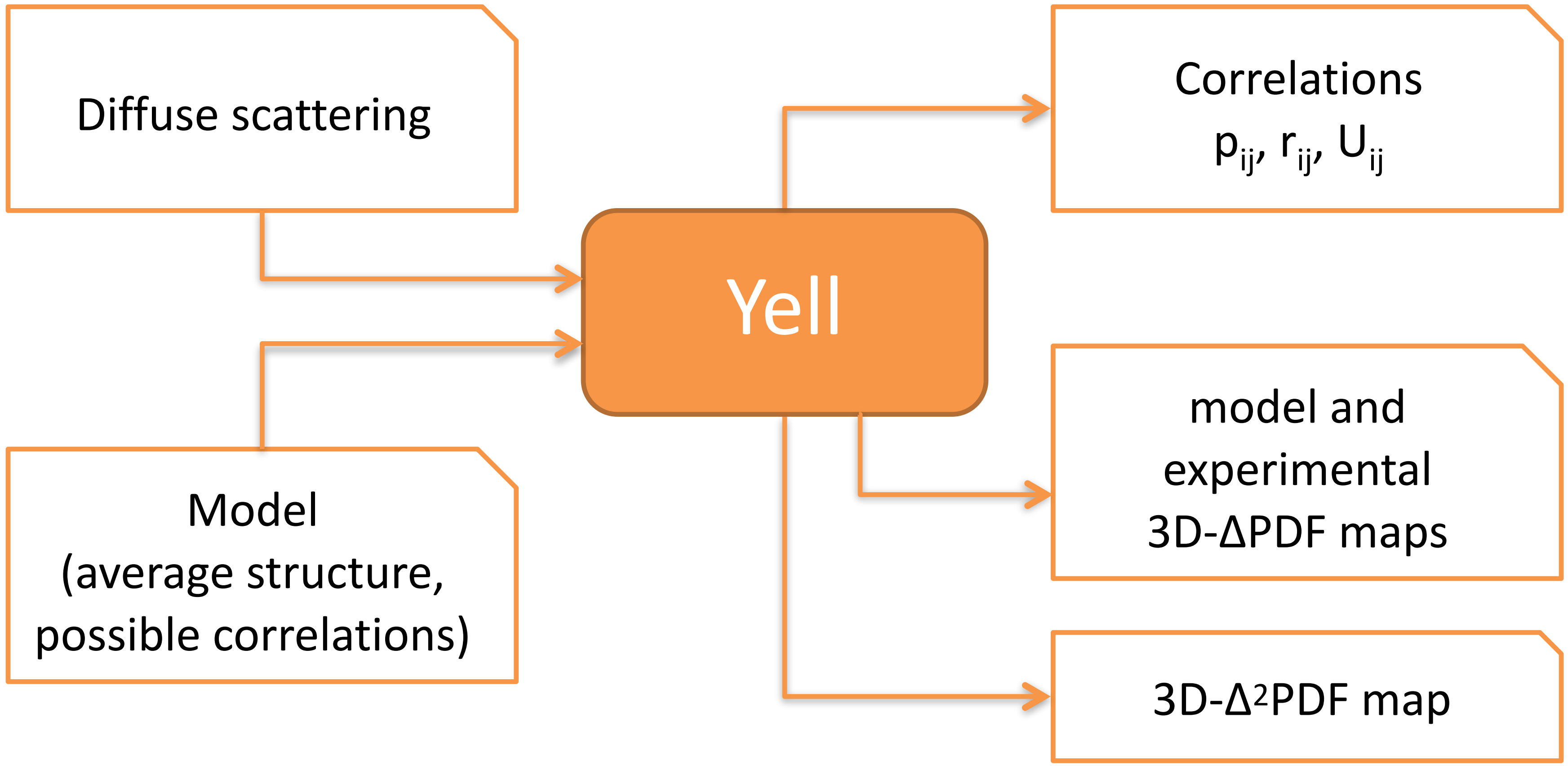

Measure scattering
Integrate
Bragg peaks
Reconstruct
diffuse scattering
Refine
average structure
Remove Bragg peaks
and background
Calculate 3D-ΔPDF
Refine pair correlations


Measure scattering
Integrate
Bragg peaks
Reconstruct
diffuse scattering
Meerkat
Refine
average structure
Remove Bragg peaks
and background
Calculate 3D-ΔPDF
Yell
Refine pair correlations

