Bulk Structure Characterization

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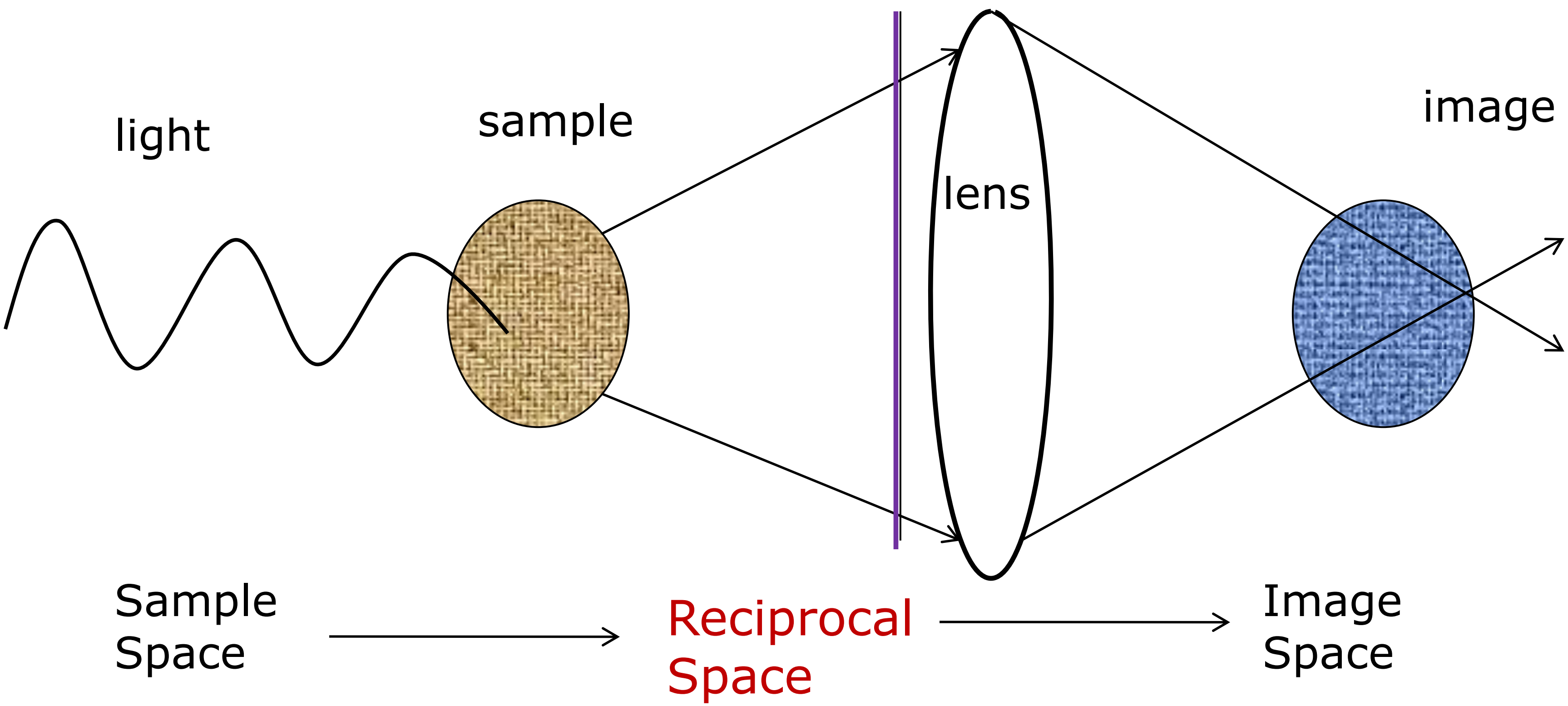
Outline

- What do diffraction peaks tell us?
- Structure Refinement Intro
- Refinement Details - Linda

Diffraction Physics

X-ray lens with resolution better than ~10nm don't exist



X-ray Scattering/diffraction is about probing the structure without a lens

Diffraction Physics

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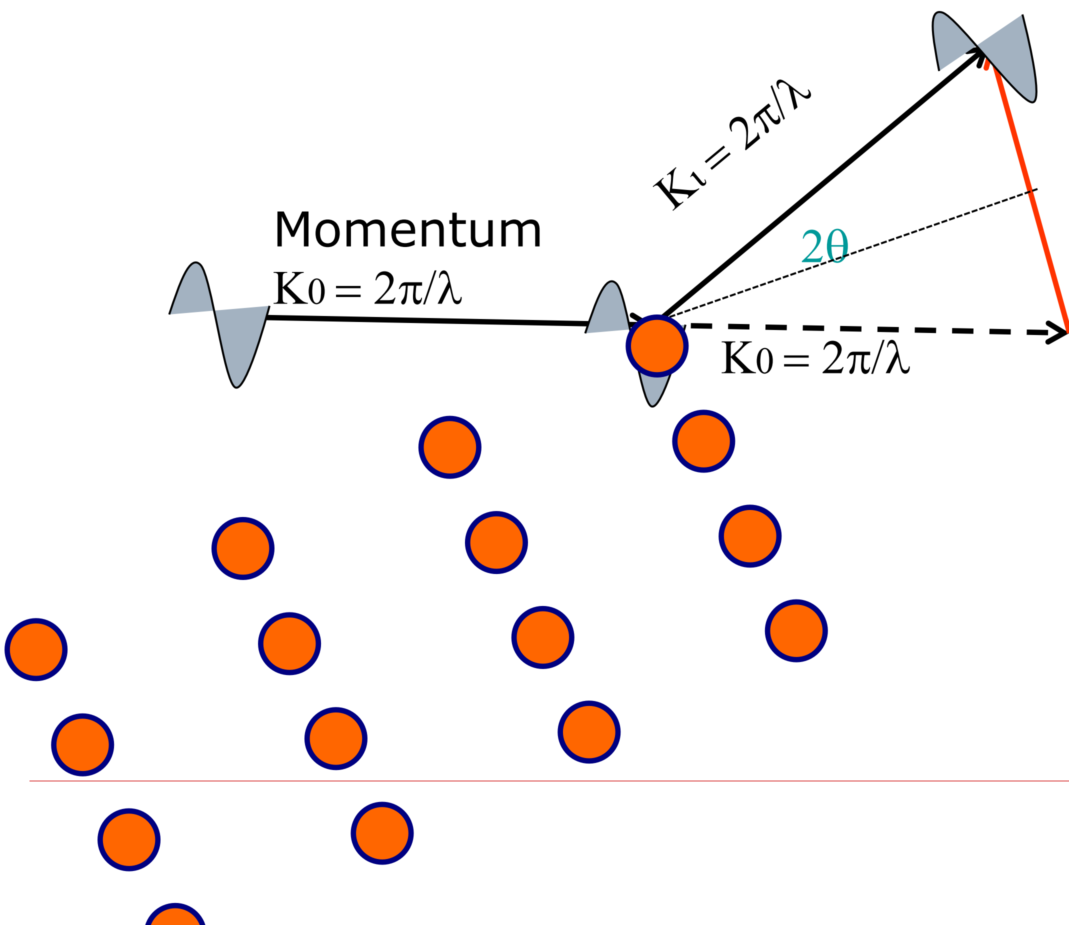
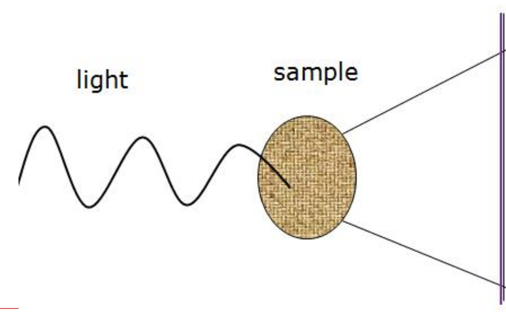
Elastic Scattering



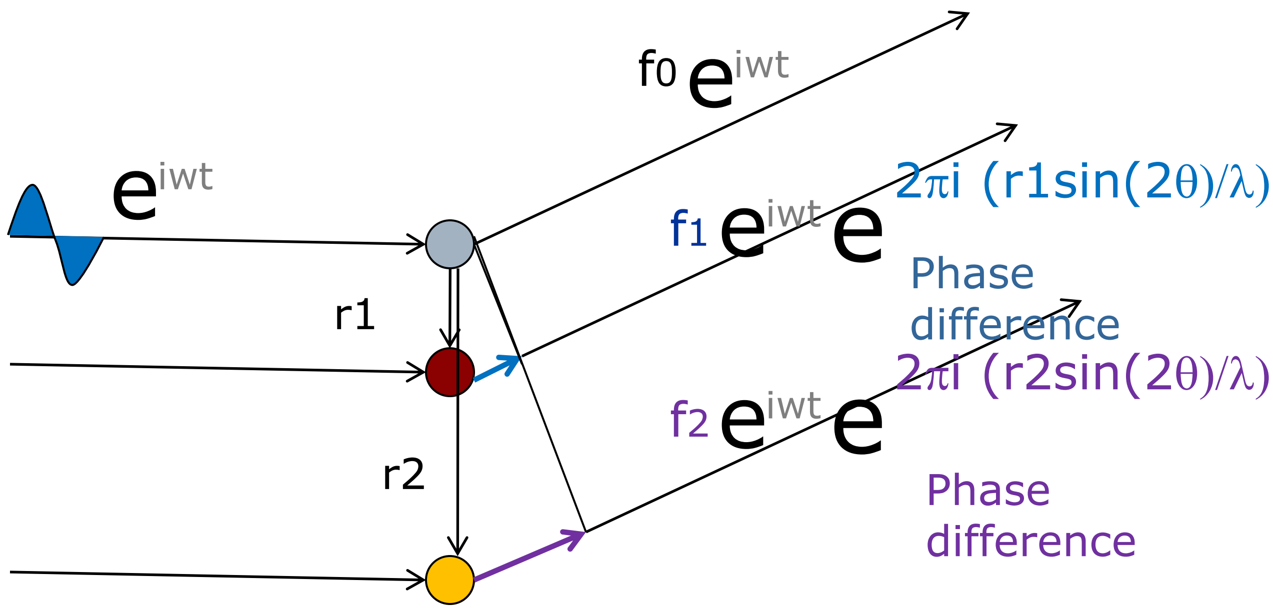
Momentum change

$\Delta K = 2\sin(\theta) * 2\pi/\lambda$

$\Delta K = Q = 4\pi \sin(\theta) / \lambda$



Diffraction Physics



$\Delta K = Q = 4\pi \sin(\theta)/\lambda$

$$A(\Delta K = (s - s0)) = e^{iwt} \sum f_i e^{2\pi i (r_i \sin(2\theta)/\lambda)}$$

amplitude

$$A(\Delta K) = \sum f_i \, e^{i (r_i \bullet Q)}$$

A(Q) = Fourier Transform (ri)

