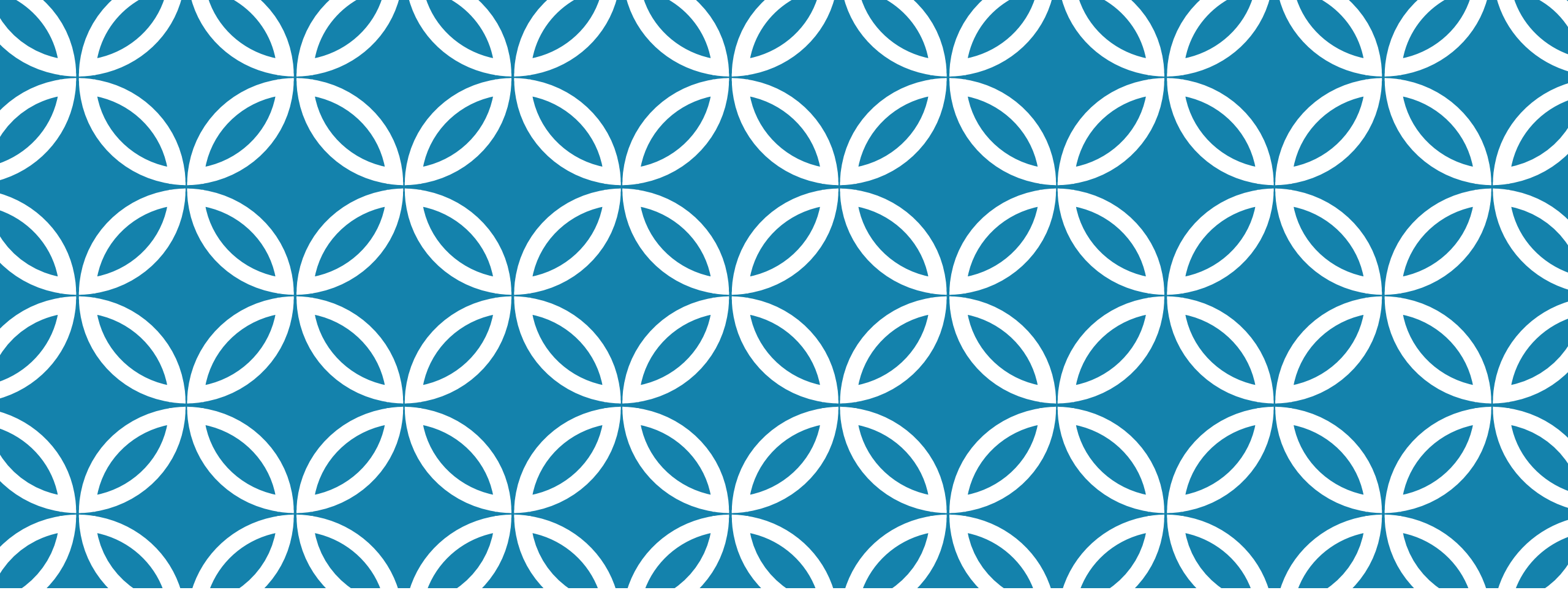


INTRODUCTION TO THE PAIR DISTRIBUTION FUNCTION

June 2024

INTRODUCTIONS

Anna Herlihy

anna.herlihy@diamond.ac.uk

Beamline Scientist on I15-1

Interests: High pressure PDF, solid oxides



INTRODUCTIONS

Dan Irving

daniel.irving@diamond.ac.uk

Beamline Scientist on I15-1

Interests: Liquids, crystallization, Dissolve, instrument development



INTRODUCTIONS

Phil Chater

philip.chater@diamond.ac.uk

Crystallography Group Leader

Interests: Beamline development, energy materials

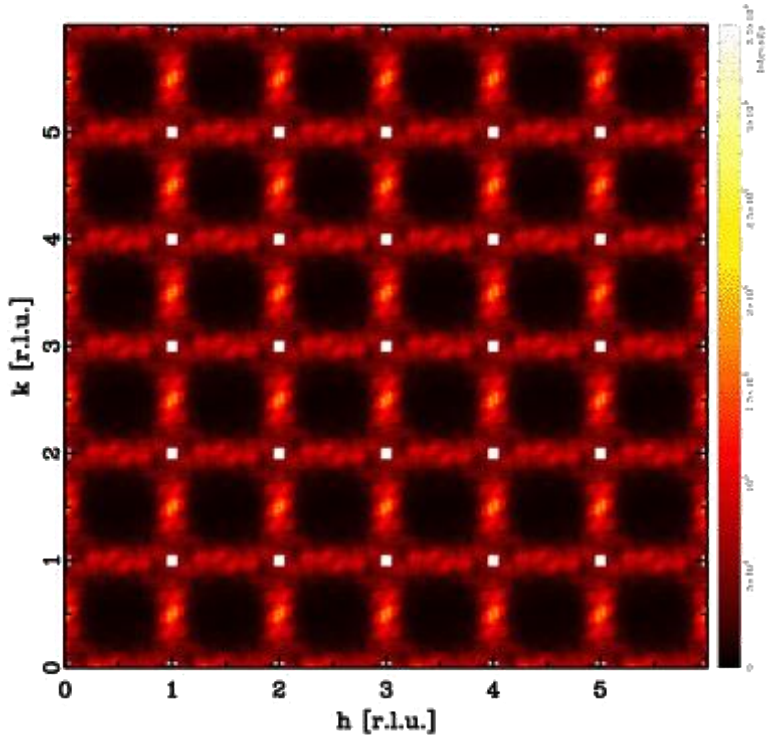


CONTENTS

- Total scattering & Fourier transforms
- What is a PDF?
- PDF forms
- What makes a good PDF?
- XPDF Beamline

Slides courtesy of Phil Chater and Dean Keeble

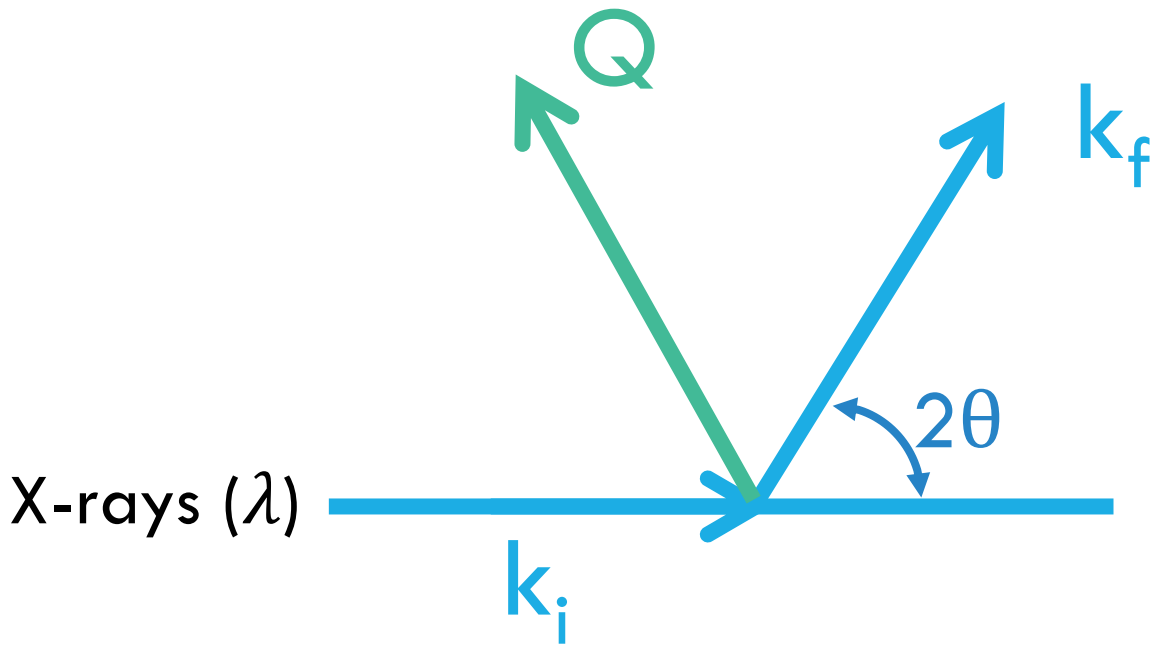
WHAT IS TOTAL SCATTERING?



- Bragg scattering
  - Sharp peaks – long-range periodicity
- Diffuse scattering
  - Weak features – short- and medium-range order
- Total scattering
  - Considering both Bragg and diffuse scattering together

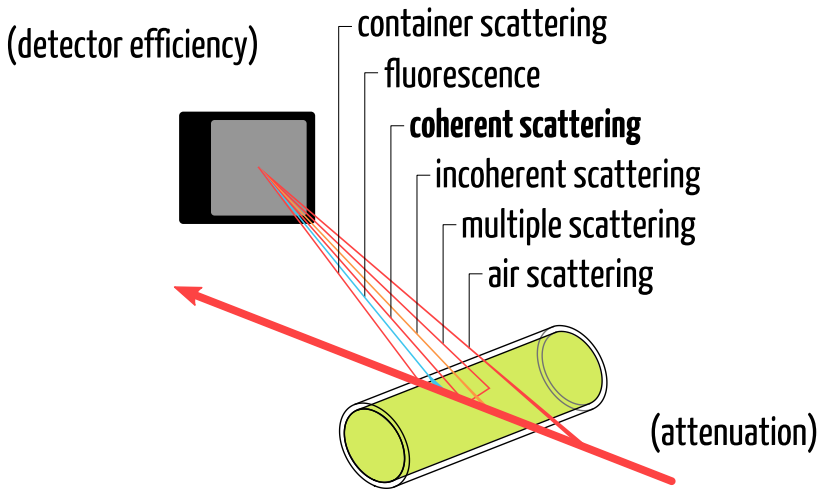
SCATTERING VECTOR, Q

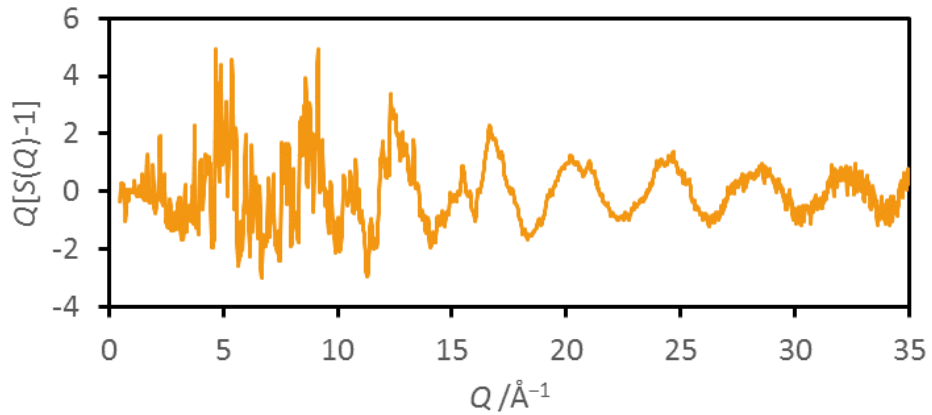
- Difference between incident wavevector k_i and scattered wavevector k_f
- $Q=k_f-k_i$



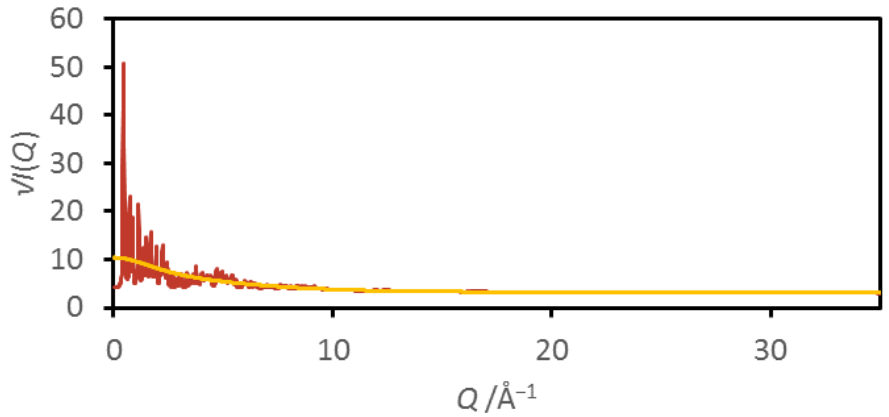
$$Q = \frac{4\pi sin\theta}{\lambda}$$

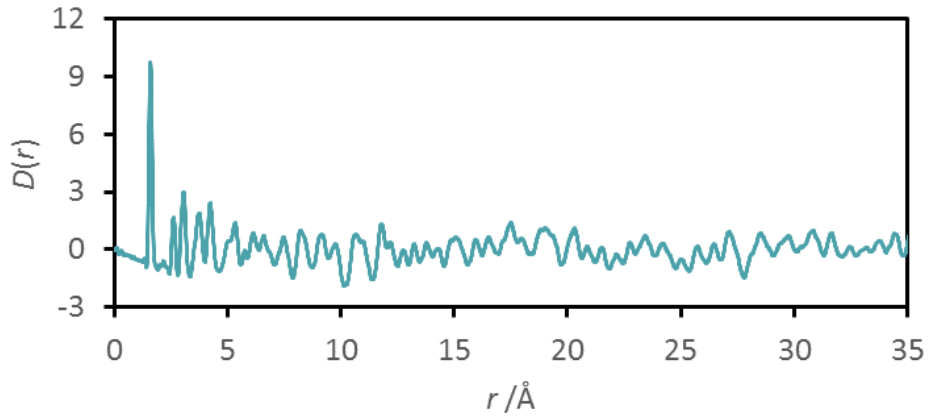
WHAT IS TOTAL SCATTERING?





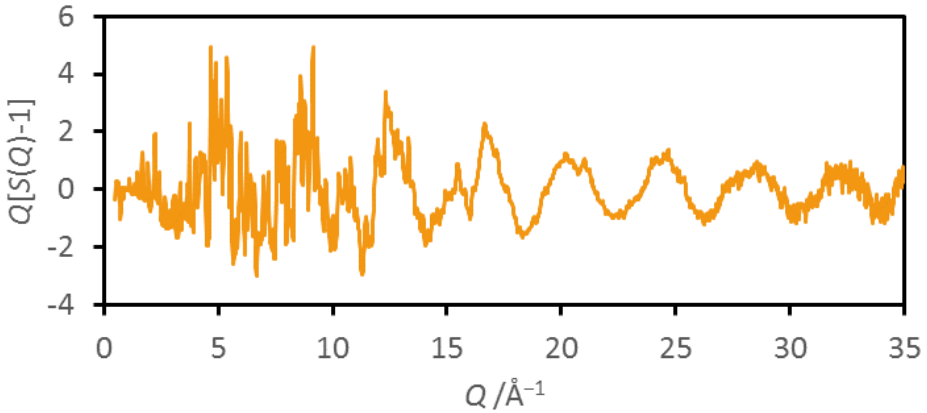
$$D(r) = \frac{2}{\pi} \int Q[S(Q) - 1] \sin(Qr) \, . \, dQ$$





WHAT IS TOTAL SCATTERING?