Meerkat

- reconstructs 3D space
- works in crystallographic coordinates
- hard-drive backed if needed
- polarization, solid angle corrections

written in python,
uses fabio and hdf5 libraries


Diffuse scattering
Model
(average structure,
possible correlations)
Yell
Correlations
p_{ij}, r_{ij}, U_{ij}
model and
experimental
3D-ΔPDF maps
3D-Δ^2PDF map

Yell

- Yell finds short range order correlations which are not captured by the average structure
- Contains fast FFT-based calculation algorithm
- Works on Windows, Mac and Linux
- No installation required

https://github.com/YellProgram/Yell

Yell input: program settings

```
Cell 5 5 5 90 90 90
LaueSymmetry 2/m
DiffuseScatteringGrid -10 -10 0 1/10 1/10 1 200 200 1

CalculationMethod exact
Refine true #If you chose false, Yell will calculate diffuse scattering
```

Yell input: refineable parameters

```
RefinableVariables
[
adp=0.003;
...
]
```

Yell input: average structure

```
UnitCell
[
  V = Variant[
    (p=0.5)
    Au = Au 1  0 0 0  adp

    (p=0.5)
    Cu = Cu 1 0 0 0  adp
  ]
]
```

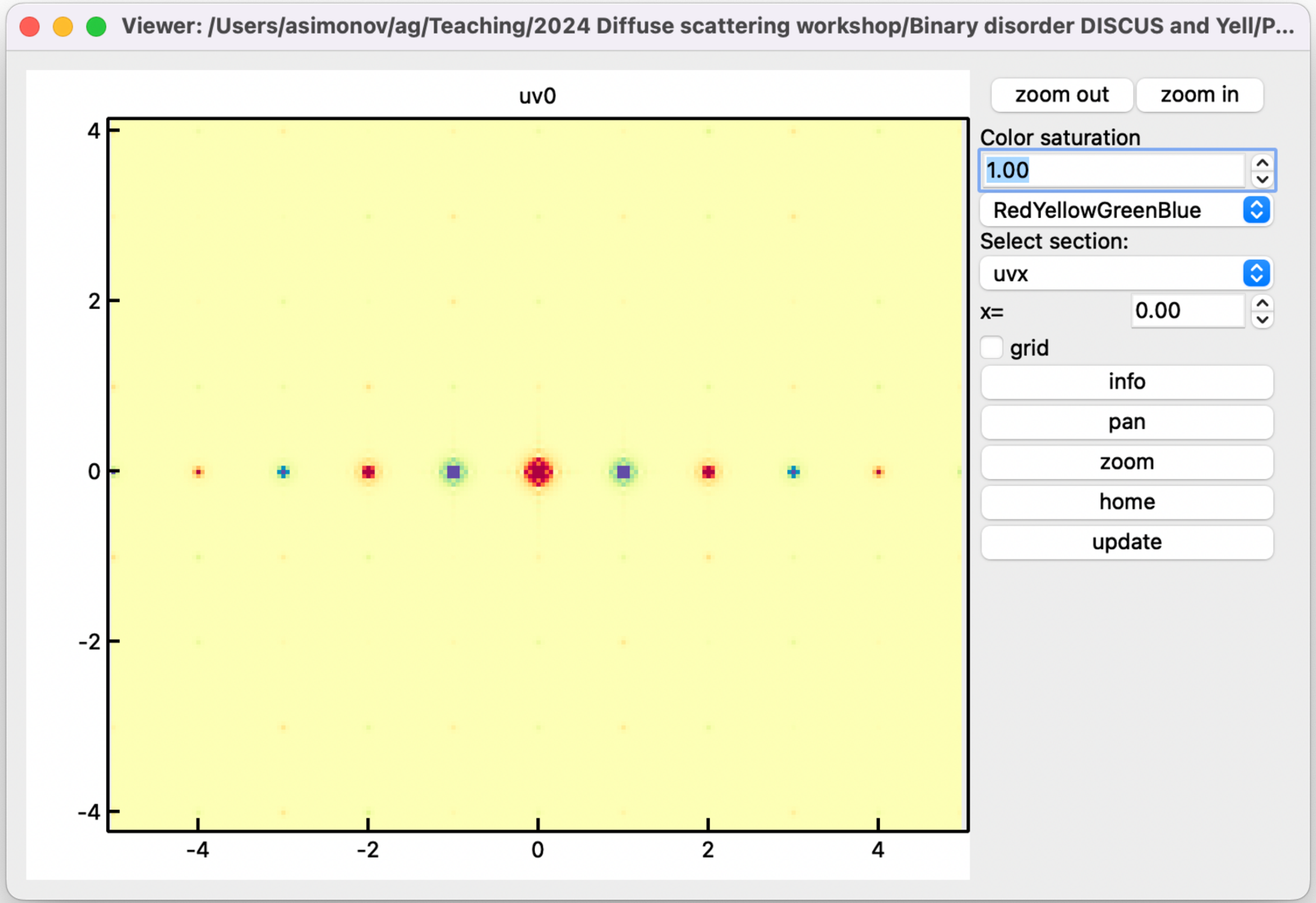
Modes of displacement

```
Modes[
    Au_x = TranslationalMode(Au, x)
    Au_y = TranslationalMode(Au, y)
    Cu_x = TranslationalMode(Cu, x)
    Cu_y = TranslationalMode(Cu, y)
]
```