Fourier Transform Recap

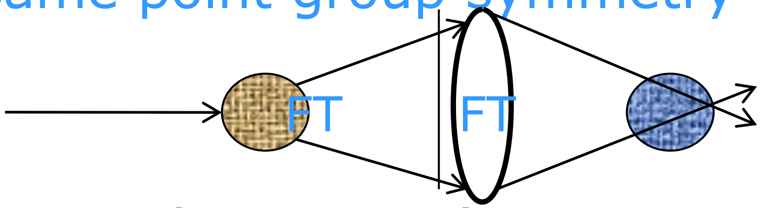
- FT (large) ~ 1/large → small

  large structures in real space → small in reciprocal space

- FT (periodic fn) ~ periodic

  Reciprocal and space have the same point group symmetry

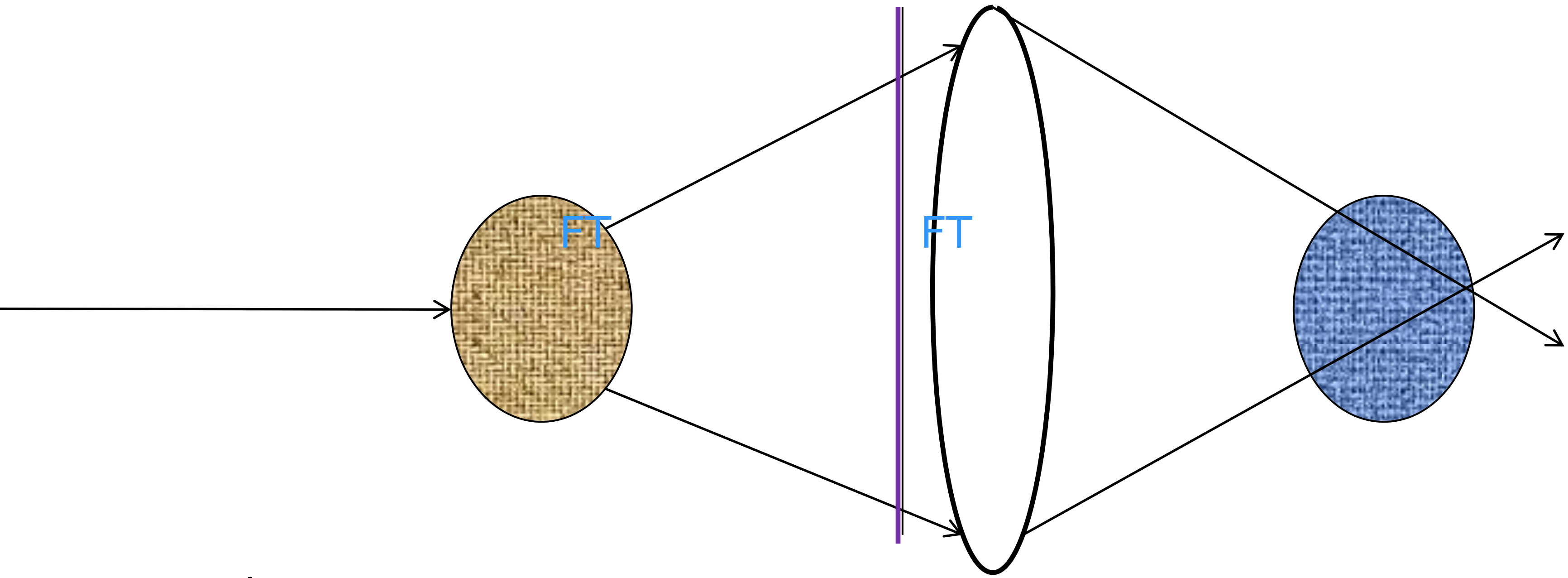
- FT (FT (S)) ~ S



FT (real space) → reciprocal space: FT (rec. space) → image of real space

- Convolution Theorem:
  - FT (a multiply b) = FT (a) conv FT (b)
  - FT (a conv b) = FT (a) mult FT (b)