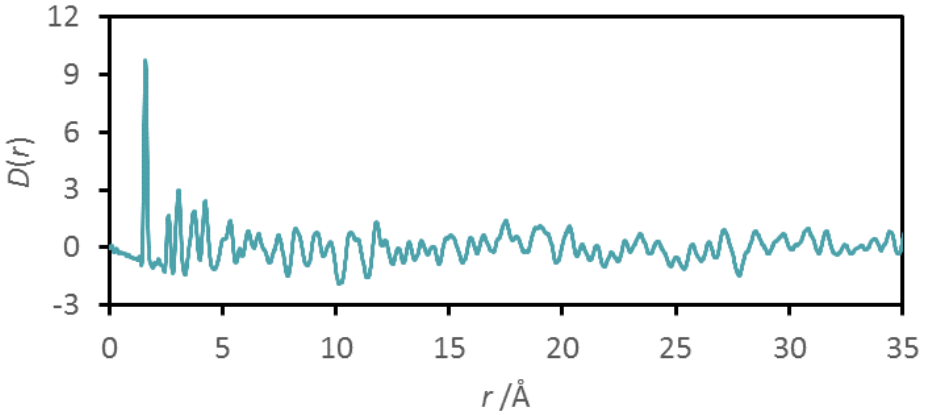
$$I(q) = \sum_{i=1}^{N}\sum_{j=1}^{N} f_i(q) f_j(q) \left[\frac{sin(qr_{ij})}{qr_{ij}}\right]$$



$$D(r) = \frac{2}{\pi}\int Q[S(Q) - 1]\sin(Qr)\,.\,dQ$$

$$D(r) = 4\pi r[\rho(r) - \rho_0]$$

$$D(r) = 4\pi r\rho_0 \sum_{i,j=1}^{n} c_i c_j b_i b_j \left[\frac{n_{ij}(r)}{4\pi r^2 \mathrm{d}r\rho_i} - 1\right]$$





THÉORIE

ANALYTIQUE

DE LA CHALEUR,

PAR M. FOURIER.

ASTOR LIBRARY
NEW-YORK

A PARIS,

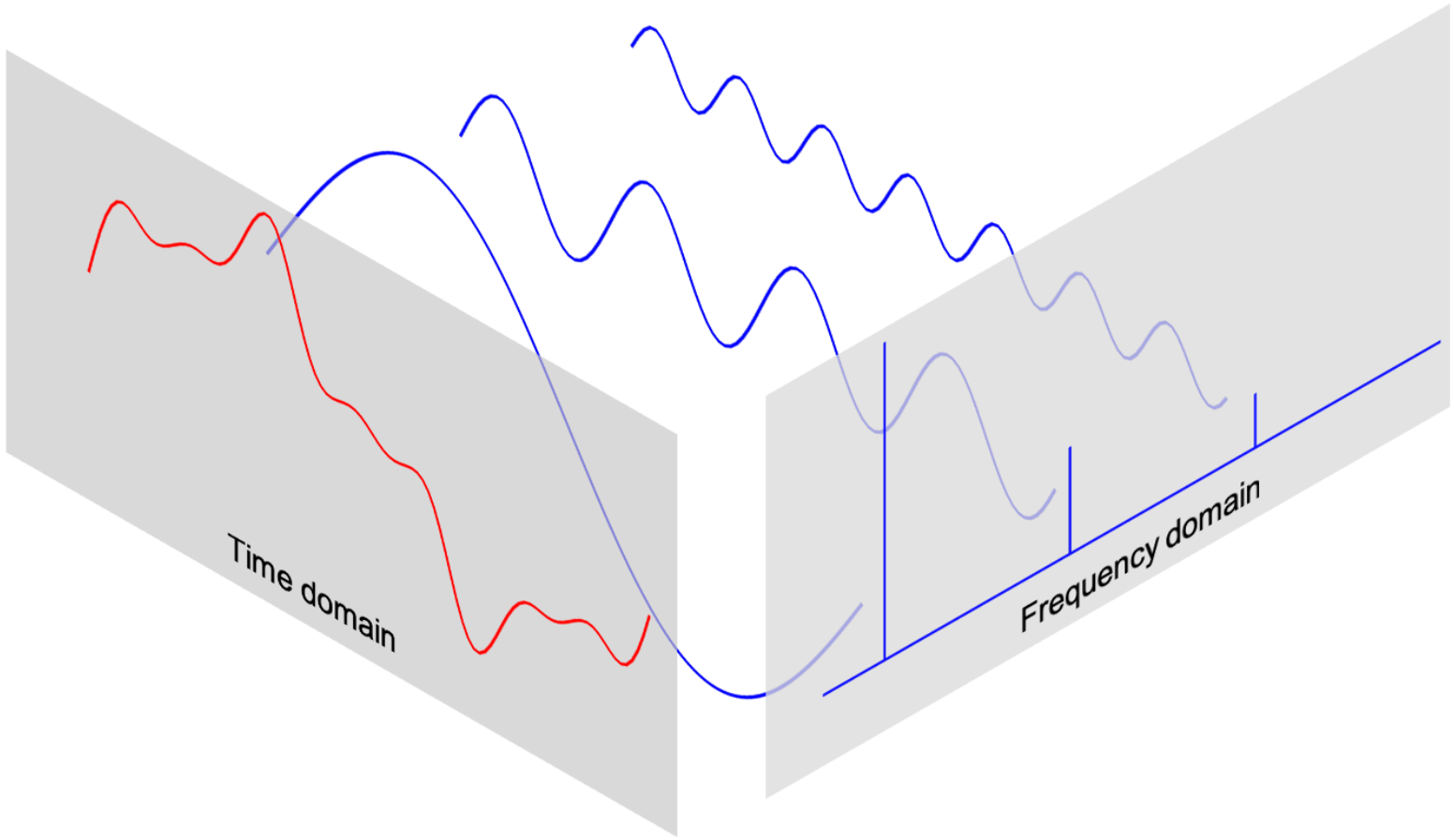
CHEZ FIRMIN DIDOT, PÈRE ET FILS,

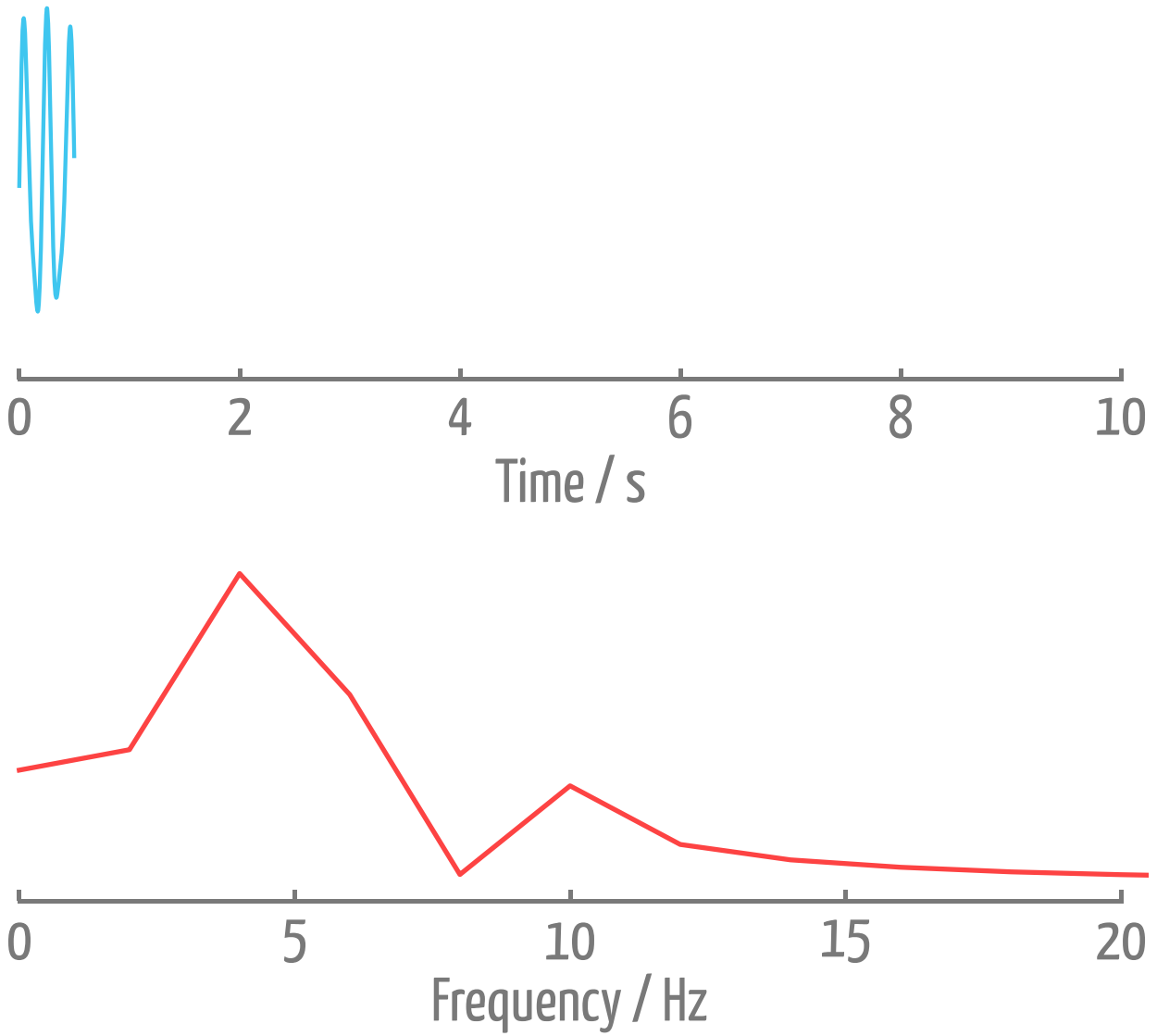
LIBRAIRES POUR LES MATHÉMATIQUES, L'ARCHITECTURE HYDRAULIQUE ET LA MARINE, RUE JACOB, N° 24.

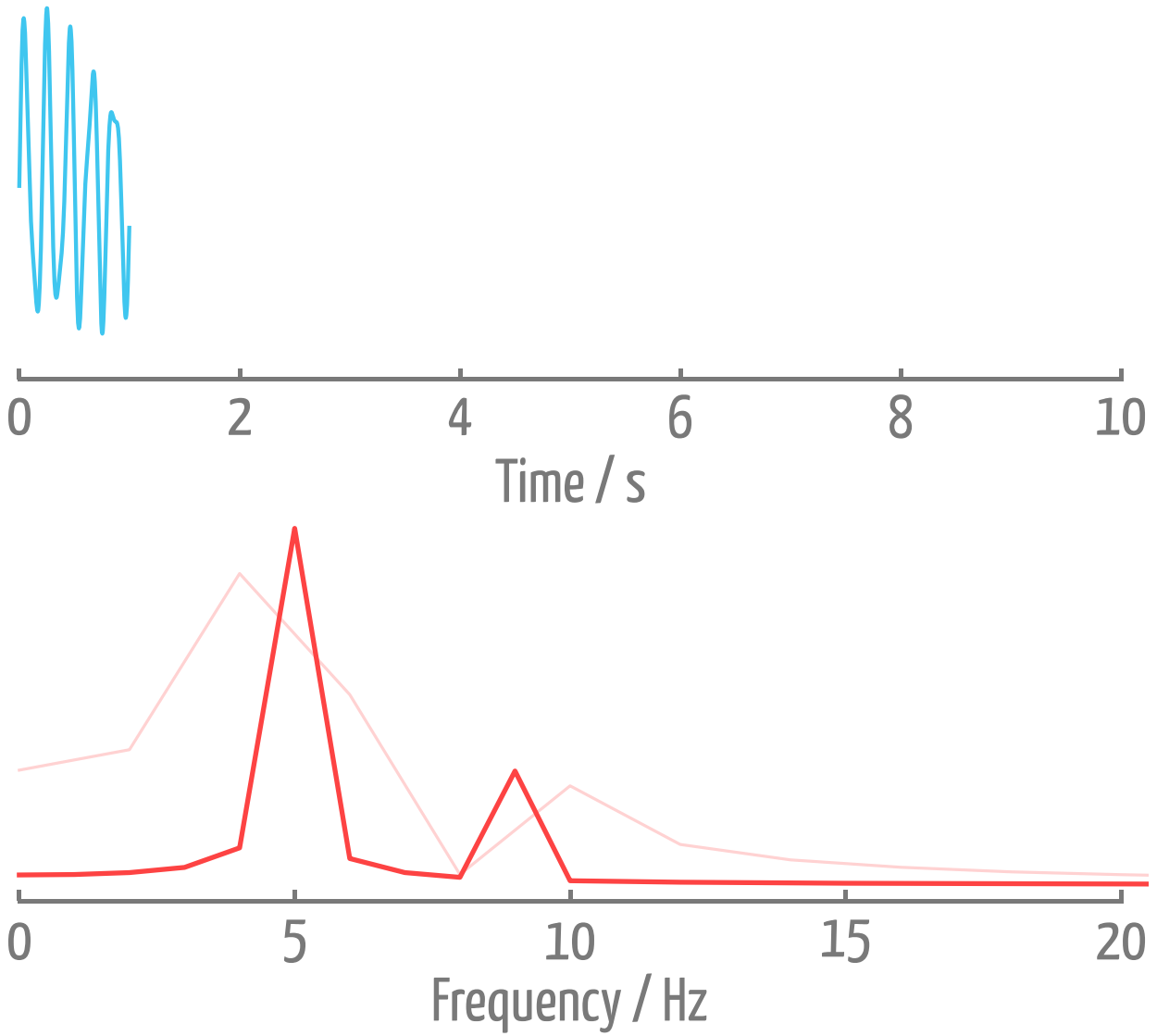
1822.

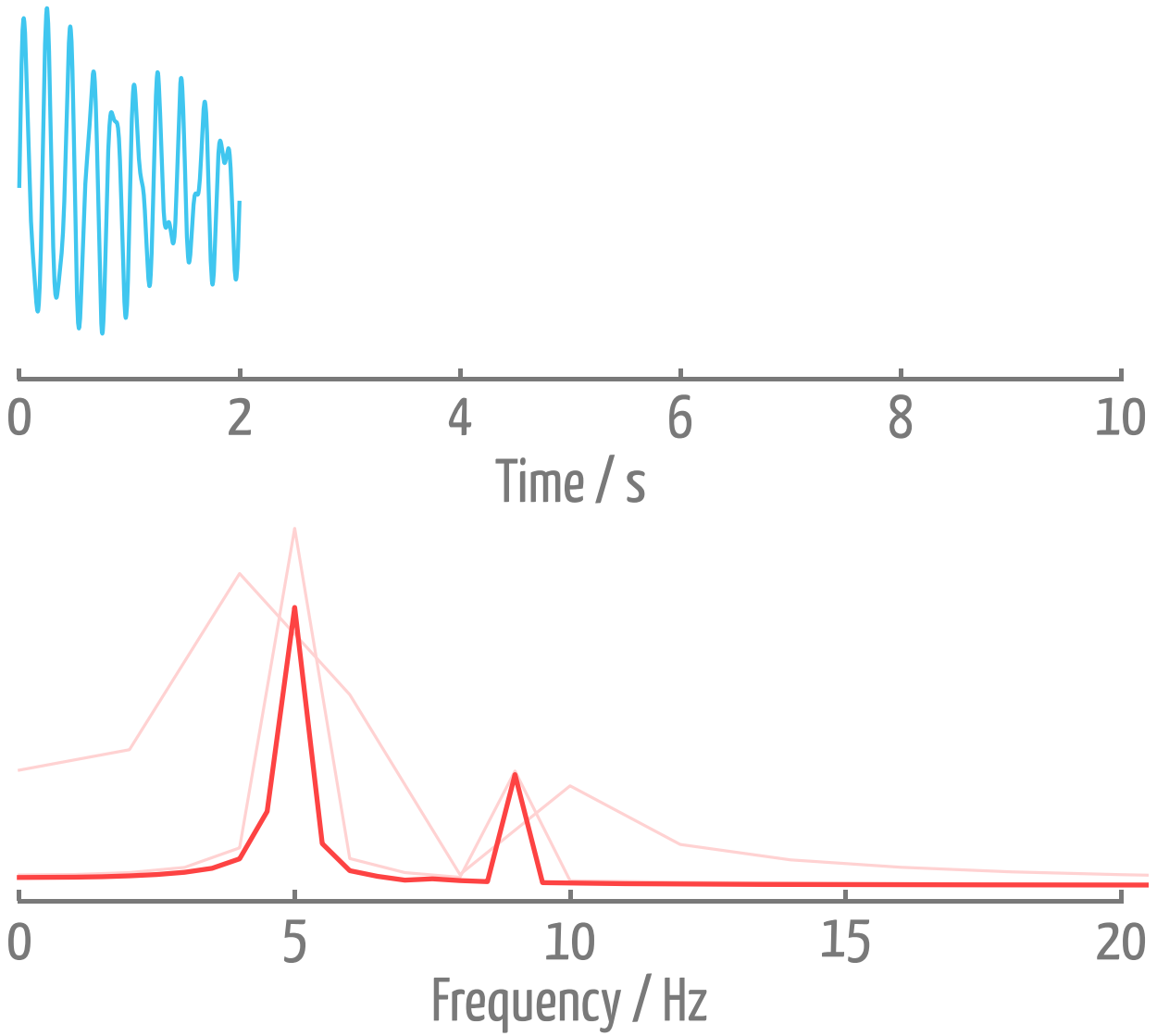
By Louis-Léopold Boilly - https://www.gettyimages.com.au/license/169251384, Public Domain, https://commons.wikimedia.org/w/index.php?curid=33084447