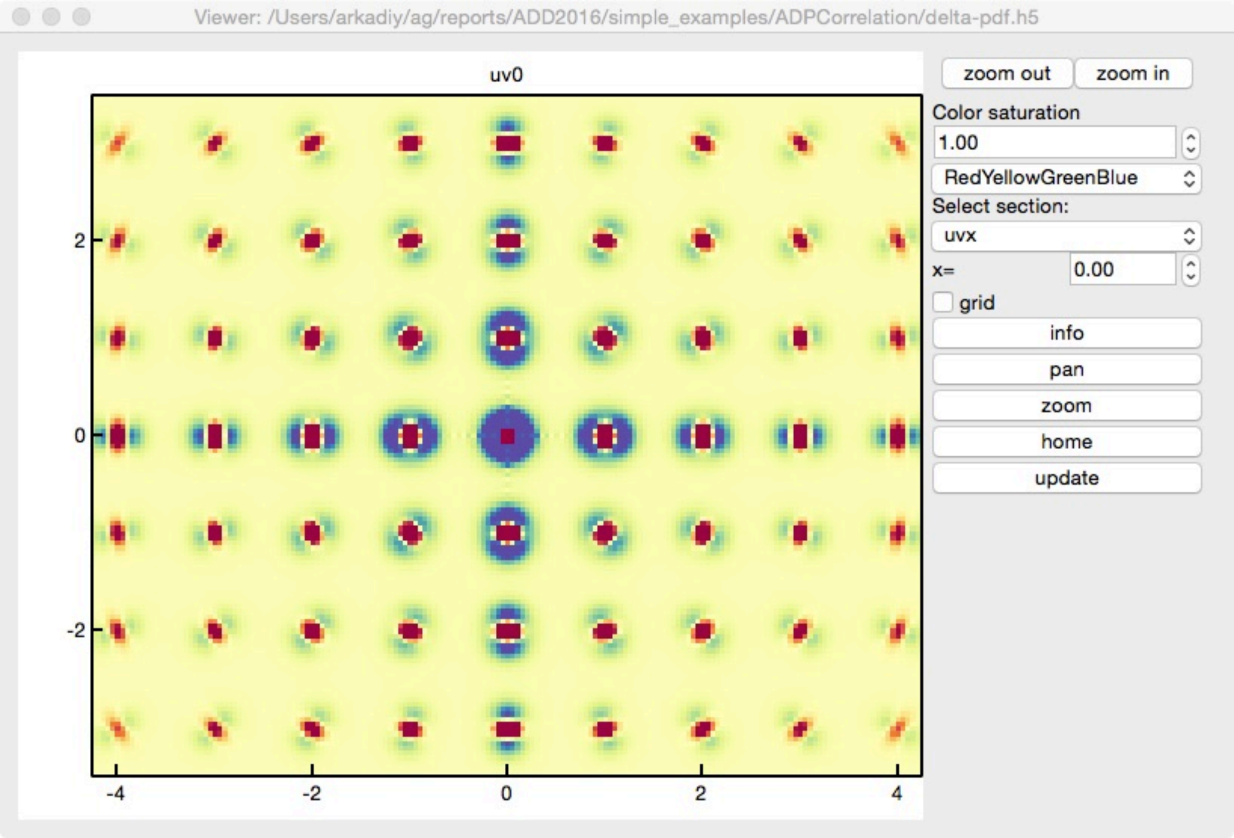
Correlations

```
[(1,0,0)
  Multiplicity 4
  SubstitutionalCorrelation(Var, Var, P_au_au_100)
  SizeEffect(Au, Au_x,  dx1)
  SizeEffect(Cu, Cu_x, -dx1)
  ADPCorrelation(Au_x, Au_x, dadp1_xx)
  ADPCorrelation(Au_y, Au_y, dadp1_yy)
  ...
  #ADP correlations for Cu-Cu Au-Cu and Cu-Au pairs
 ]
```