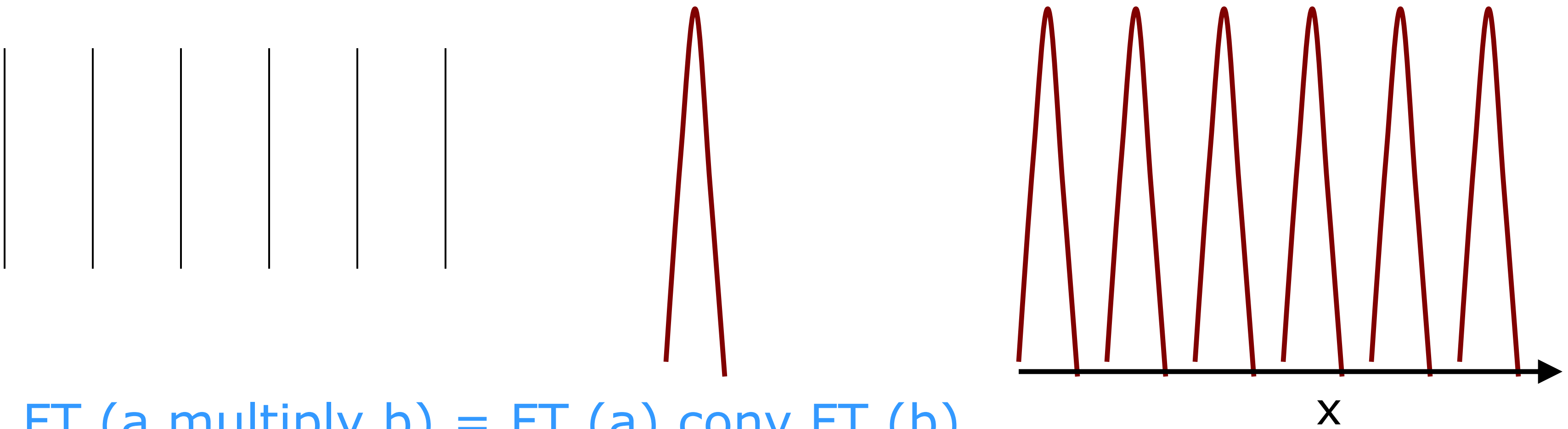
Diffraction Physics



Sample Space → Scattering Space

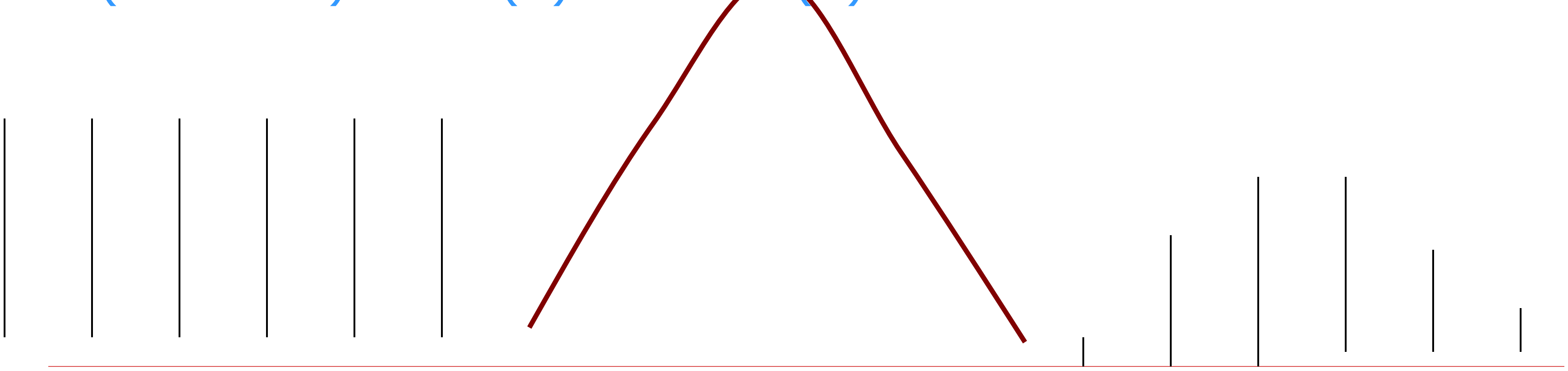
Fourier Transform

Multiplication vs Convolution



Convolution

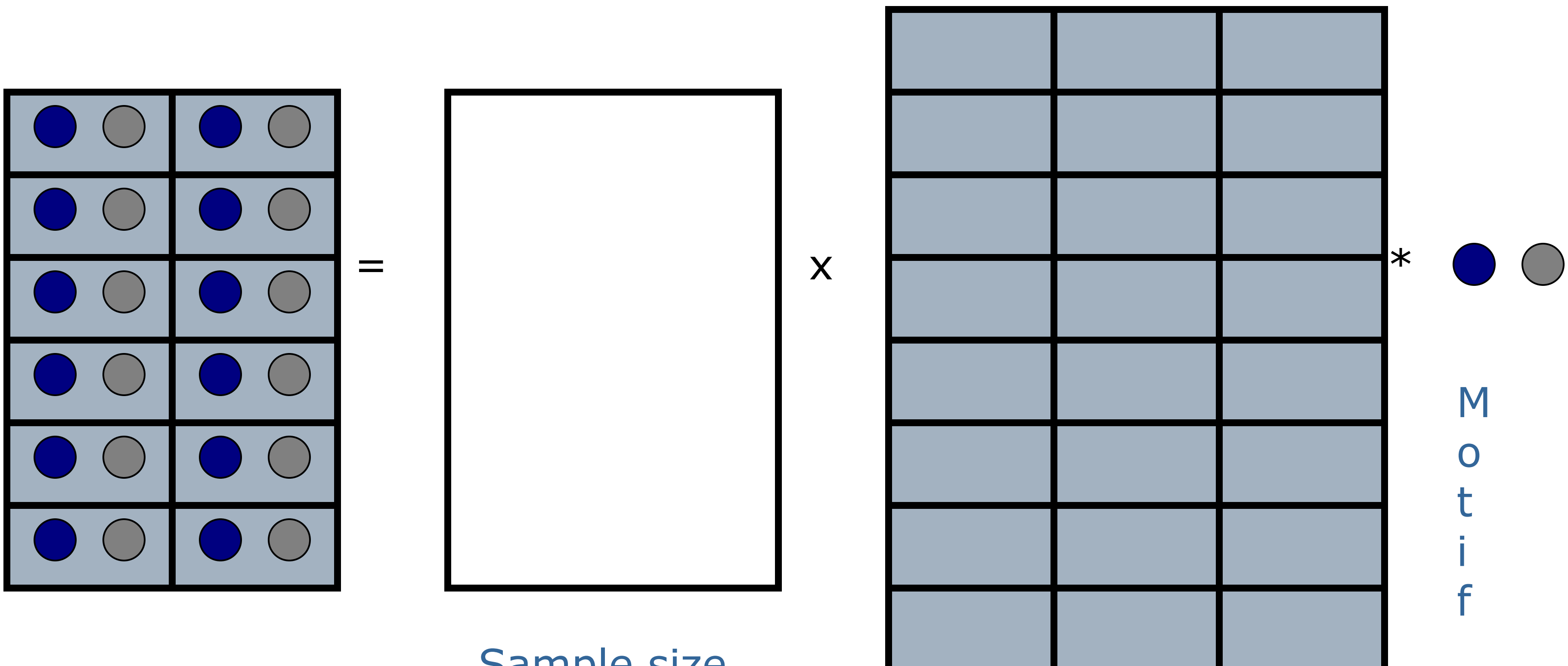
FT (a multiply b) = FT (a) conv FT (b)
FT (a conv b) = FT (a) mult FT (b)



Multiplication

Deconstructing the Sample space

Sample = S x P * M

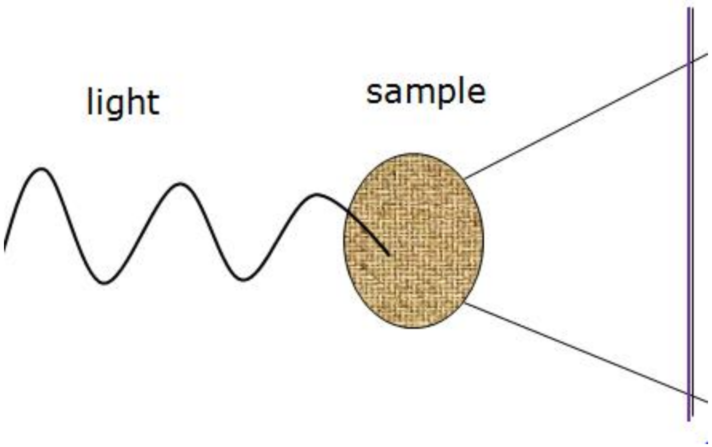


Sample size (S)

Infinite Periodic Lattice (P)

(M)

Reciprocal Space Peaks



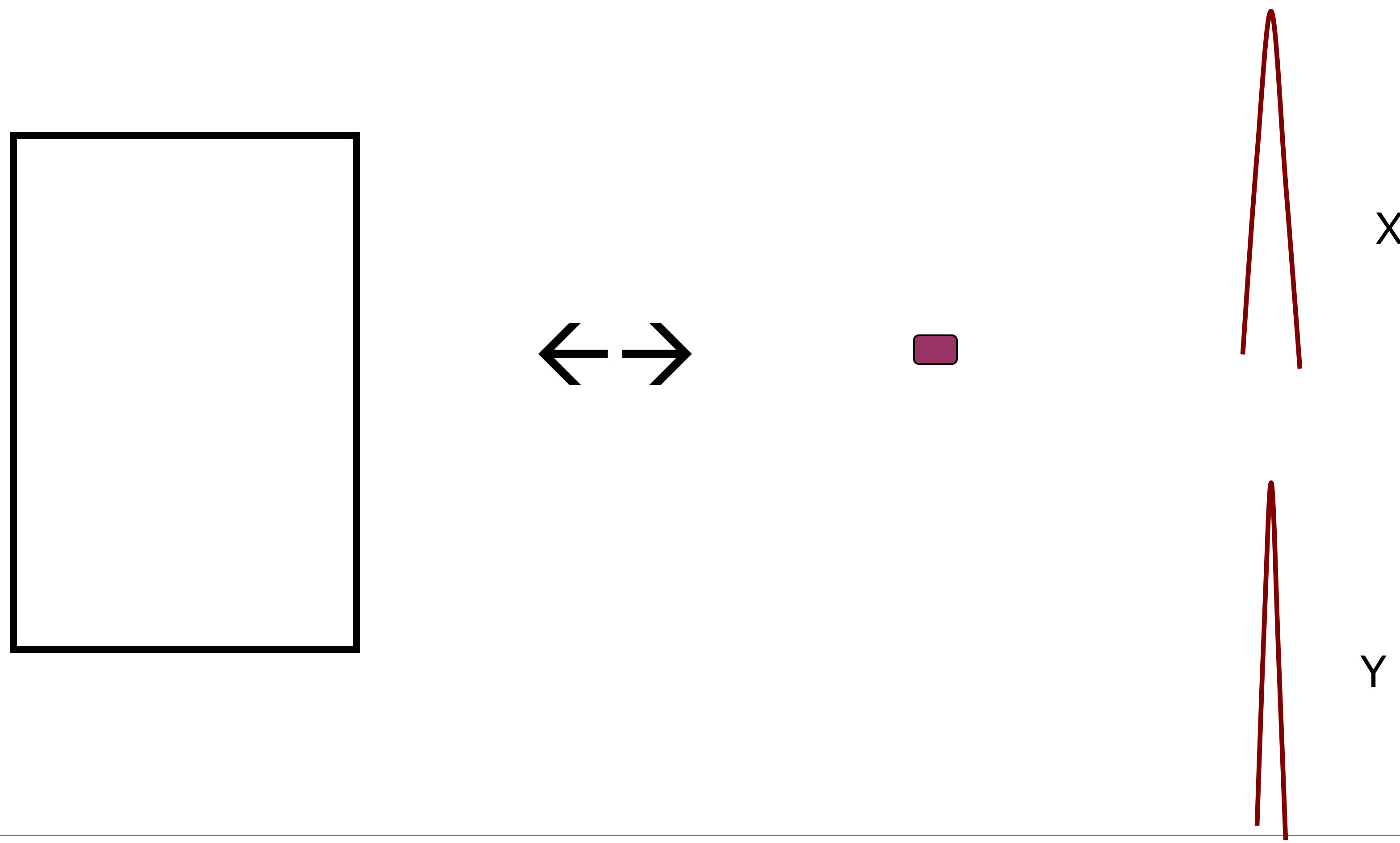
$$I\ (Q) = FT(sample) \times FT(sample)$$

$$= FT\ (\ S \times P * M) \times FT\ (\ S \times P * M)$$

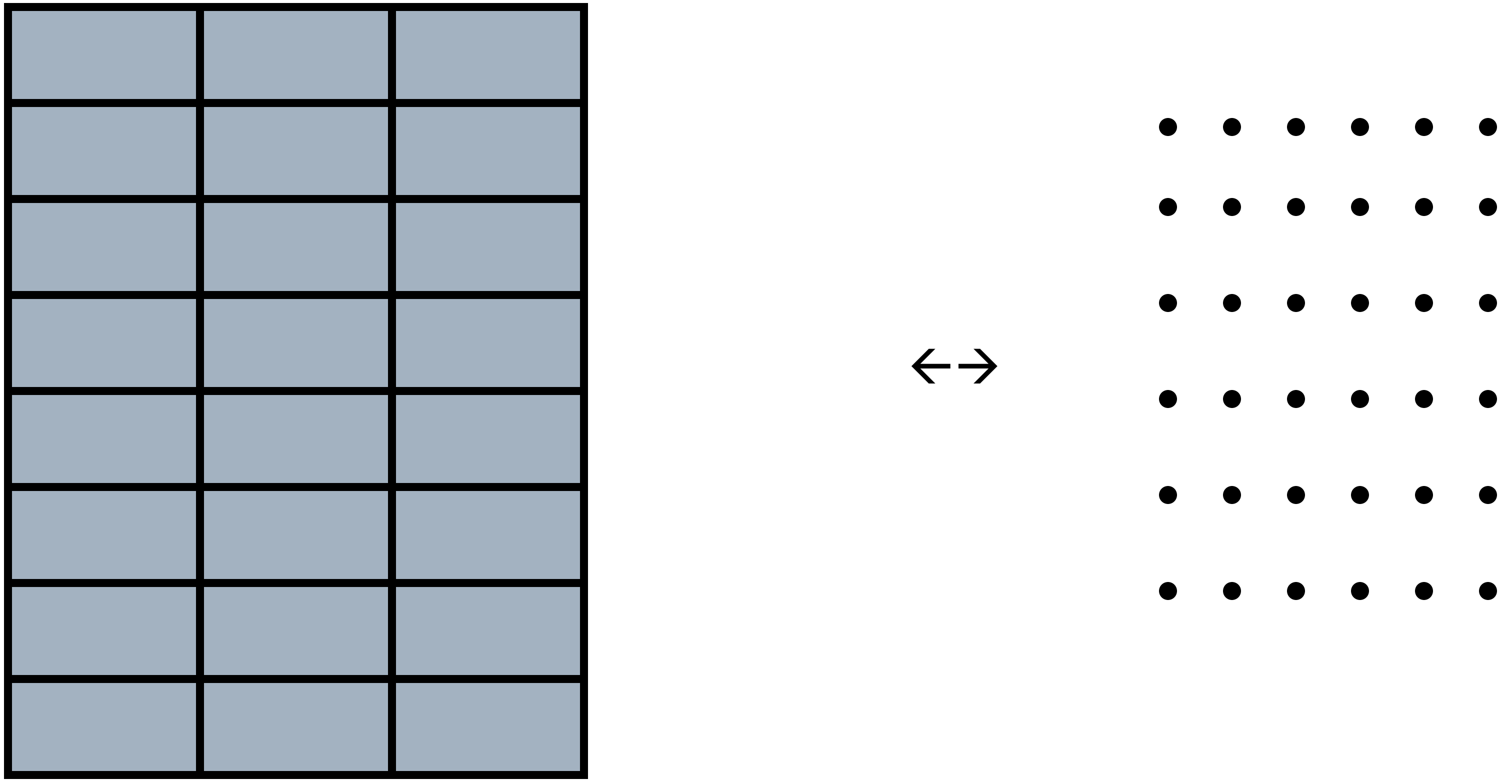
$$= \{FT\ (S \times P) \times FT\ (M)\}\ \{\ ....\}$$