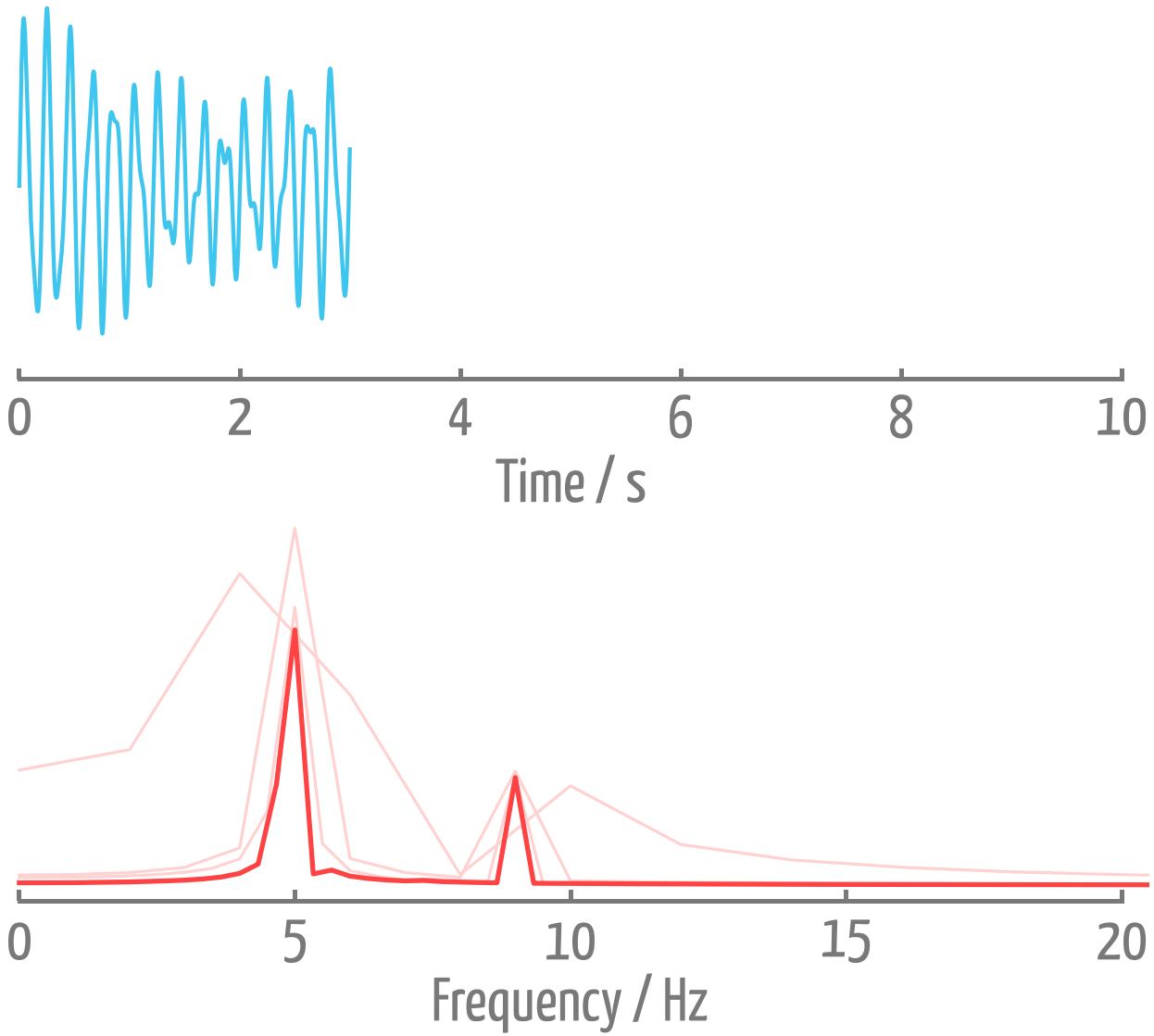
FOURIER TRANSFORMS

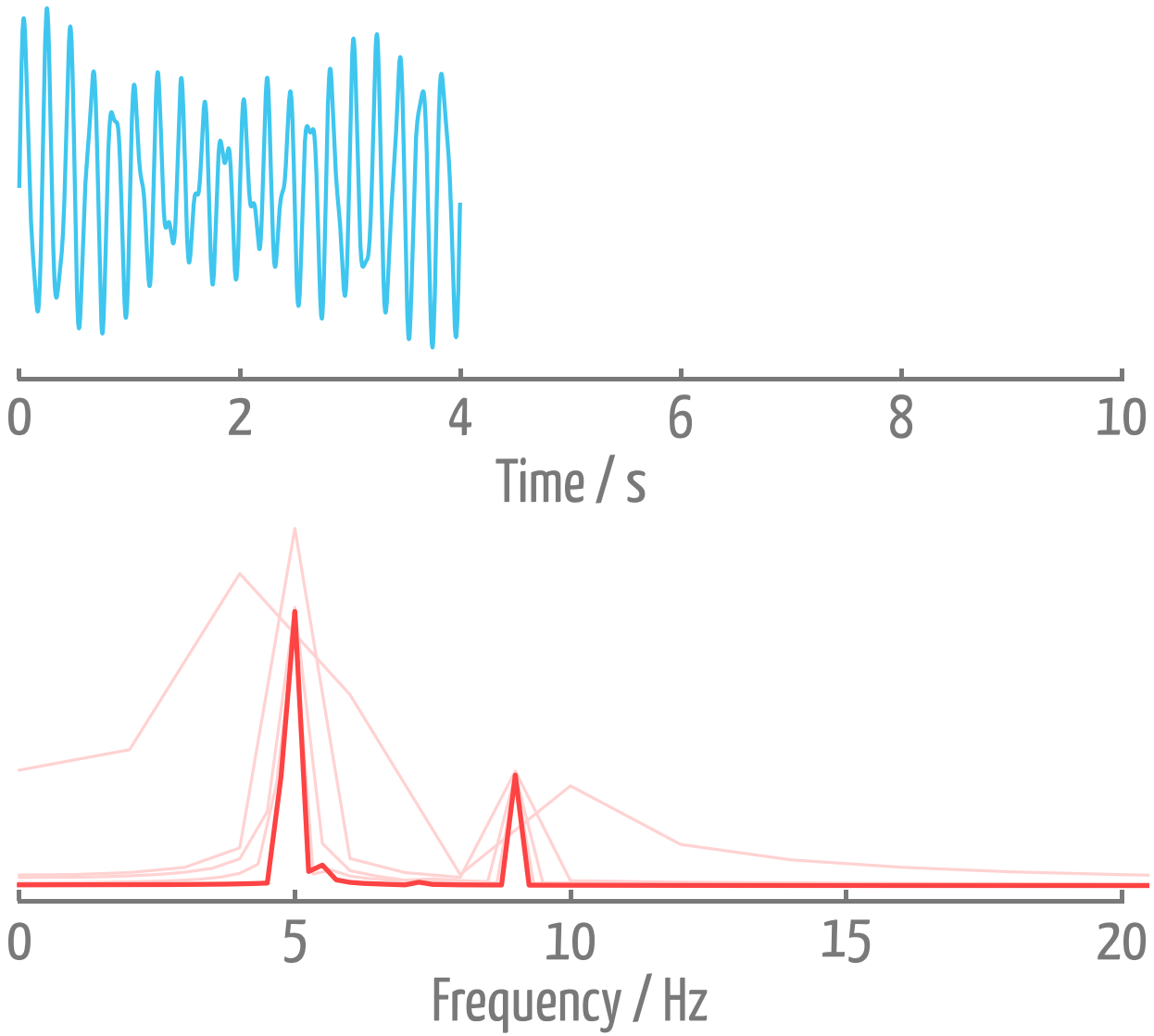


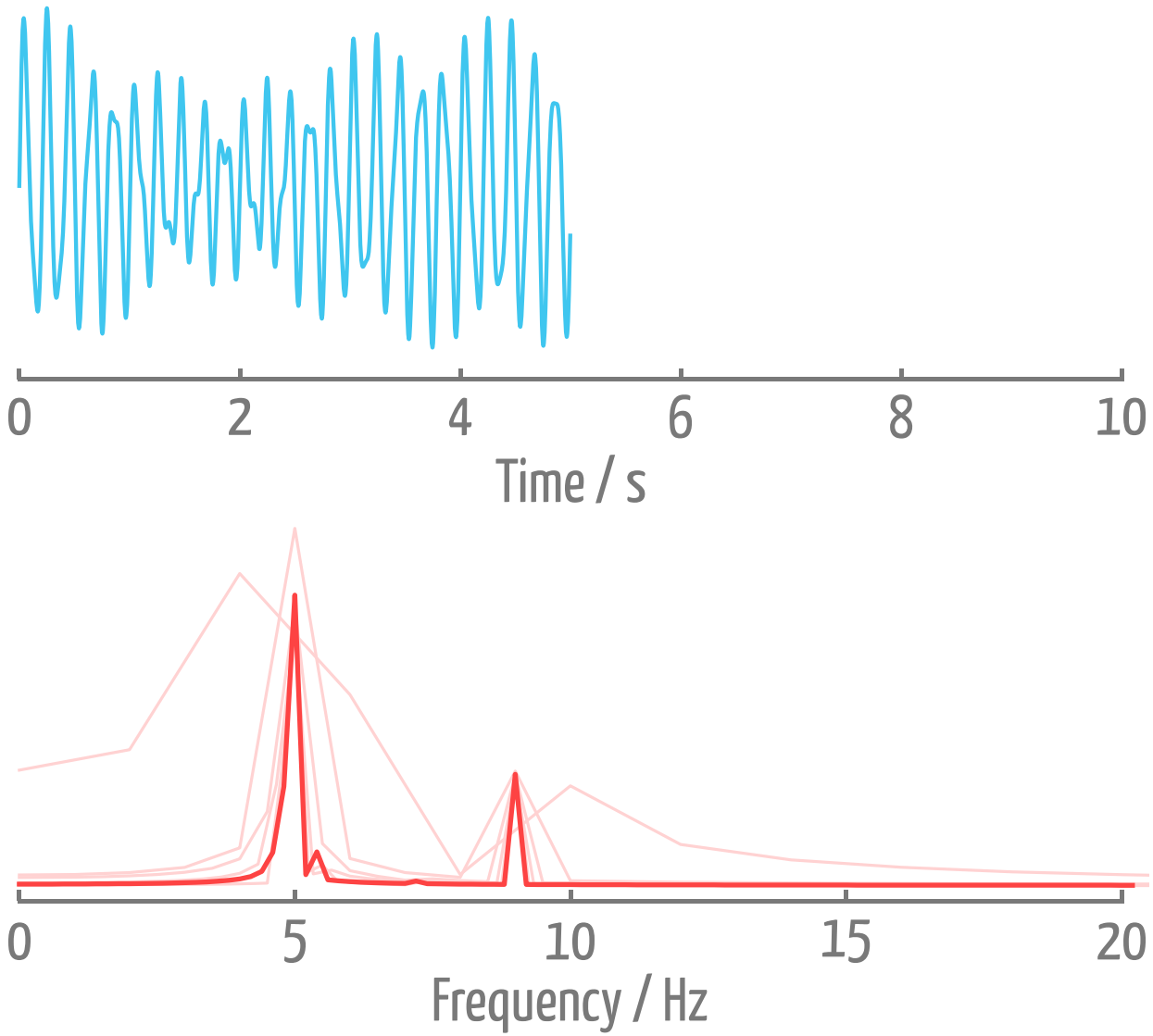

0
2
4
6
8
10
Time / s
0
5
10
15
20
Frequency / Hz

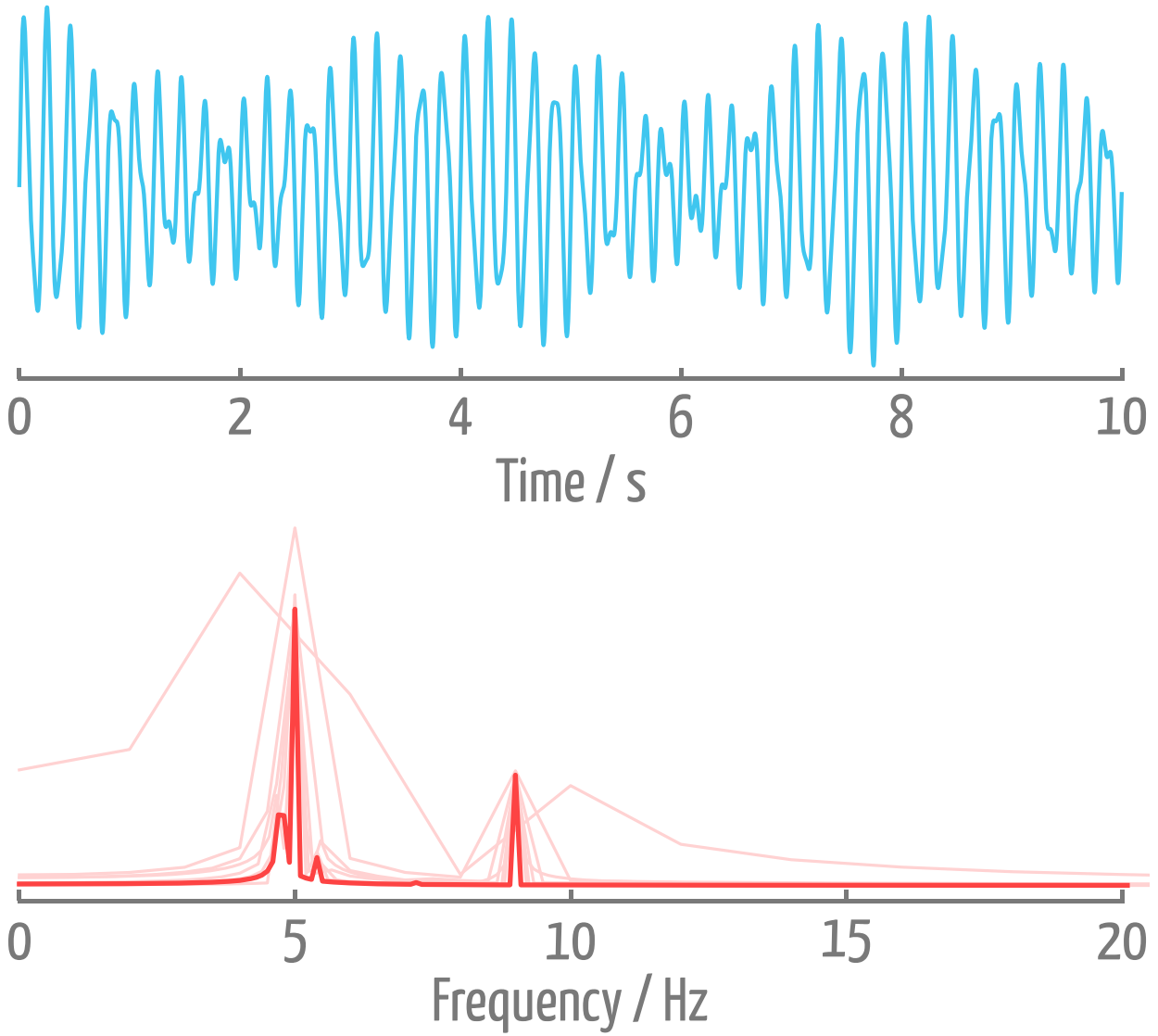

0
2
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Time / s
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Frequency / Hz