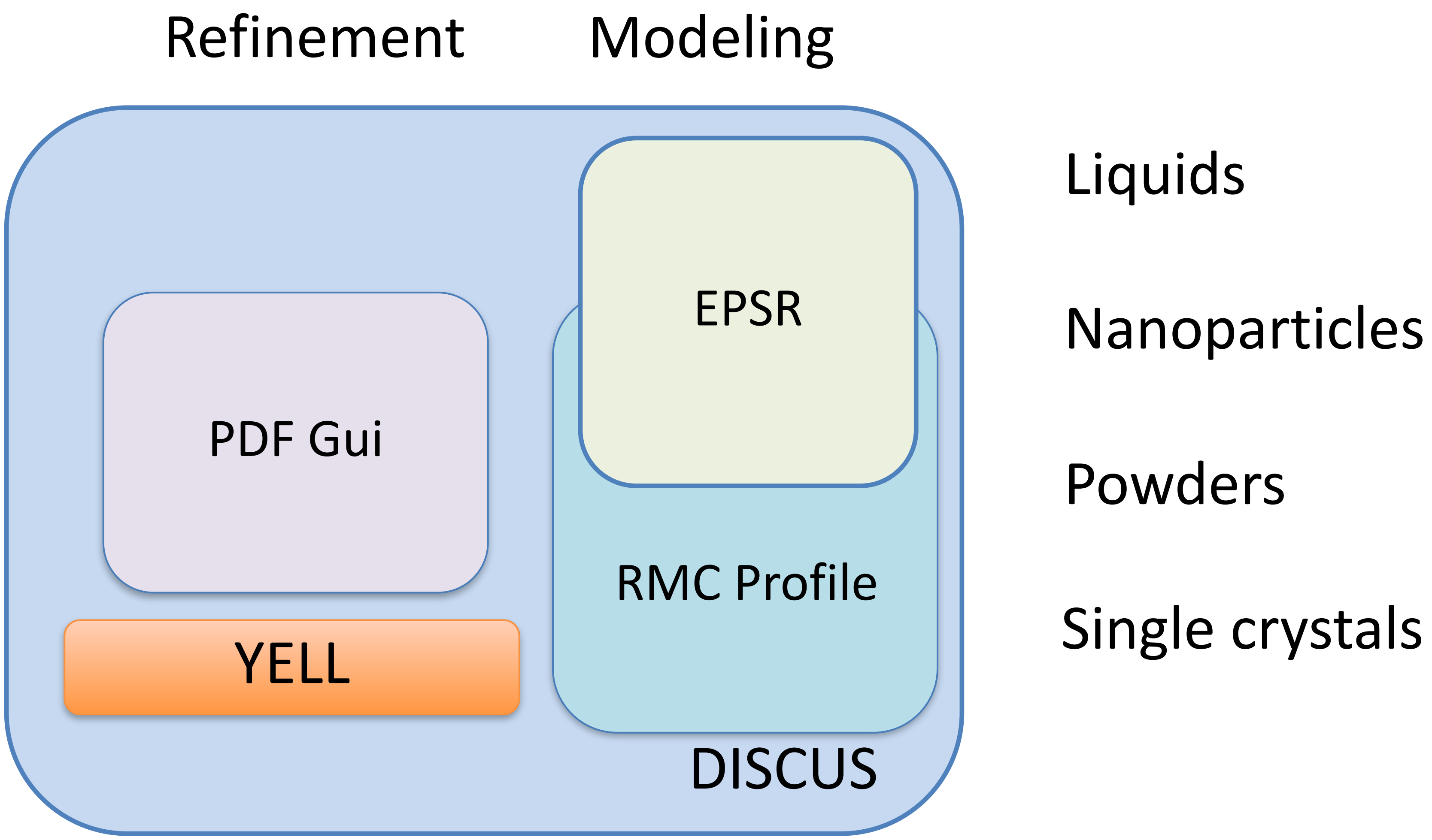
Yell strategy: refine what you see



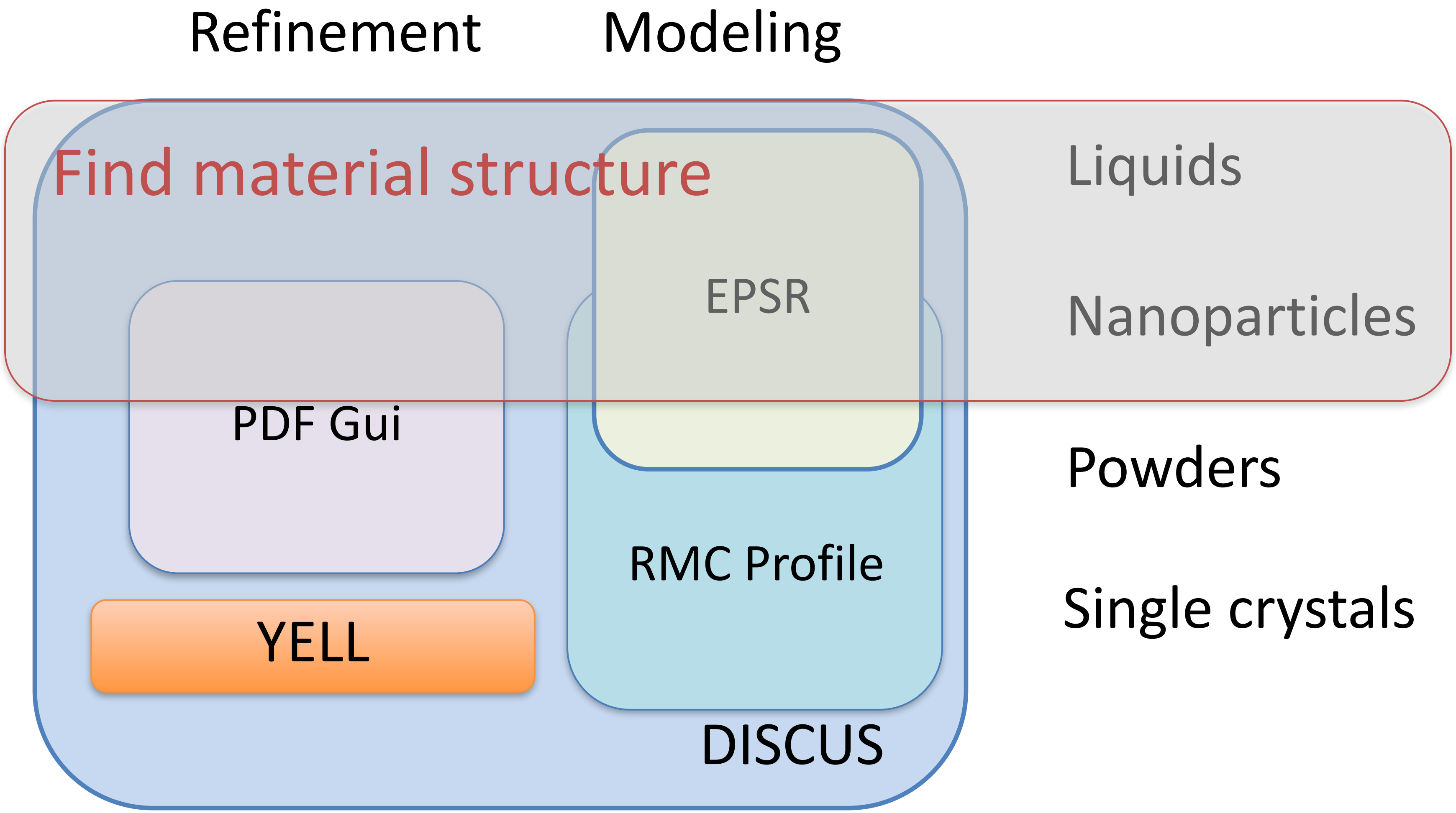
```
Cell 3.101 3.101 1  90 90 90
LaueSymmetry 4/mmm
DiffuseScatteringGrid -30 -30 0 0.1 0.1 1 600 600 1

CalculationMethod exact
Refine false

UnitCell
[
adp_au=0.02;
  Variant[
    (p=1)
    Au = Au 1  0 0 0  adp_au
  ]
]

Modes[
Au_x = TranslationalMode(Au,x)
Au_y = TranslationalMode(Au,y)
]

Correlations
[
[(0,0,0)
Multiplicity 1
   ADPCorrelation(Au_x,Au_x, 0.01*2 )
   ADPCorrelation(Au_y,Au_y, adp_au)
]

  [(1,0,0)
   Multiplicity 4
   ADPCorrelation(Au_x,Au_x, 0.01)
   ADPCorrelation(Au_y,Au_y, 0.005)
  ]
```