$$= \{FT(S) * FT(P) \times FT(M)\}\ \{.....\}$$

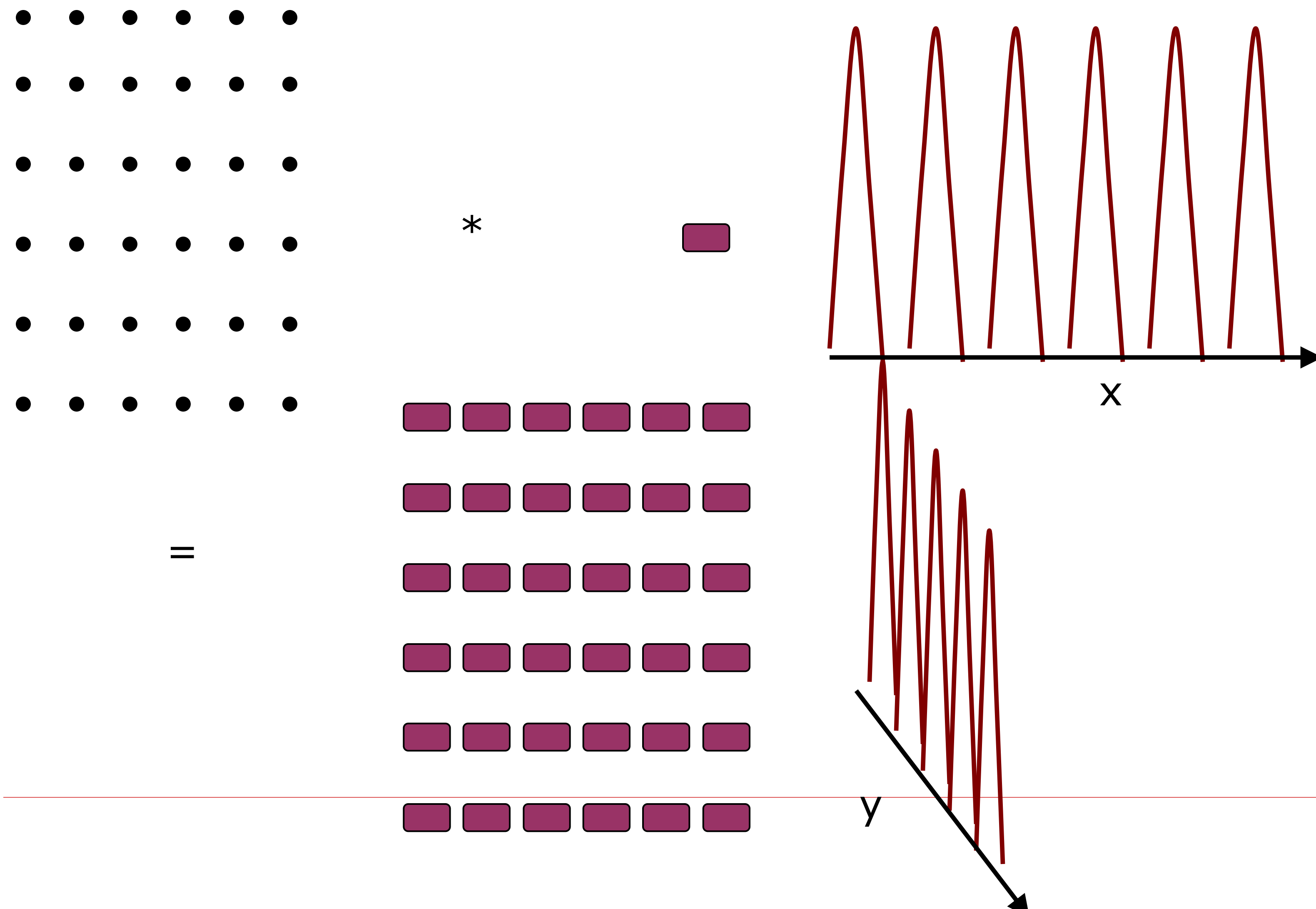
FT(S)



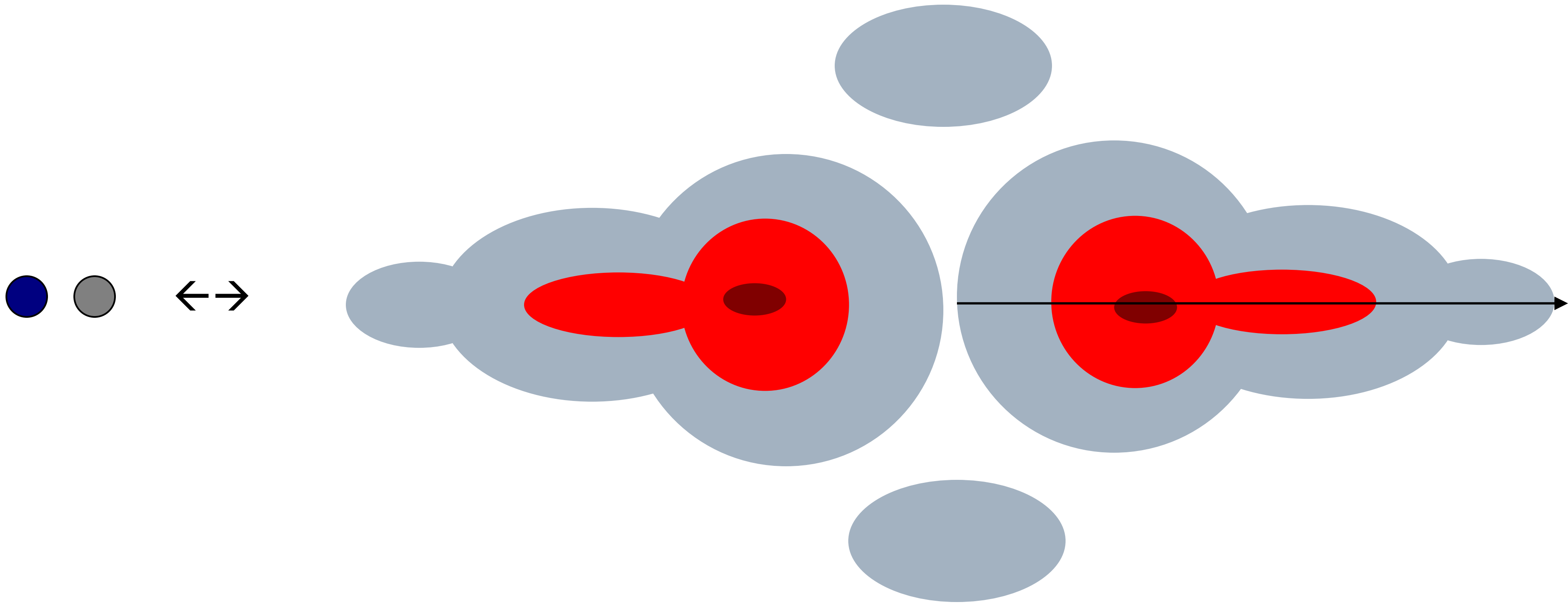
FT(P)