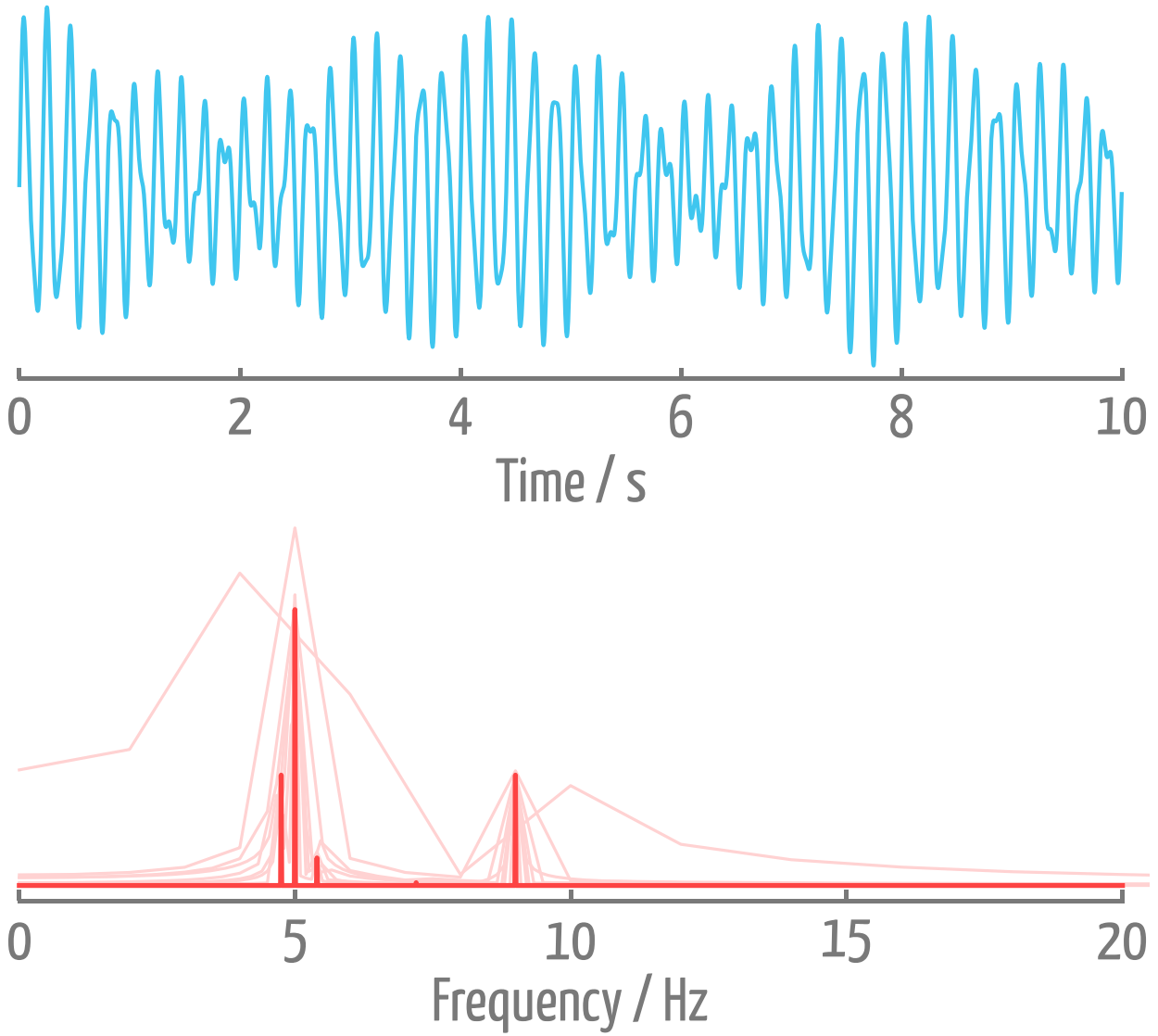

0
2
4
6
8
10
Time / s
0
5
10
15
20
Frequency / Hz


0
2
4
6
8
10
Time / s
0
5
10
15
20
Frequency / Hz


0
2
4
6
8
10
Time / s
0
5
10
15
20
Frequency / Hz


0
2
4
6
8
10
Time / s
0
5
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15
20
Frequency / Hz


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4
6
8
10
Time / s
0
5
10
15
20
Frequency / Hz