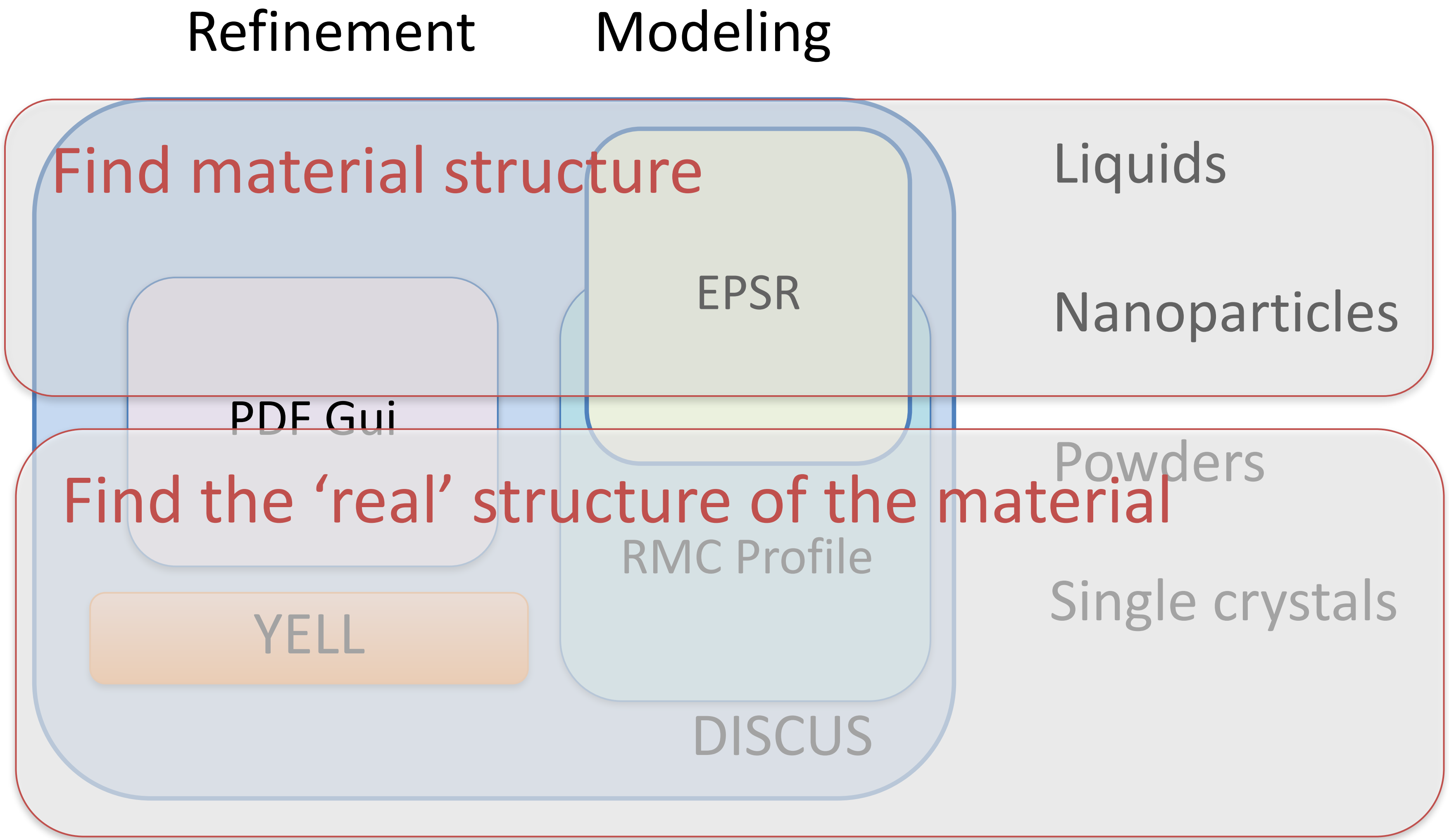
Direct space programs



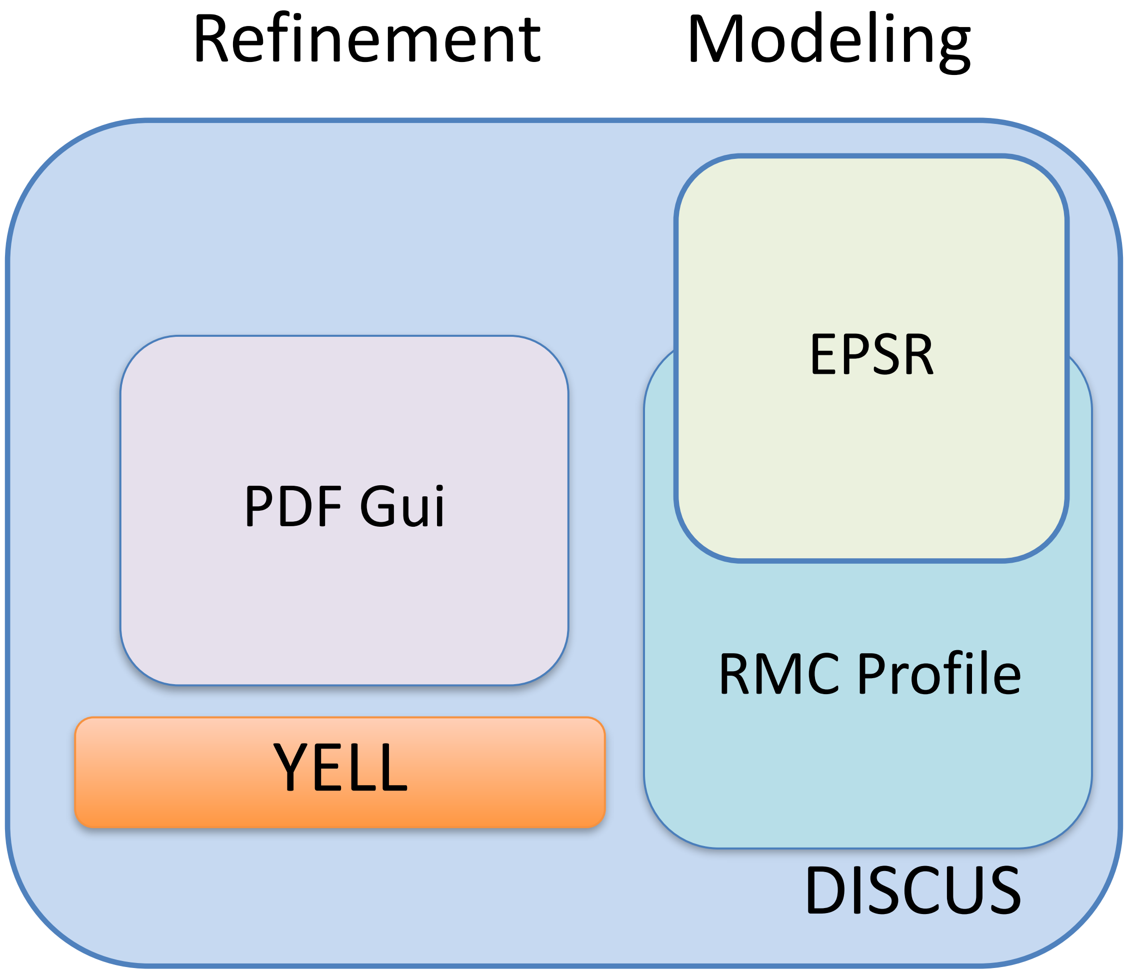
Direct space programs



Direct space programs



Direct space programs



Liquids

Nanoparticles

Powders

Single crystals