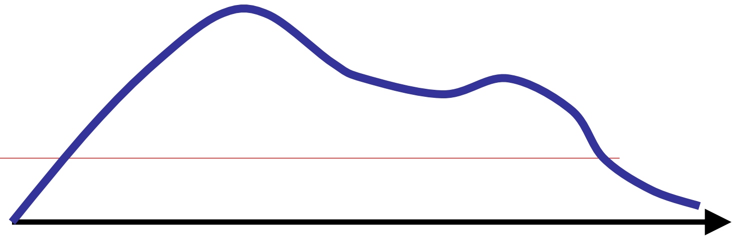


$FT(S \times P) = FT(S) * FT(P)$



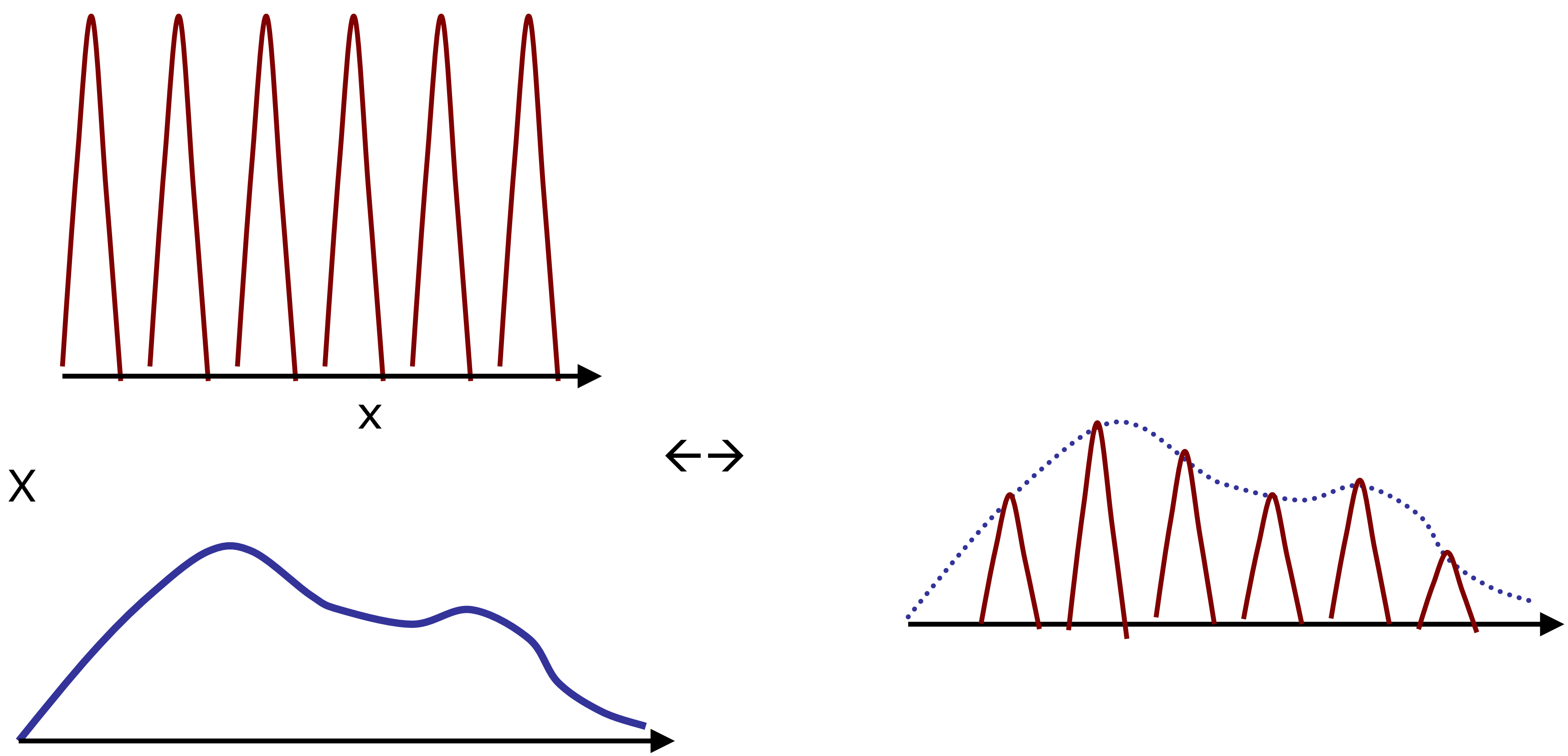
FT(M)



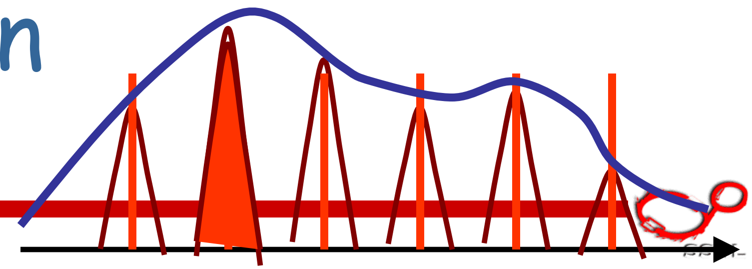


FT(sample) = FT(S x P) x FT(M)

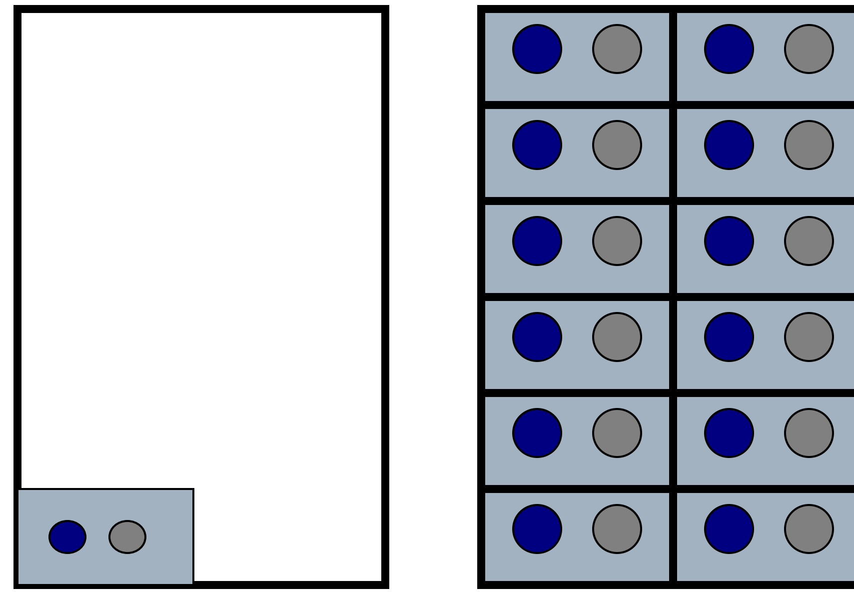
Along X direction

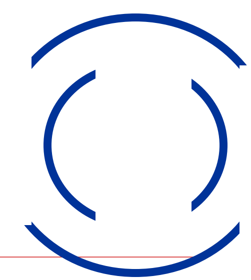


What does a diffraction pattern tell us?



- Peak Shape & Width:
  - crystallite size
  - Strain gradient
- Peak Positions:
  - Phase identification
  - Lattice symmetry
  - Lattice strain
- Peak Intensity:
  - Structure solution
  - Crystallite orientation





Questions?

Bulk Structure via powder diffraction

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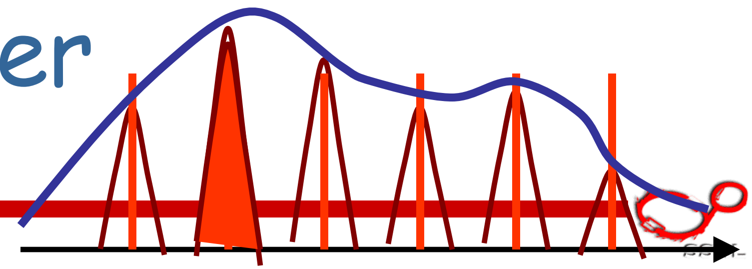

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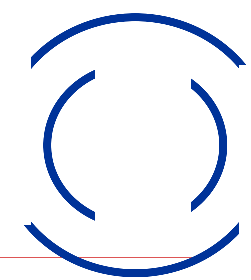
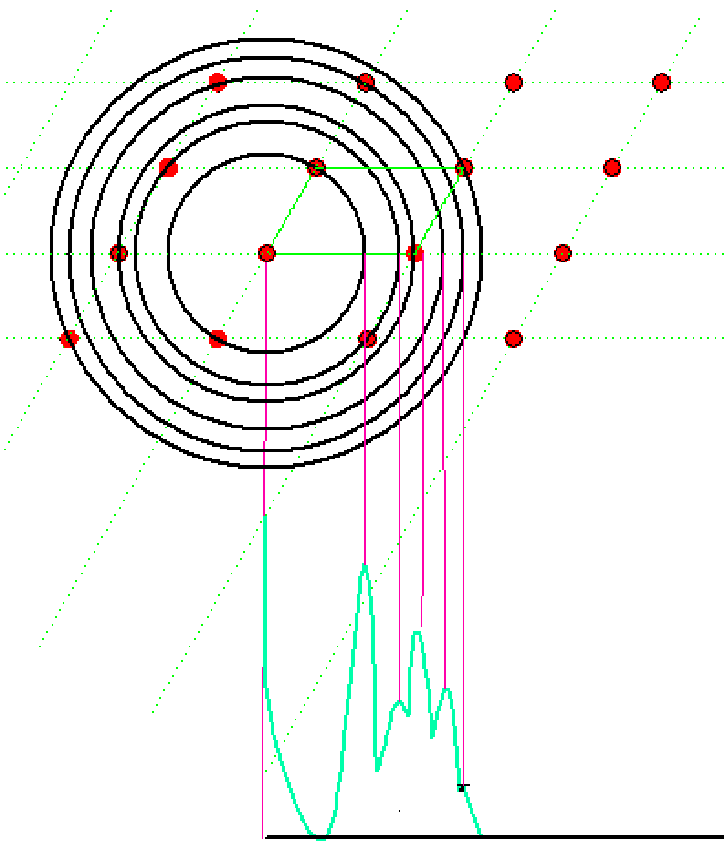
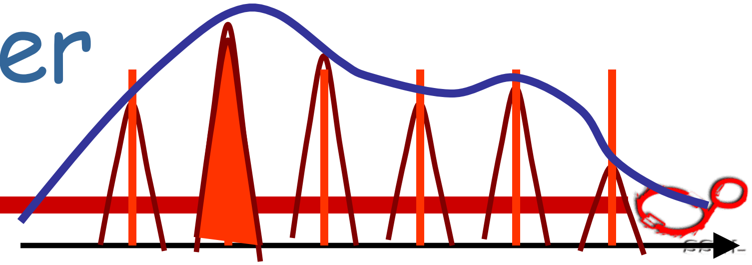