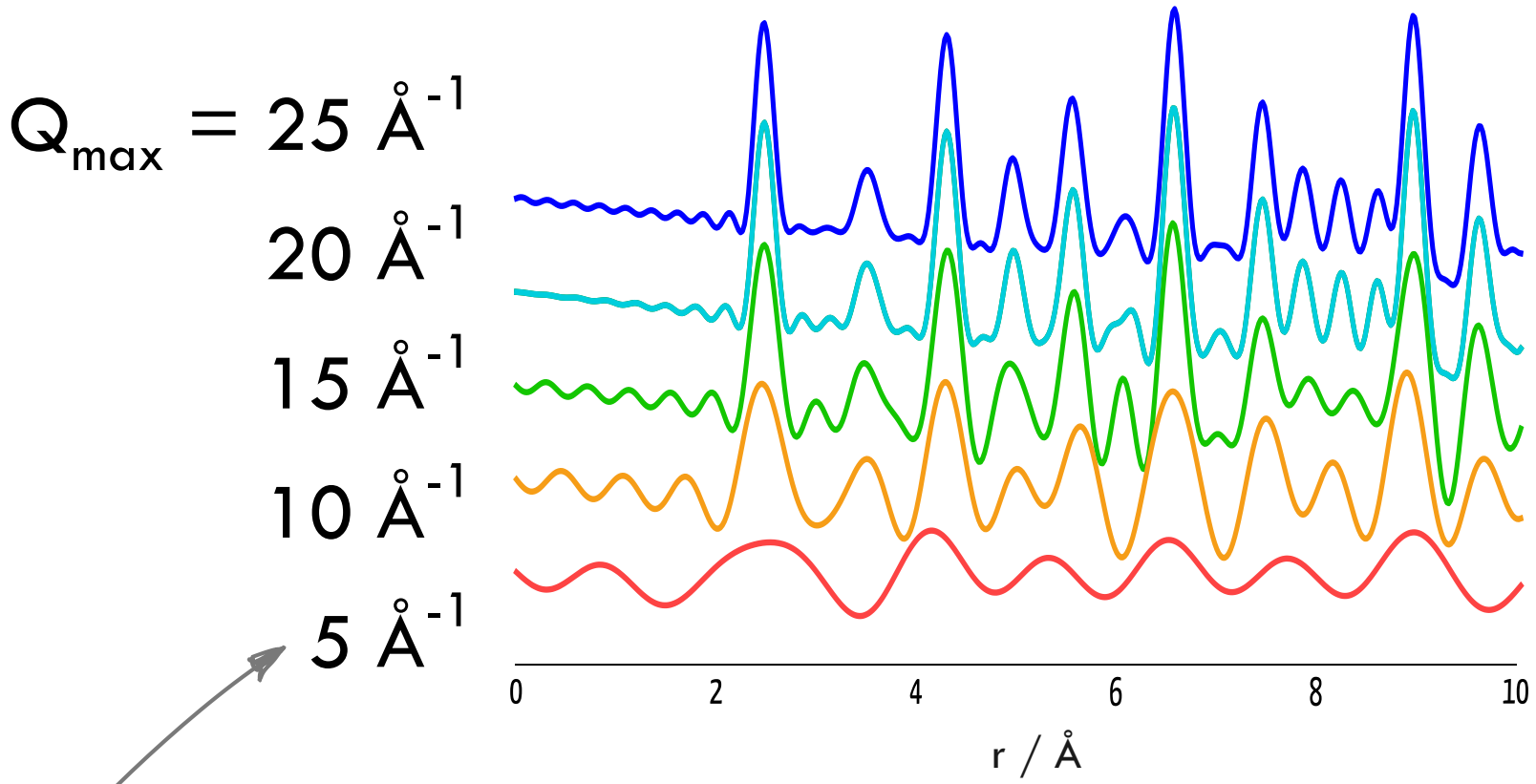

0
2
4
6
8
10
Time / s
0
5
10
15
20
Frequency / Hz

Real-space resolution

depends on

Reciprocal-space extent

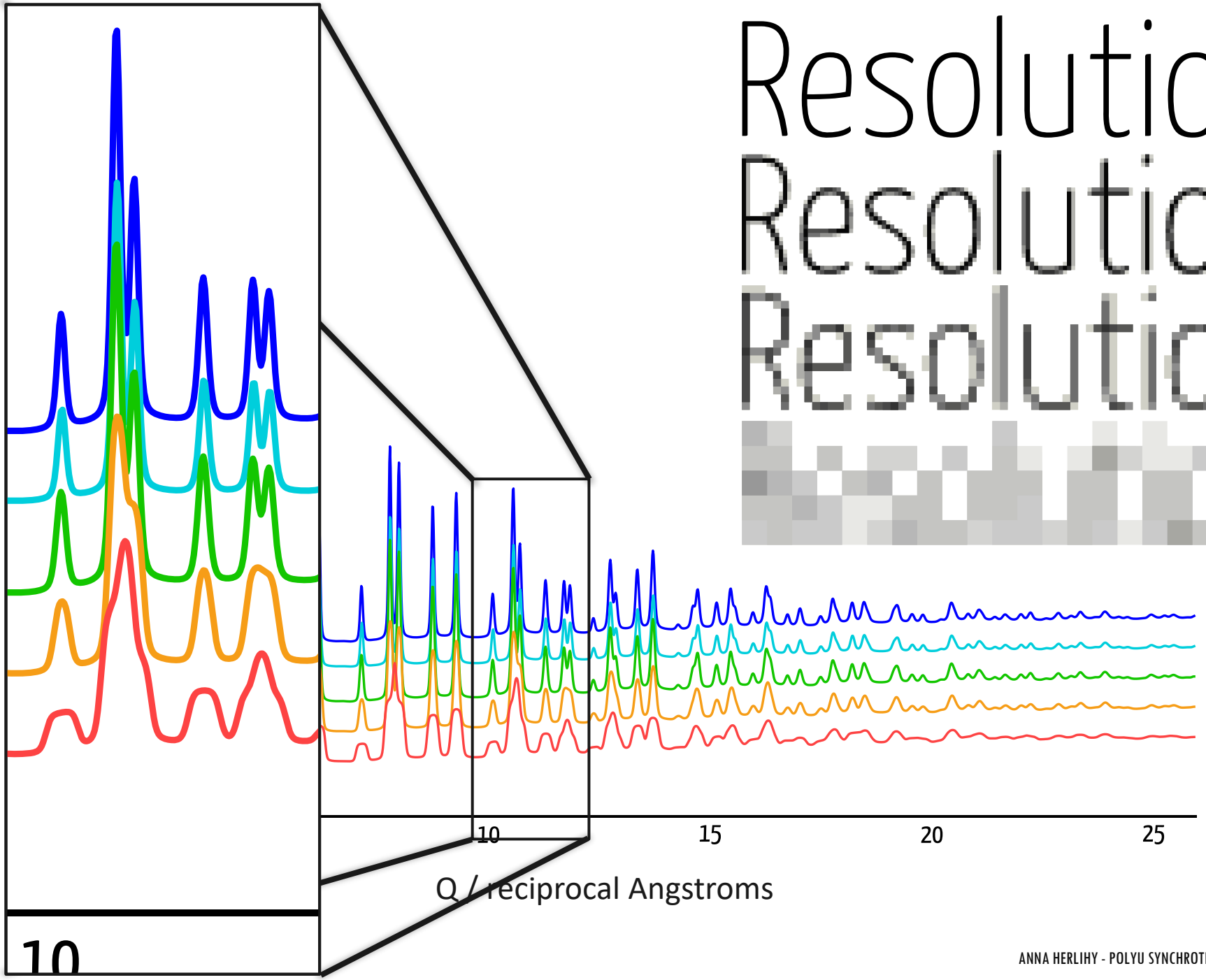
REAL SPACE RESOLUTION ⟷ RECIPROCAL-SPACE EXTENT

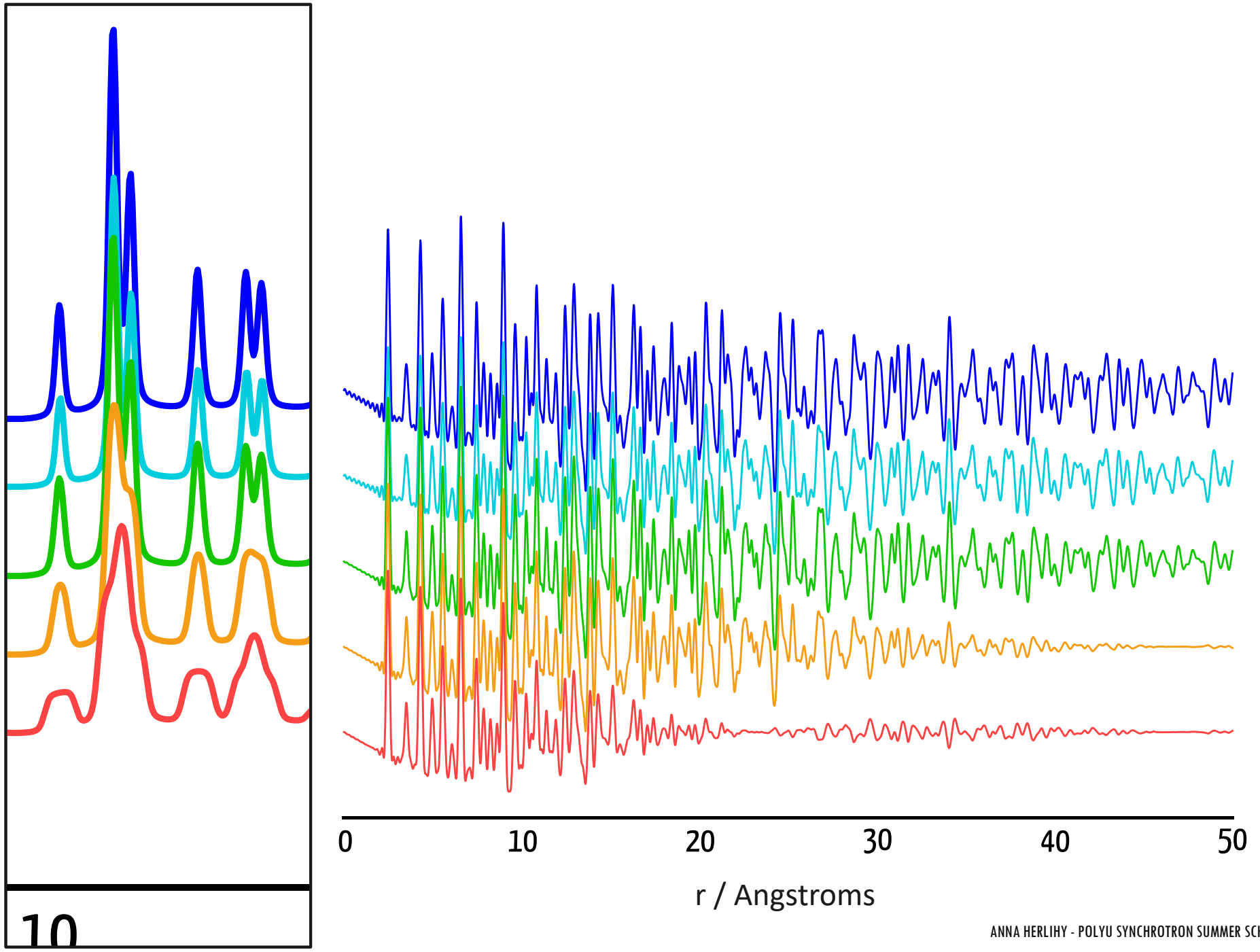


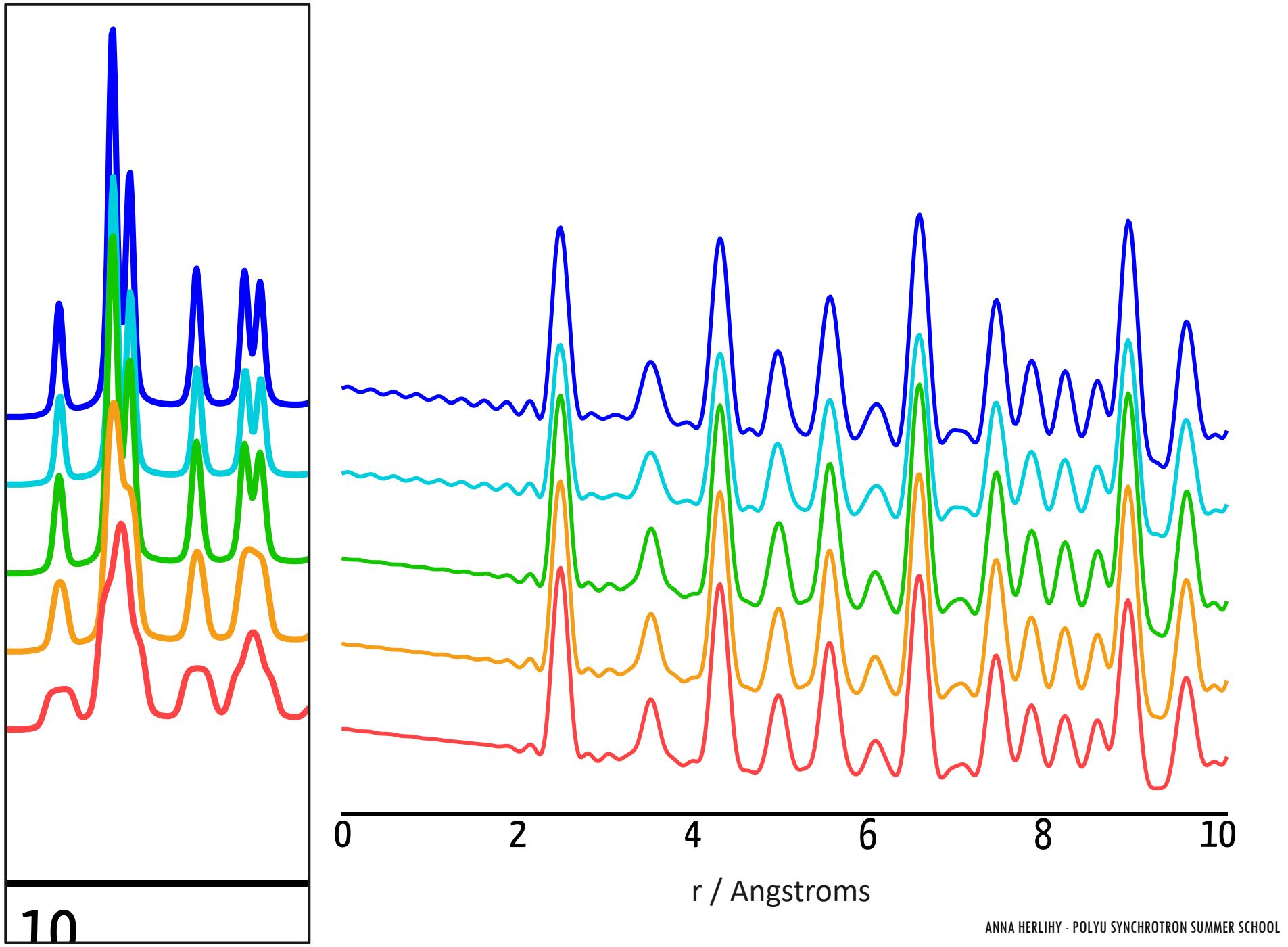
Bragg angle of 76° 2θ for CuKα radiation

Resolution

Resolution
Resolution
Resolution




10
0
10
20
30
40
50
r / Angstroms


10
0
2
4
6
8
10
r / Angstroms

Real-space **extent**

depends on

Reciprocal-space **resolution**

FOURIER TRANSFORMS : A SUMMARY

Fourier transforms move from a *space* to its *reciprocal space*; the easiest example being time and frequency

We're interested in the PDF which exists in real space, and we transform from momentum transfer space (or Q-space, or reciprocal-space)

FOURIER TRANSFORMS : A SUMMARY

To measure the frequencies (lengths) accurately we need to collect for a long time (momentum transfer)

To measure high frequencies (lengths) we need to collect very small time (momentum transfer) steps

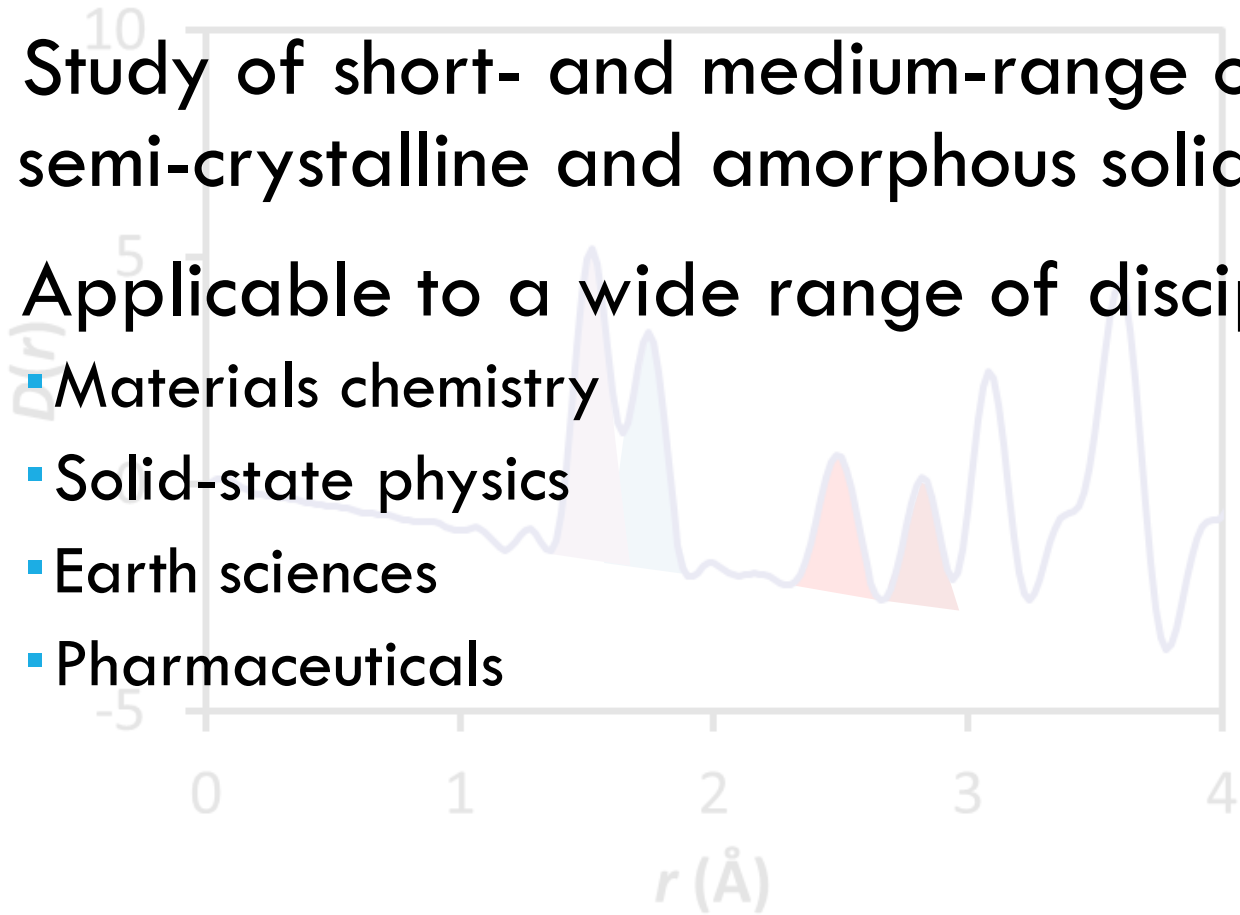
WHAT IS A PDF?

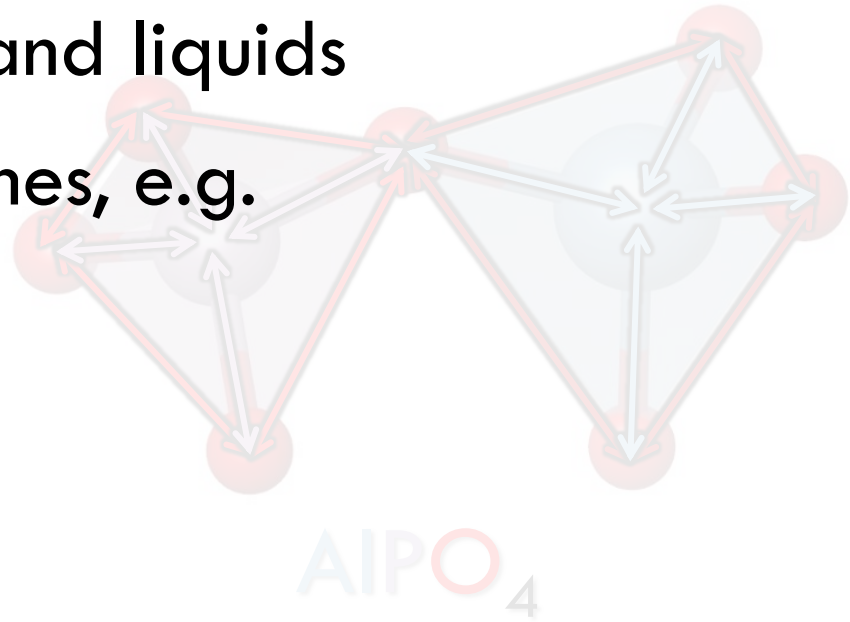
Probability of finding two atoms at a given separation, *r*

Study of short- and medium-range order in crystalline, semi-crystalline and amorphous solids and liquids

Applicable to a wide range of disciplines, e.g.

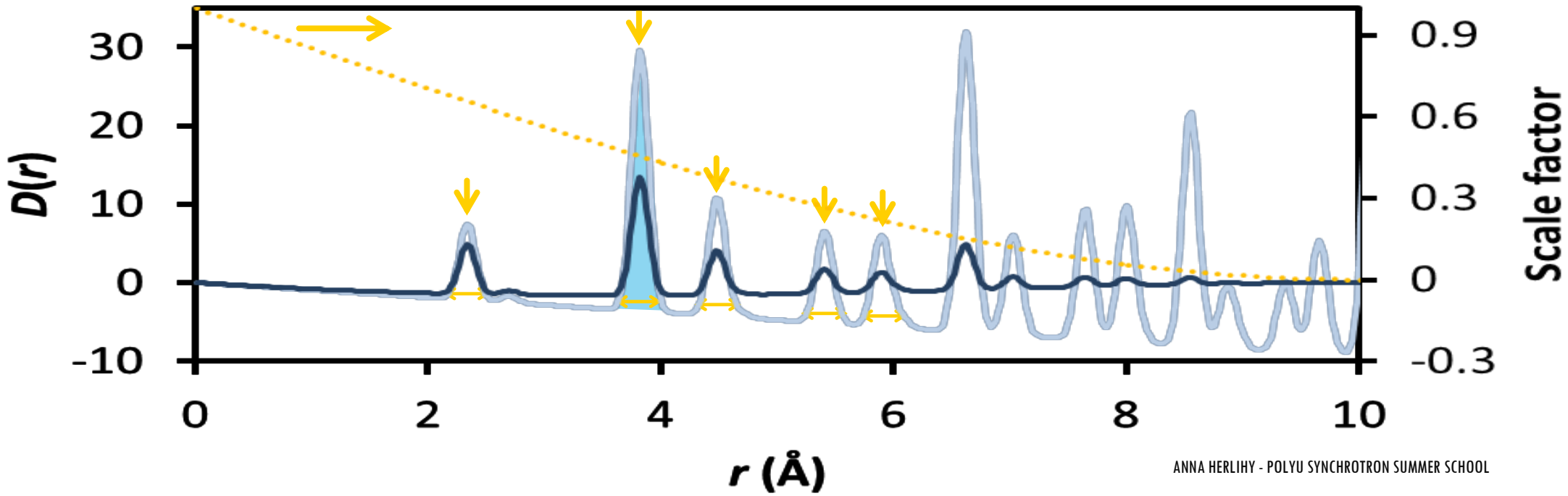
- Materials chemistry
- Solid-state physics
- Earth sciences
- Pharmaceuticals



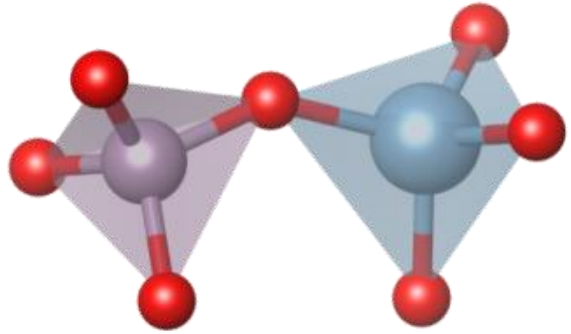


WHAT IS A PDF?

- Peak positions: Bond lengths, geometry, unit cell
- Peak areas: Coordination number, occupancies
- Peak widths: Vibrations, phonons, disorder
- Peak damping: Size, shape

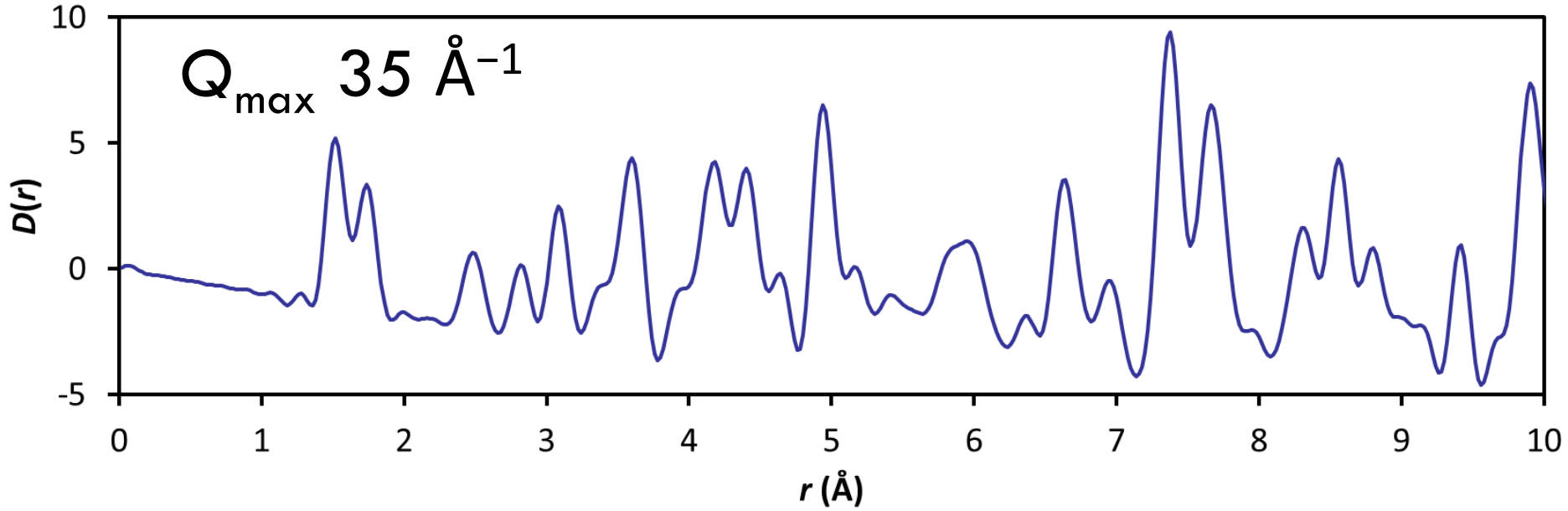


REQUIREMENTS FOR QUALITY PDF DATA



- High Q_{max}
  - Resolution of a PDF is dominated by Q_{max}
    - $Q = 2\pi/d = 4\pi\sin\theta/\lambda$
    - $\Delta r \approx 2\pi/Q_{max}$
    - Sample limited resolution if $Q_{max} > 3/\langle\langle u^2\rangle\rangle^{1/2}$ †

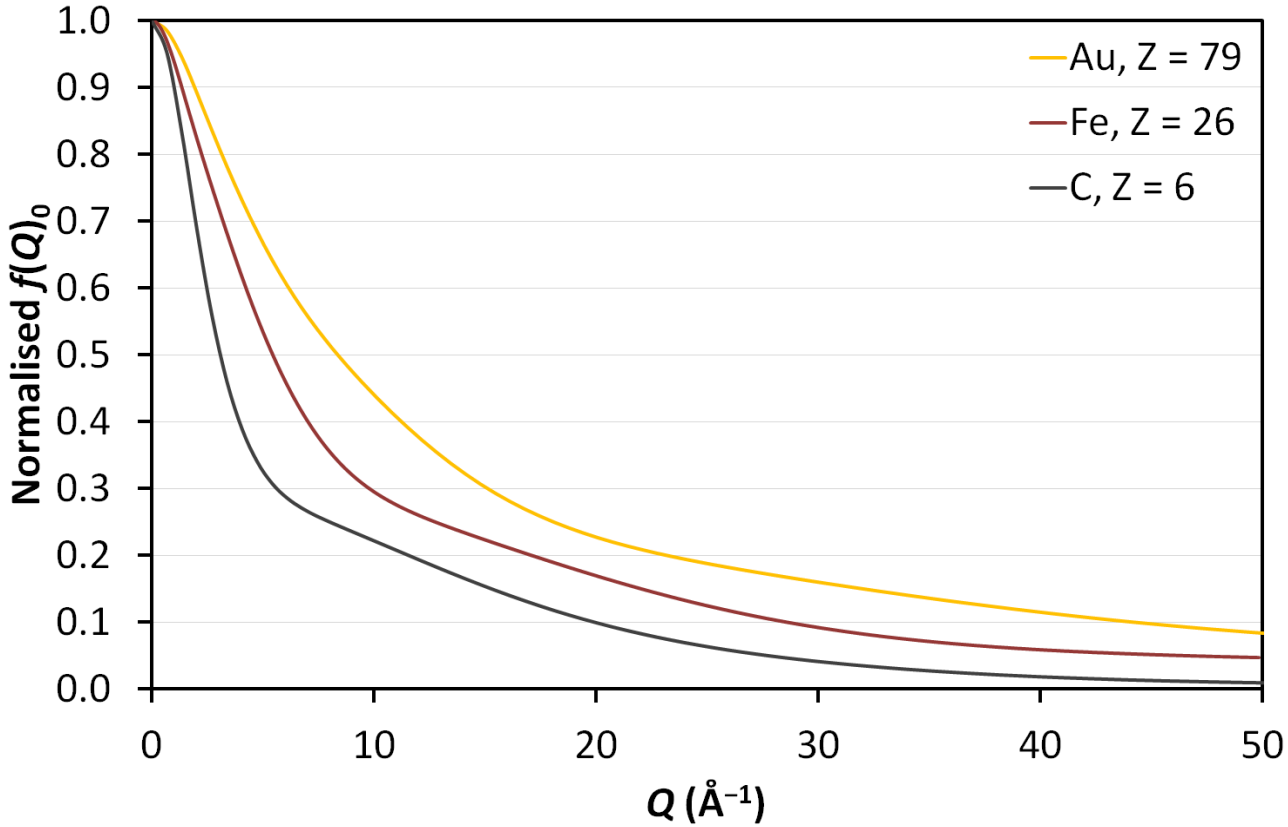
$\Delta r = 0.18$ Å



†B. H. Toby and T. Egami, *Acta Cryst. A*, **48** (1992) 336

REQUIREMENTS FOR QUALITY PDF DATA

- High Q_{max}
- High flux
  - X-ray form factors fall off dramatically with Q



REQUIREMENTS FOR QUALITY PDF DATA

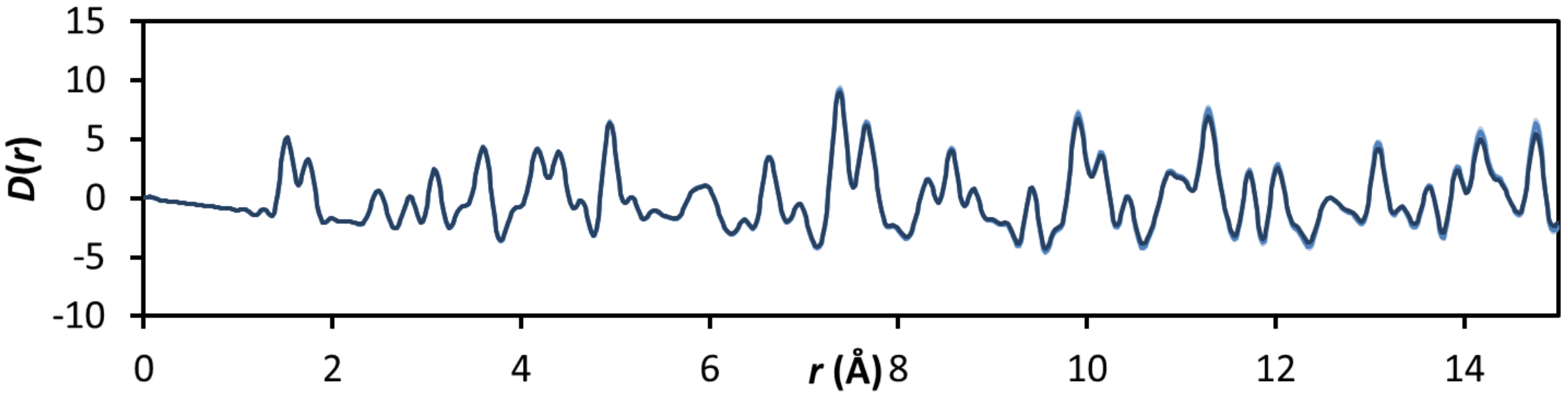
- High Q_{max}
- High flux
- Low (and reproducible) background

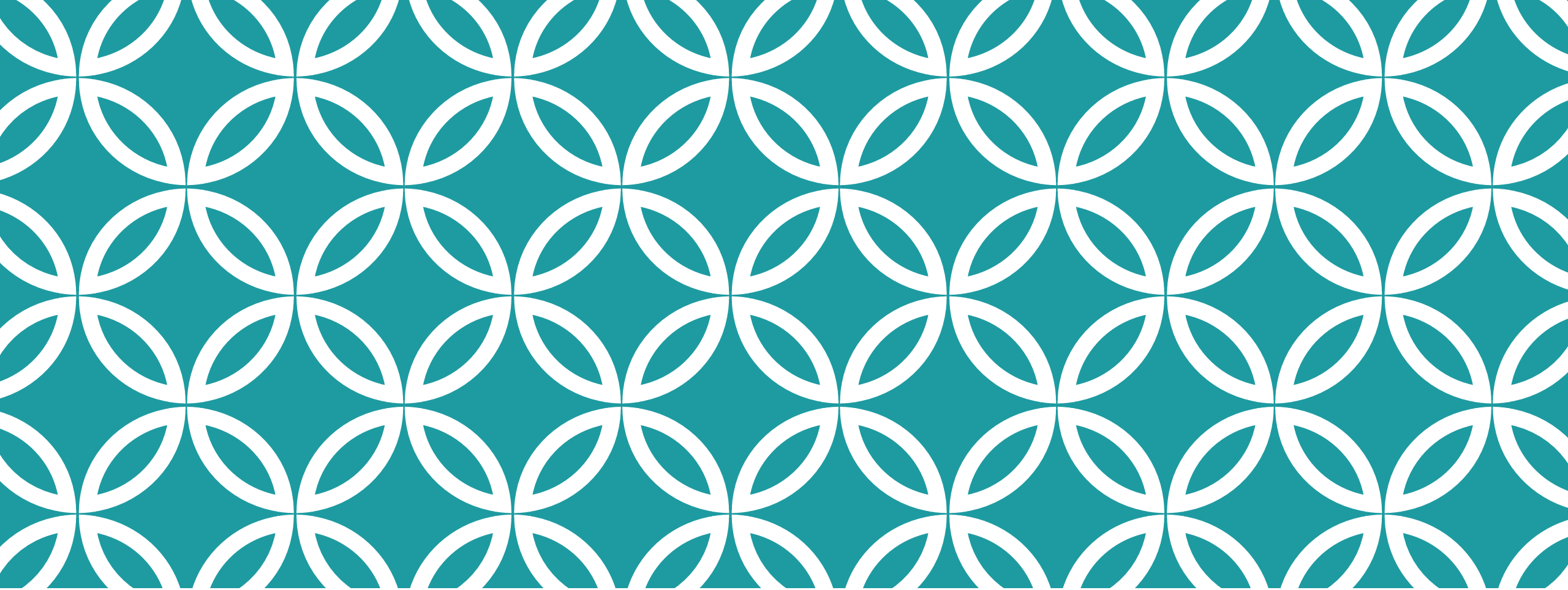




REQUIREMENTS FOR QUALITY PDF DATA

- High Q_{max}
- High flux





TYPES OF PDF

D(r), G(r), G'(r), etc

research papers

Journal of
Applied
Crystallography

ISSN 0021-8898

Received 31 July 2000
Accepted 8 December 2000

A comparison of various commonly used correlation functions for describing total scattering

David A. Keen

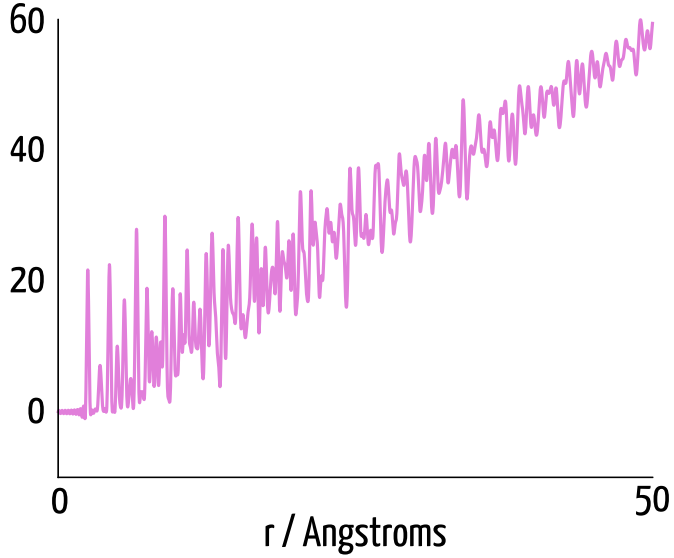
ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, England.
Correspondence e-mail: d.a.keen@rl.ac.uk

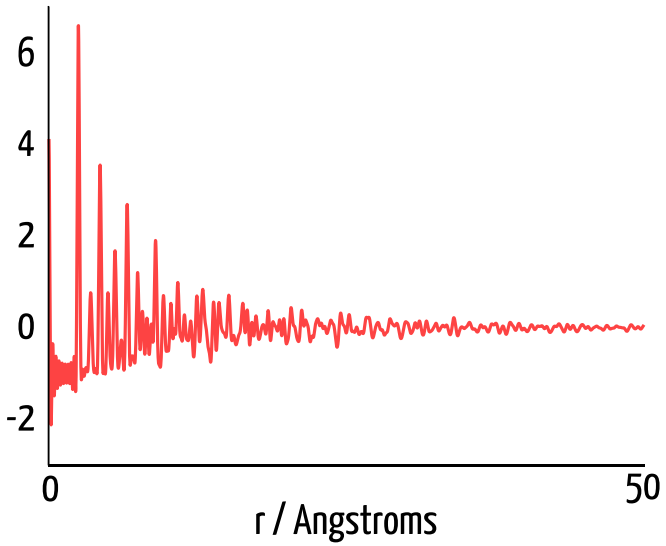
Total scattering, an increasingly important crystallographic research area, is defined theoretically in terms of correlation functions. Different researchers use different definitions for these functions, frequently leading to confusion in the literature. Here, a consistent set of equations for total-scattering correlation functions are developed and explicitly compared with other, often encountered, definitions. It is hoped that this will lead to increased transparency for newcomers to the field of total scattering.

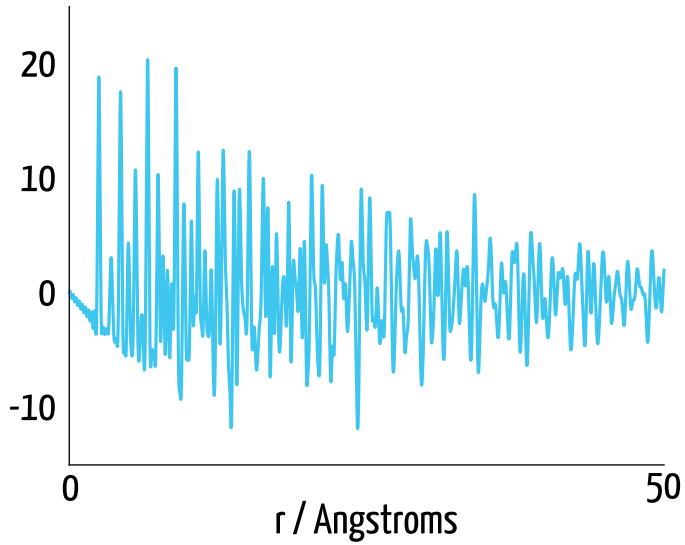
© 2001 International Union of Crystallography
Printed in Great Britain – all rights reserved