Powder Pattern



- Loss of angular information
  - Not a problem as peak position = fn(a, b & α)
- Peak Overlap :: A problem
  - High Resolution Synchrotron measurements help
  - But can be useful for precise lattice parameter measurements

Bulk Structure via powder diffraction



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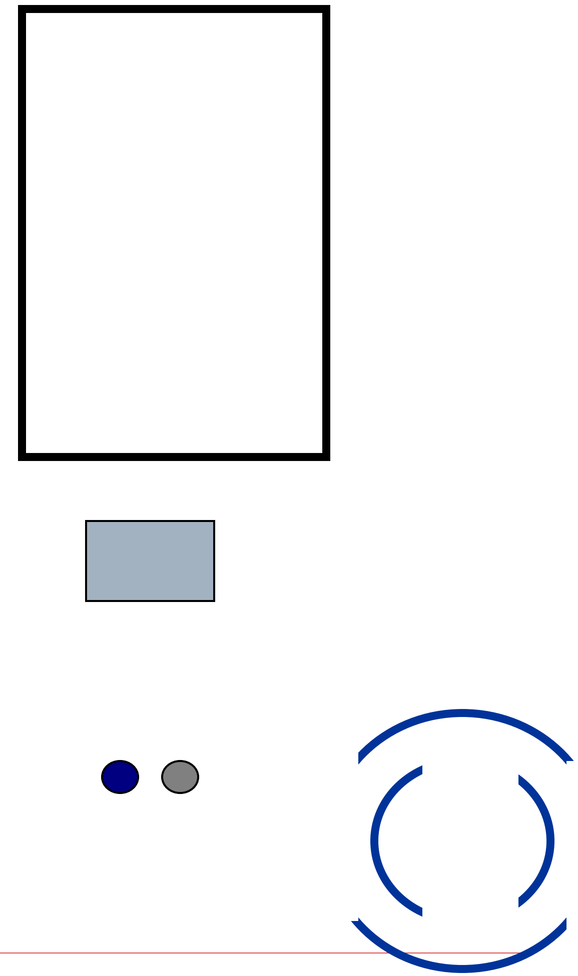
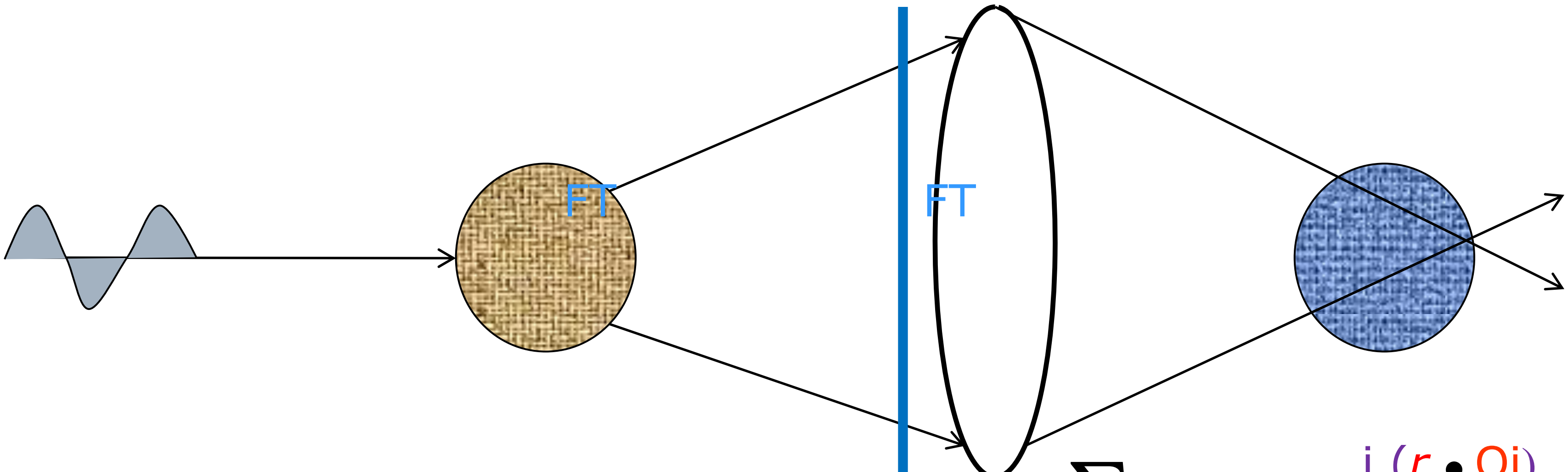


Diffraction Physics



$$A(\Delta K) = \sum f_i e^{2\pi i (r_i \sin(2\theta)/\lambda)}$$

$$A(\Delta K) = \sum f_i \; e^{i (r_i \bullet Q)}$$

$$A(Q) = F_{hkl} = \text{Fourier Transform } (r_i)$$

$$A(r) = \sum F_{hkl} e^{i (r \bullet Q_i)}$$

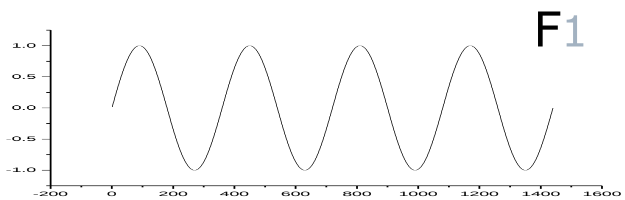
$A(Q)/F_{hkl}$ is a complex number

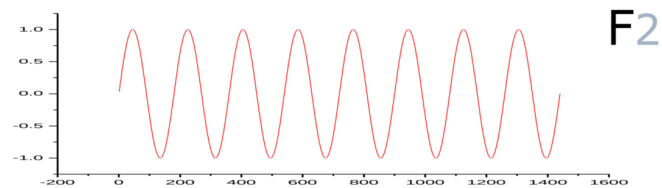
We measure $A(Q) * A(Q)$

→ amplitude but not the phase of $A(Q)$ is known

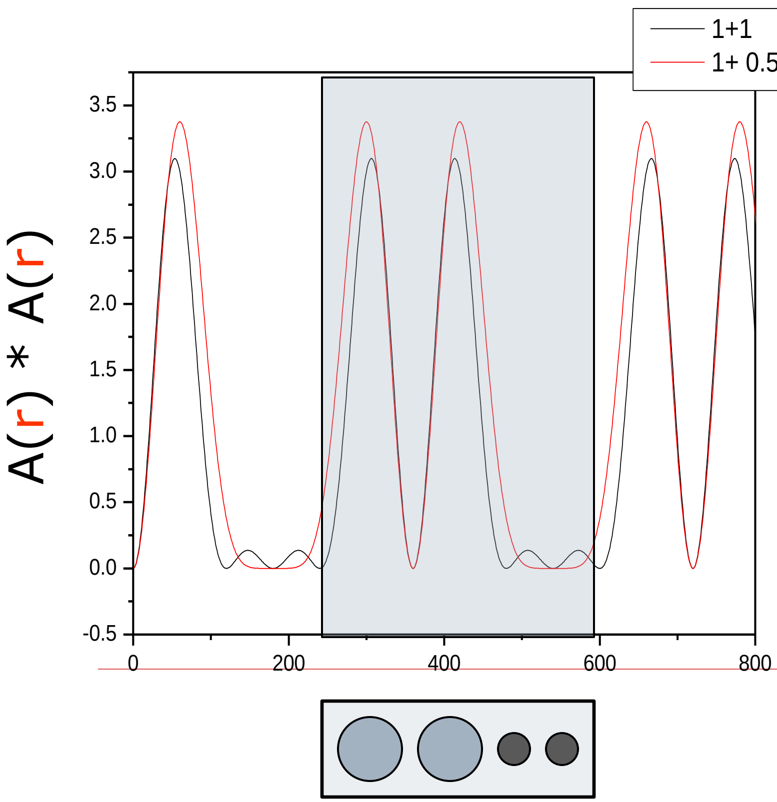
Phase Problem

$$A(r) = FT\{ F_1 + aF_2 e^{i(ph)} \}$$

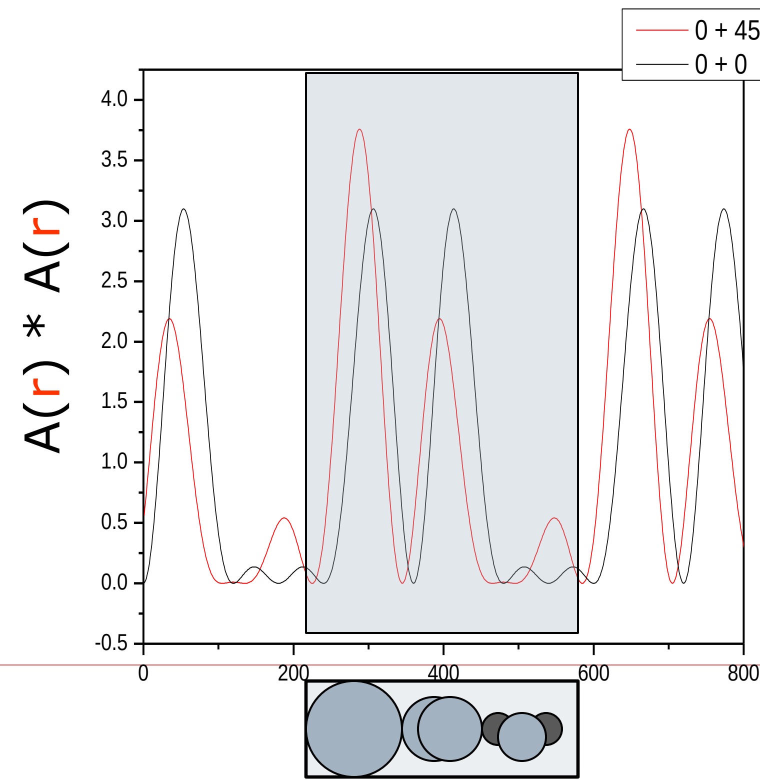




Amplitude unknown



Phase Unknown



Solution to Phase Problem

- Phase/Structure must be guessed
  - And then refined.