J. Appl. Cryst. (2001). **34**, 172-177

THE PDF NORMALLY COMES IN ONE OF THREE FLAVOURS







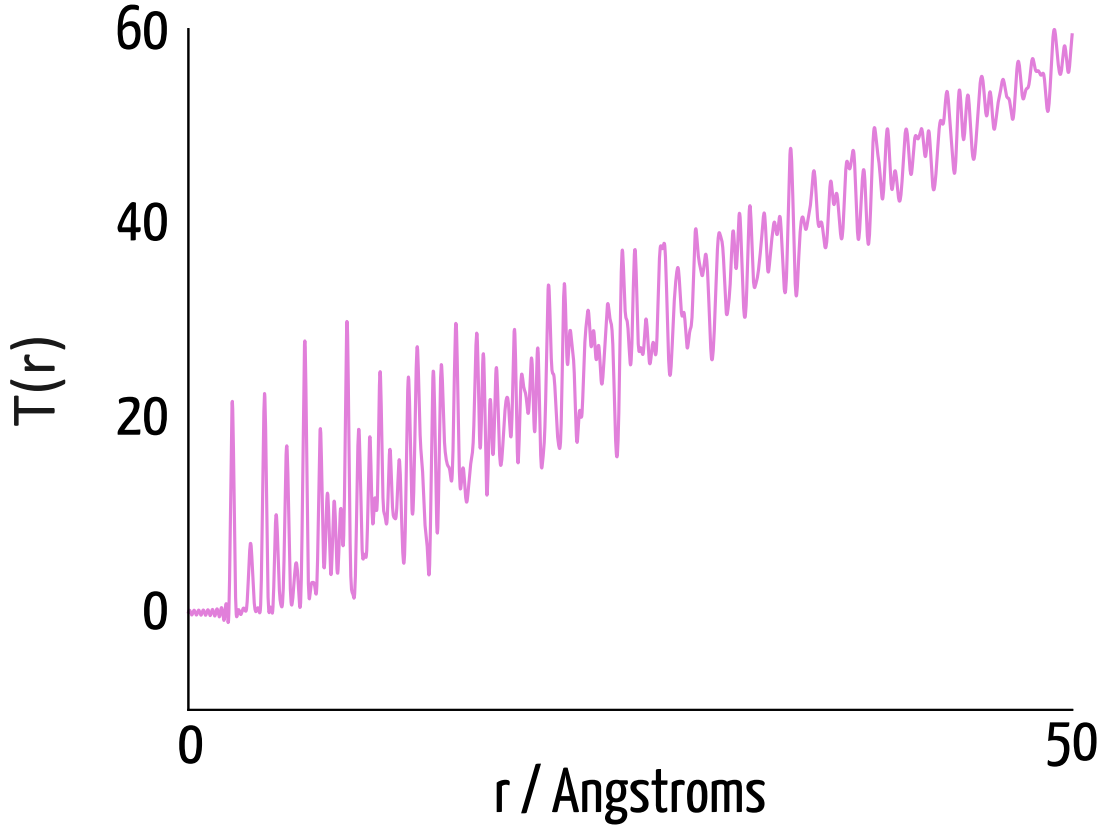
THE GLASS AND FLUIDS ONE

Starts at 0

Ends at ∞

Probably the most intuitive

Rarely used



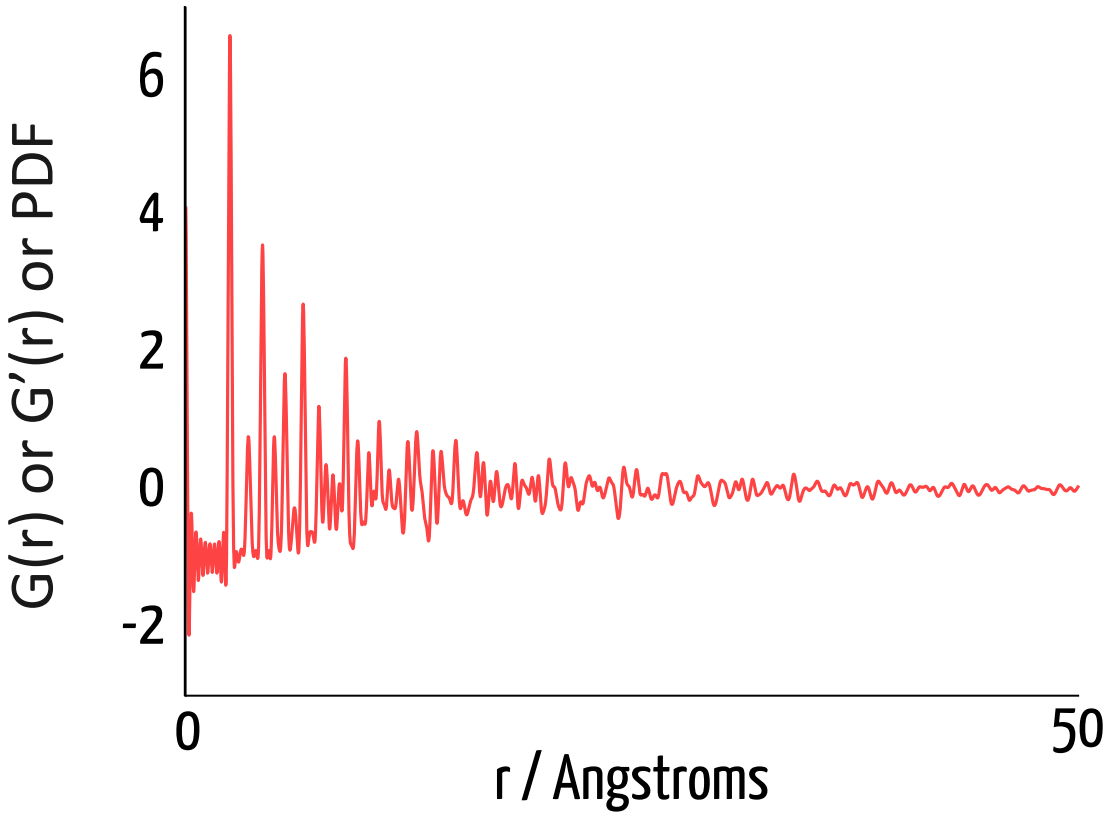
THE FLAT-LOOKING ONE

Starts at -ve *

Ends at 0 *

Emphasises low-r region

Suppresses high-r region



* normally

THE ONE WITH THE SLOPING BACKGROUND

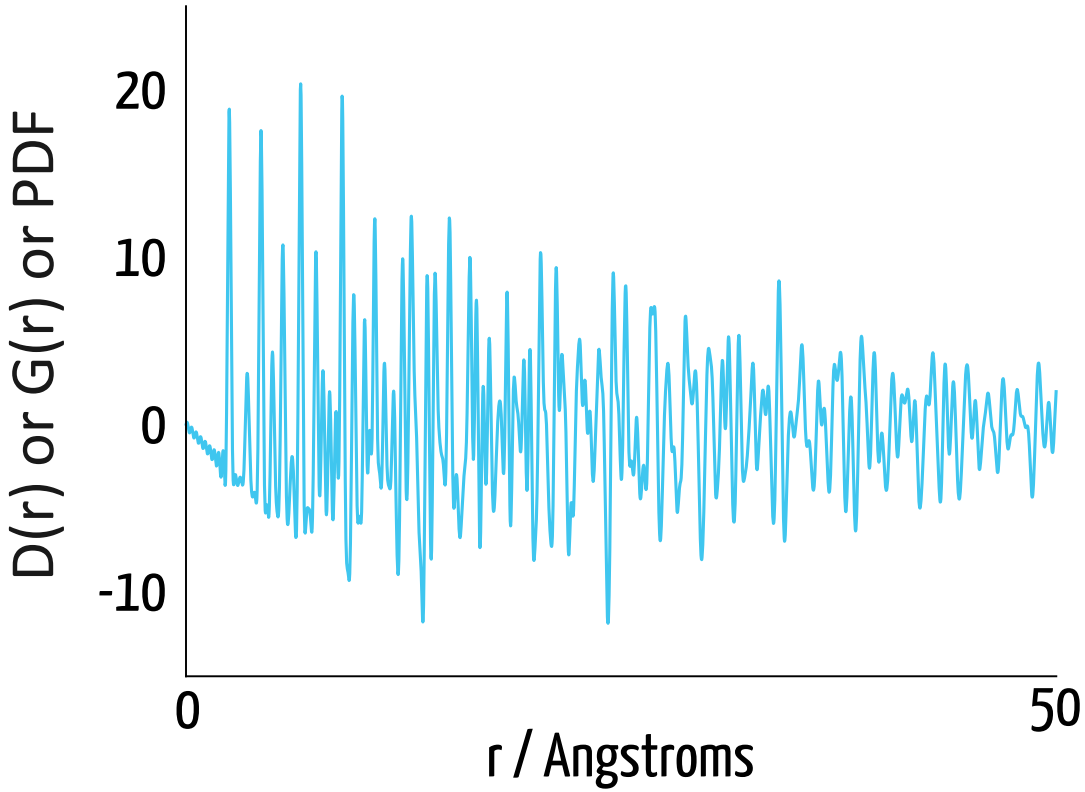
Starts at 0

Ends at 0

Emphasises high-r region

Suppresses low-r region

Is the fluids one but straightened out



REQUIREMENTS FOR QUALITY PDF DATA

- High Q_{max}
- High flux
- Low (and reproducible) background
- Moderate Q resolution

DIAMOND LIGHT SOURCE

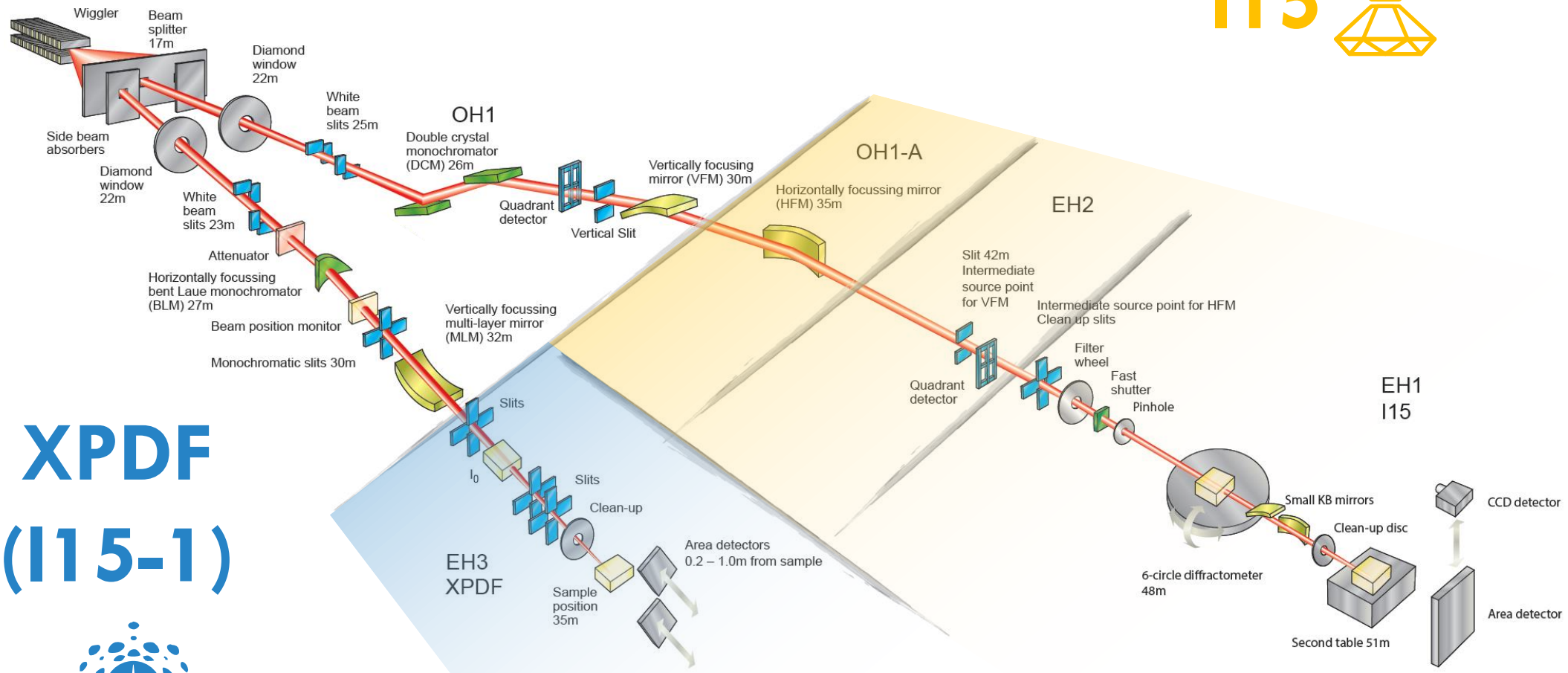


diamond

THE XPDF BEAMLINE

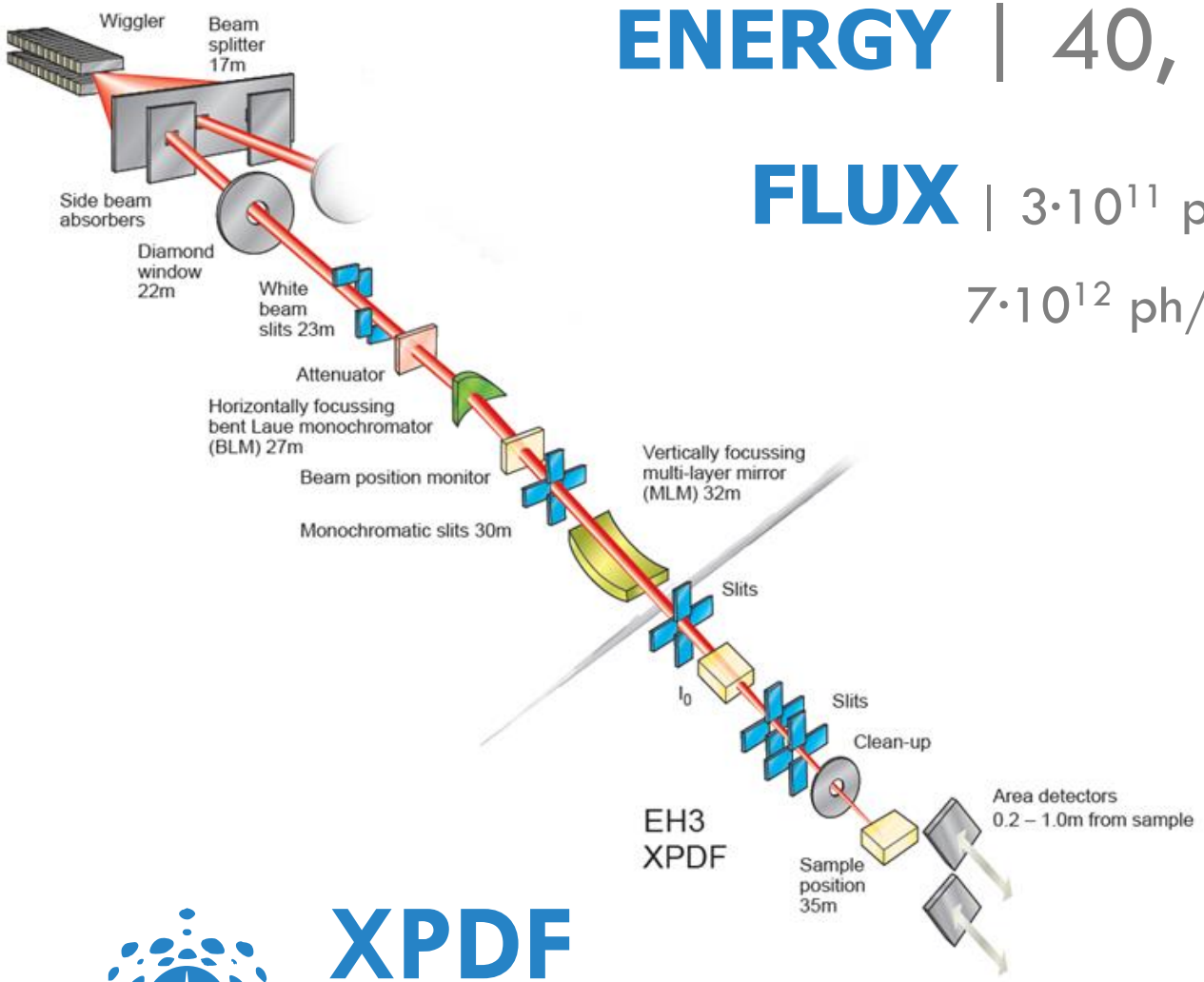
Extreme conditions

I15



XPDF

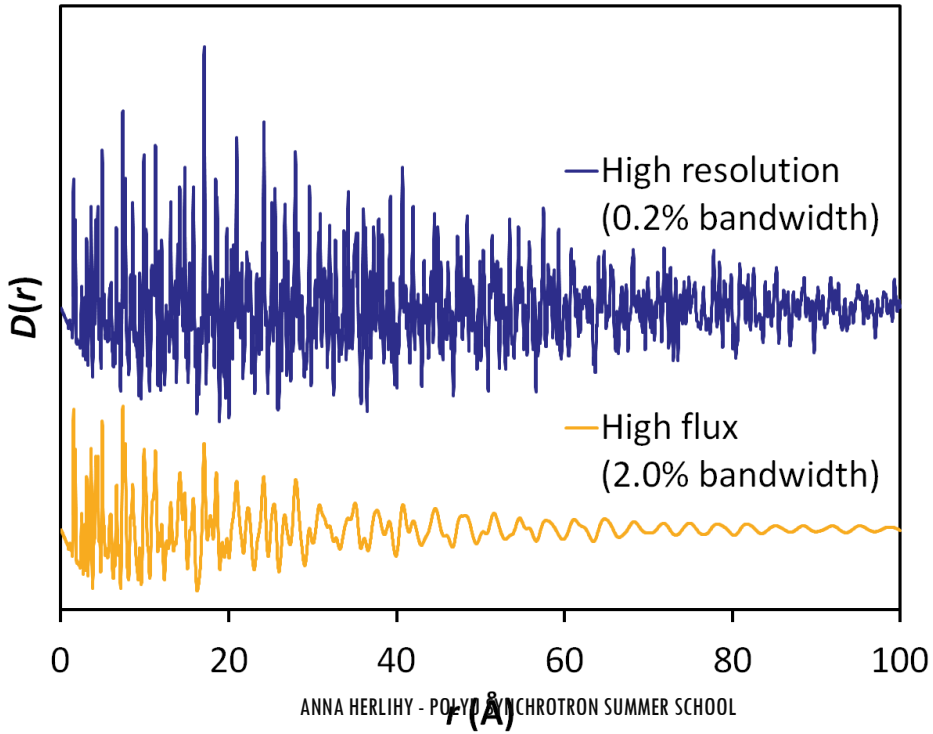
(I15-1)