- How to guess?
  - Heavy atom substitution, SAD or MAD
  - Structure with one strong scatterer – e.g. U in Phosphates matrix -
  - Similarity to homologous compounds, e.g. NaCl → KCl
  - Patterson function or pair distribution analysis. M. Michel

Structure Solution

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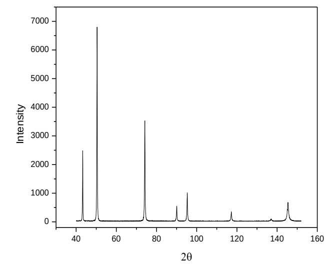
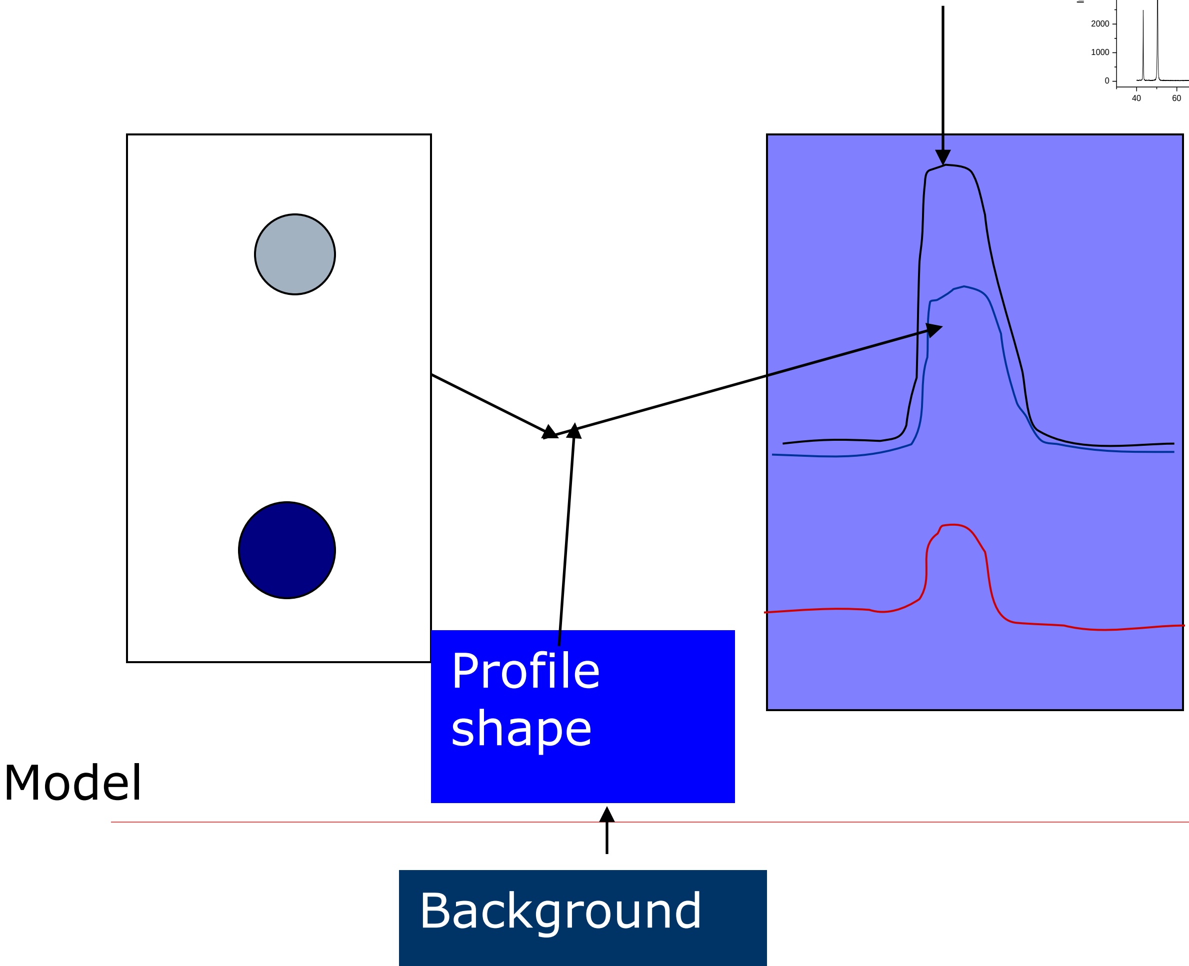
- Single Crystal
  - Protein Structure
  - Sample with heavy Z problems Due to
    - Absorption/extinction effects
  - Mostly used in Resonance mode
    - Site specific valence
    - Orbital ordering.

- Powder
  - Due to small crystallite size kinematic equations valid
  - Many materials can not be readily prepared in single-crystal form: their structures obtained via synchrotron powder diffraction
  - Peak overlap a problem – high resolution setup helps
  - Much lower intensity – loss on super lattice peaks from small symmetry breaks. (Fourier difference helps)

Inverse Modeling Method 1

- Reitveld Method Data





Profile Shape function

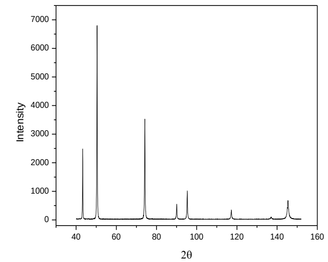
- Empirical
  - Voigt function modified for axial divergence (Finger, Jephcoat, Cox)
    - Refinable parameters – for crystallite size, strain gradient, etc…

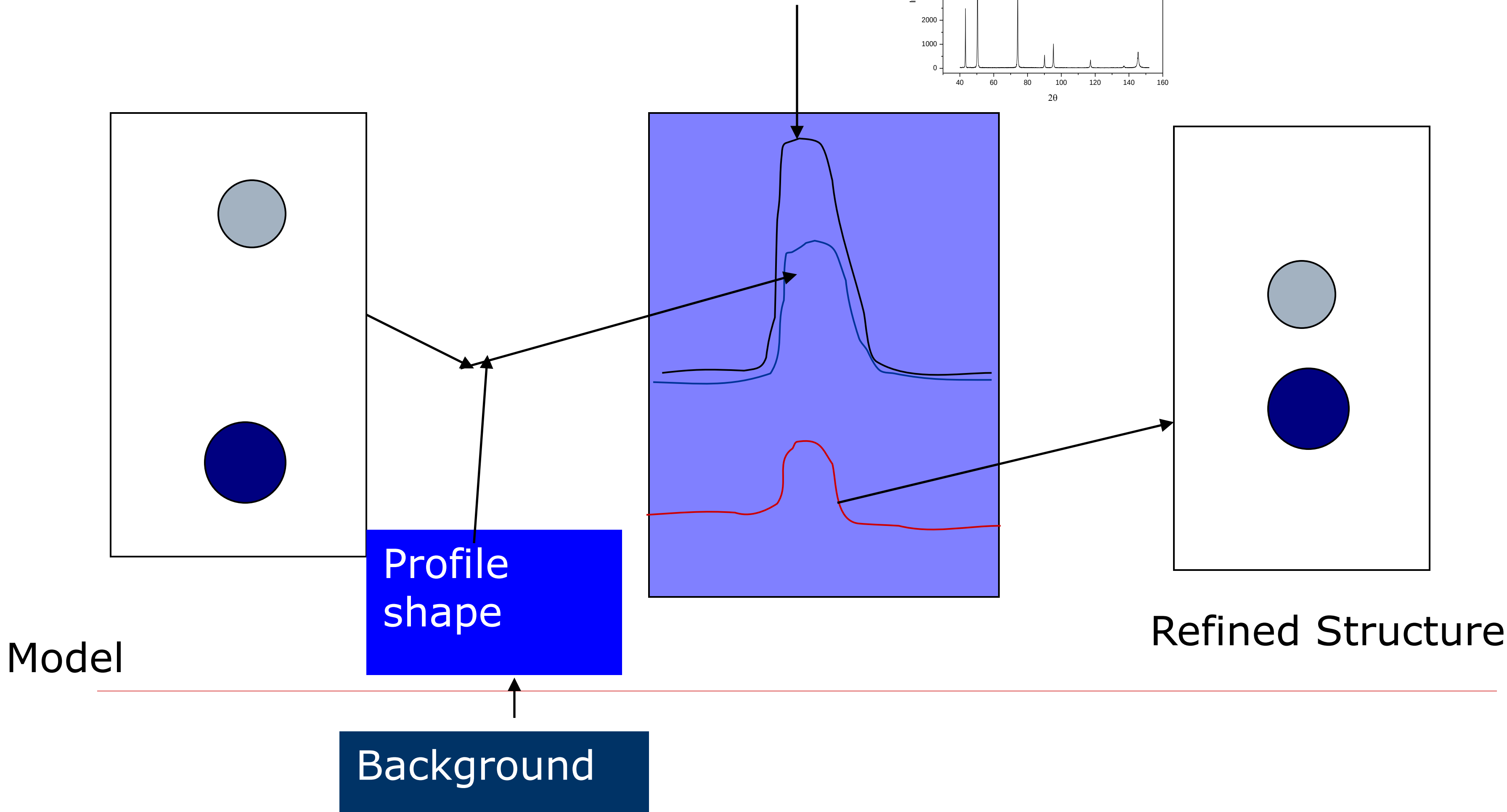
- From Fundamental Principles

Inverse Modeling Method 1

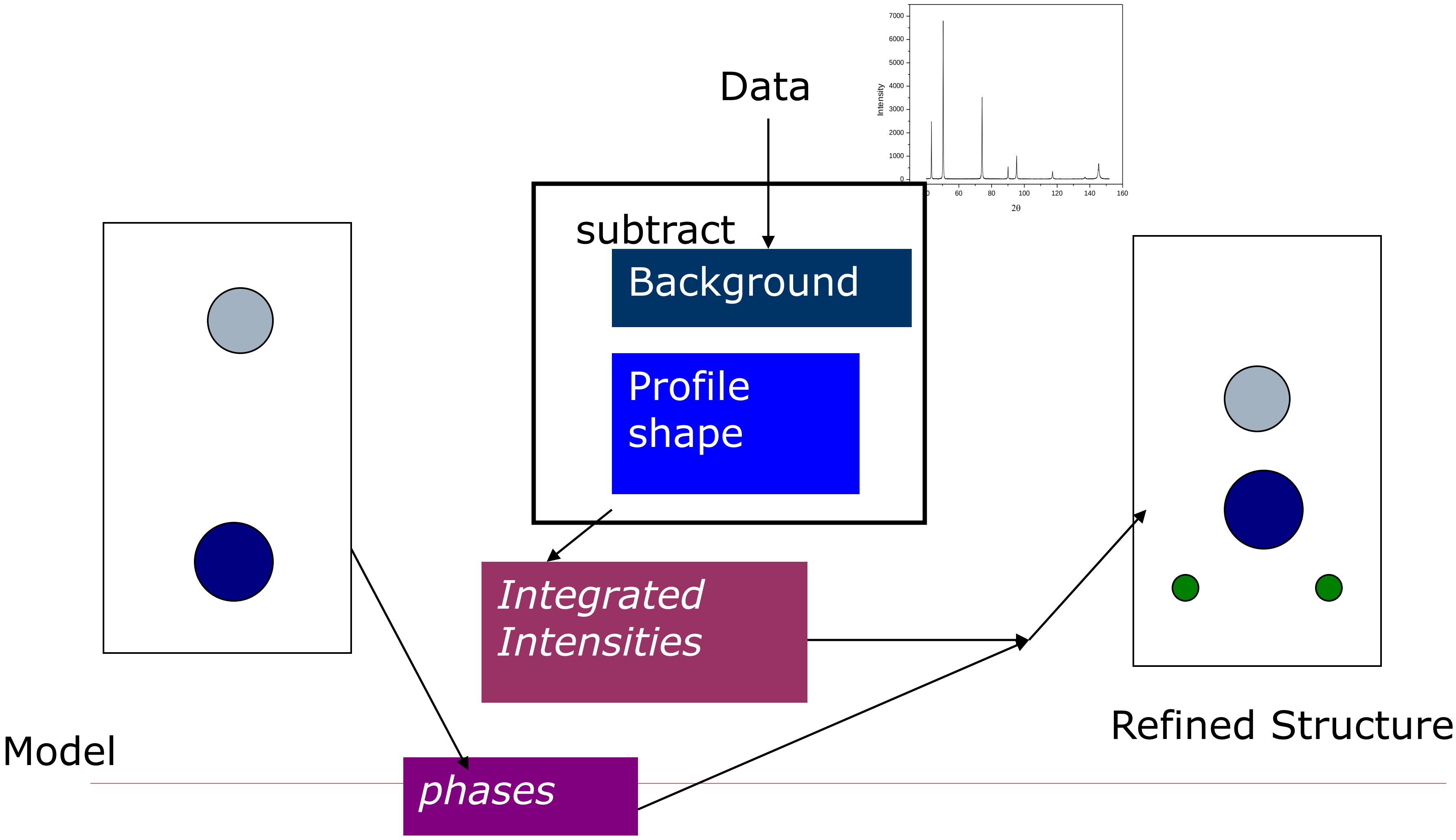
- Reitveld Method

Data





Inverse Modeling Method 2

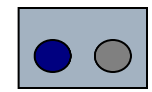


Inverse Modeling Methods

- Rietveld Method
  - More precise
  - Yields Statistically reliable uncertainties
- Fourier Method
  - Picture of the real space
  - Shows "missing" atoms, broken symmetry, positional disorder
- Should iterate between Rietveld and Fourier.
  - Be skeptical about the Fourier picture if Rietveld refinement does not significantly improve the fit with the "new" model.

Procedure for Refinement/Inverse Modeling

- Measure peak positions:
  - Obtain lattice symmetry and point group
    - Guess the space group.
      - Use all and compare via F-factor analysis



- Guess the motif and its placement
  - Phases for each hkl
- Measure the peak widths
  - Use an appropriate profile shape function
- Construct a full diff. pattern and compare with measurements

Collect data on Calibrant under the same conditions

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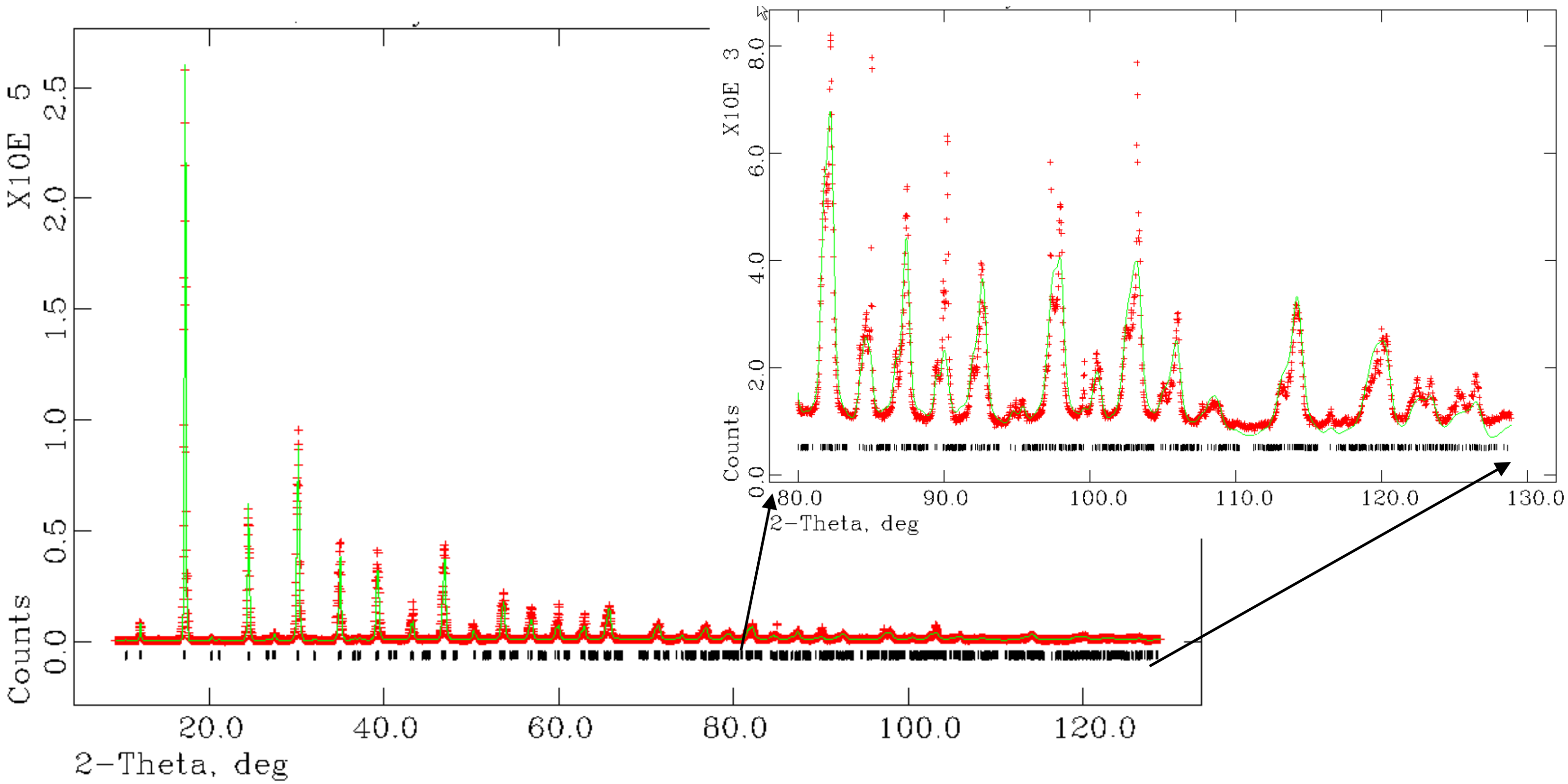
- Obtain accurate wavelength and diffractometer misalignment parameters
- Obtain the initial values for the profile function (instrumental only parameters)
- Refine polarization factor

- Tells of other misalignment and problems

Need for High Q

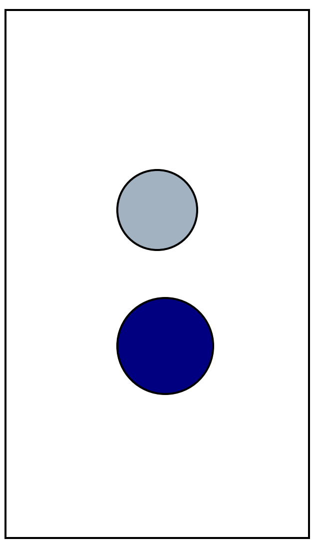


Many more reflections at higher Q.

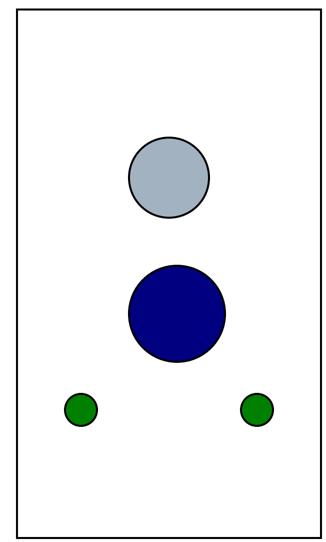
Therefore, most of the structural information is at higher Q

Structure Refinement Method

Reitveld Method



Fourier Difference Method



Thanks

Questions?