ENERGY | 40, 65 and 76 keV

FLUX | $3 \cdot 10^{11}$ ph/s @ 76 keV 0.9% bw

$7 \cdot 10^{12}$ ph/s @ 76 keV 2.0% bw



XPDF (I15-1)

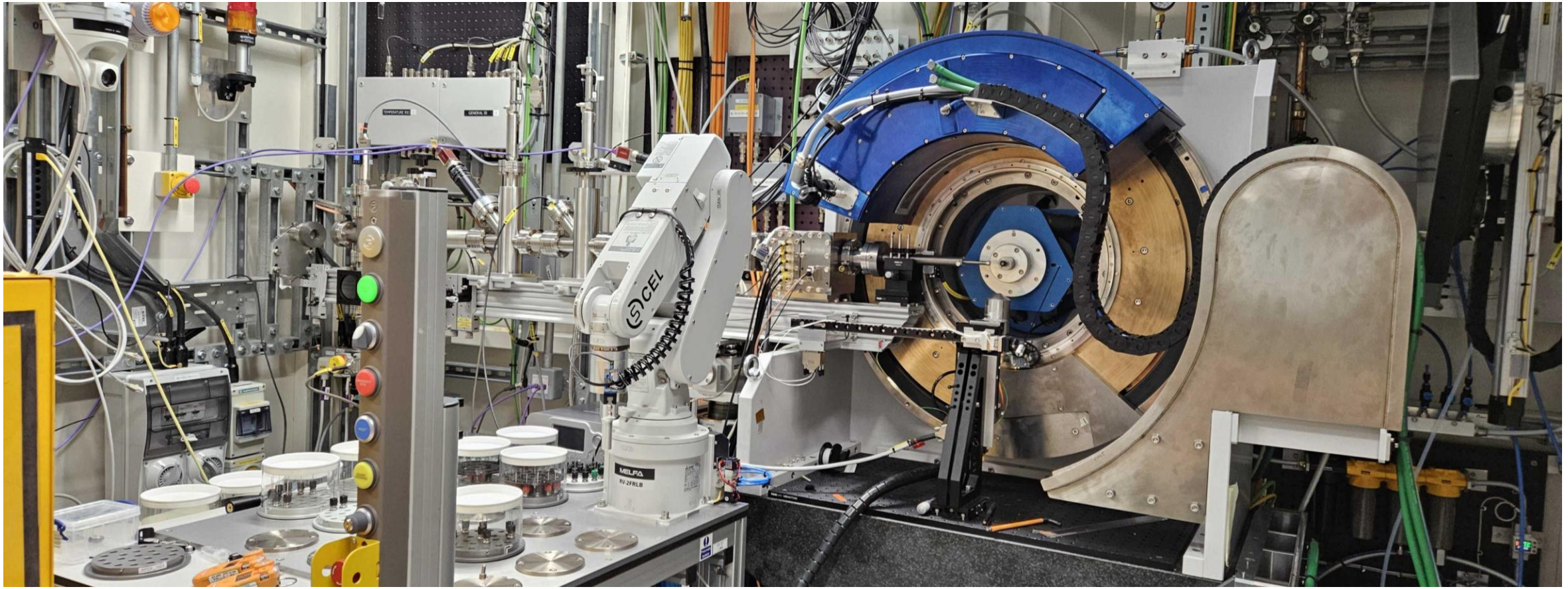
LOW BACKGROUND | Contained beam pipe

| Tunable beamstop

HIGH STABILITY | I_0 beam position control



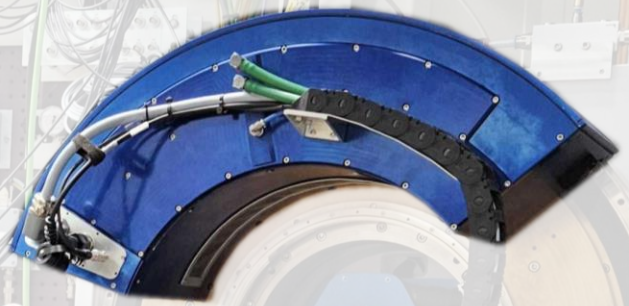
THE XPDF BEAMLINE AT DIAMOND LIGHT SOURCE



E. N. Gimenez, P. A. Chater, G. Crevatin, G. Dennis, A. Fairley, I. Horswell, D. Omar, J. Spiers, N. Tartoni, IEEE Nuclear Science Symposium and Medical Imaging Conference NSS/MIC, 2019, 1–3.

NEW ANGULARLY-RESOLVED CDTE (ARC) DETECTOR

- High real-space resolution mode: Q_{max} of 51 $Å^{-1}$ (~1 minute)
- Rapid mode: Q_{max} of 27 $Å^{-1}$ at 100 Hz (millisecond collections)



E. N. Gimenez, P. A. Chater, G. Crevatin, G. Dennis, A. Fairley, I. Horswell, D. Omar, J. Spiers, N. Tartoni, IEEE Nuclear Science Symposium and Medical Imaging Conference NSS/MIC, 2019, 1–3.

SAMPLE DELIVERY



Capillaries

Capillary holder

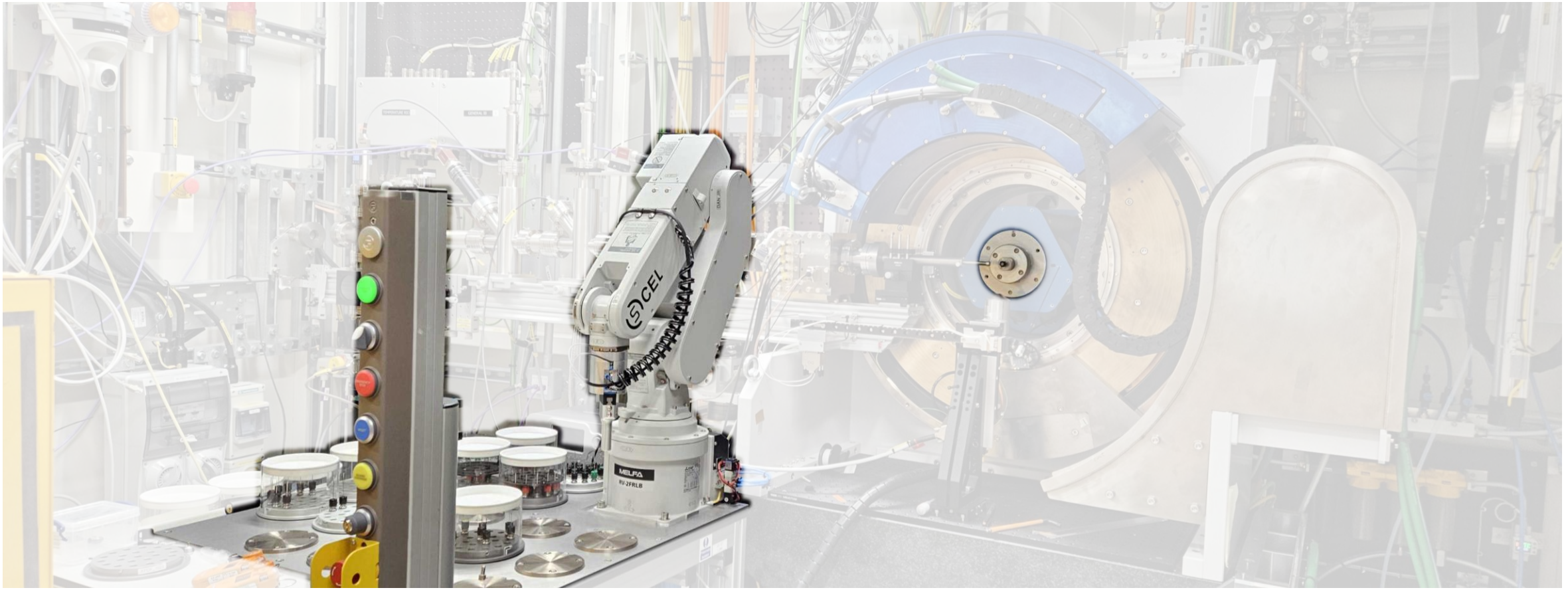


Puck



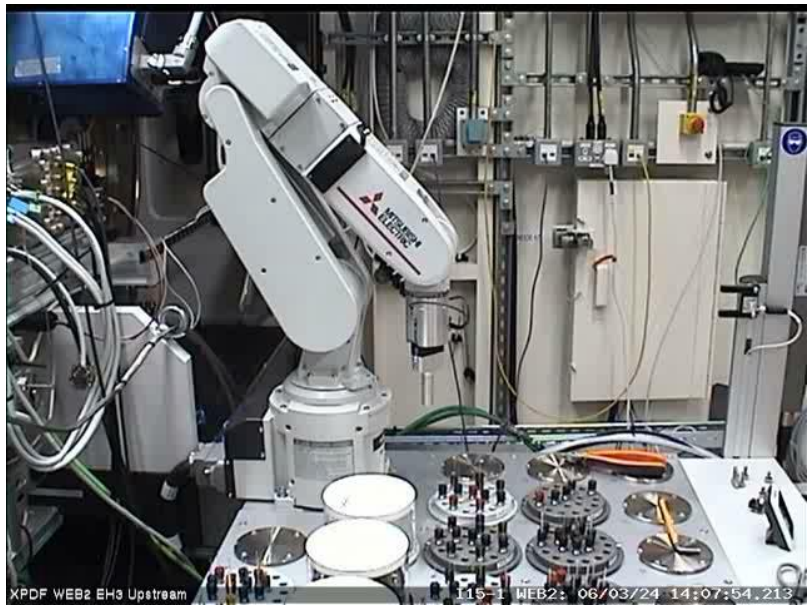
Transport box

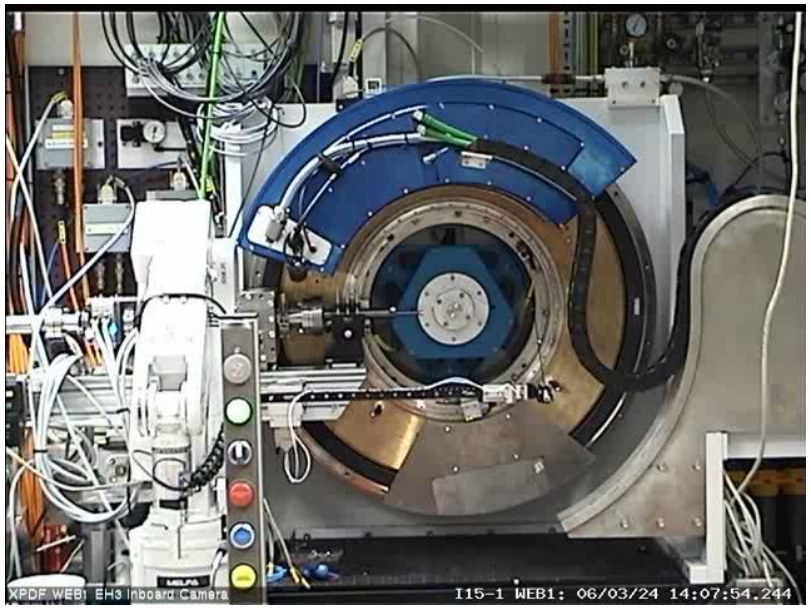
SAMPLE DELIVERY

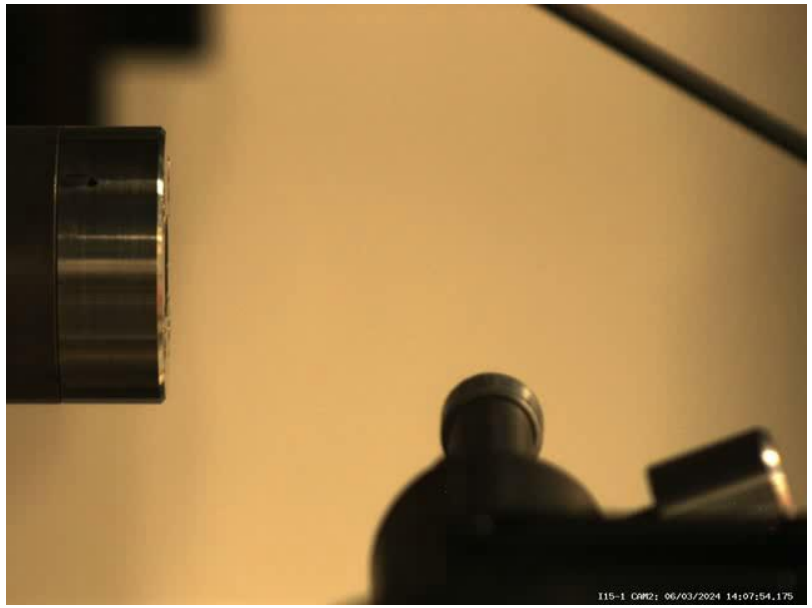


E. N. Gimenez, P. A. Chater, G. Crevatin, G. Dennis, A. Fairley, I. Horswell, D. Omar, J. Spiers, N. Tartoni, IEEE Nuclear Science Symposium and Medical Imaging Conference NSS/MIC, 2019, 1–3.

SAMPLE LOADING

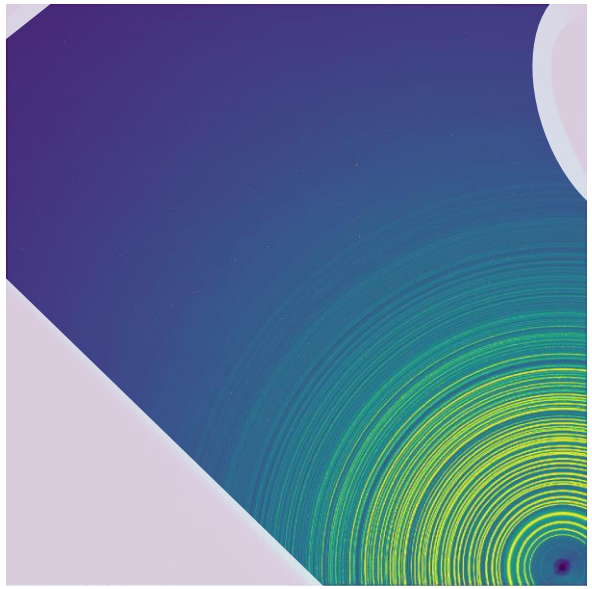


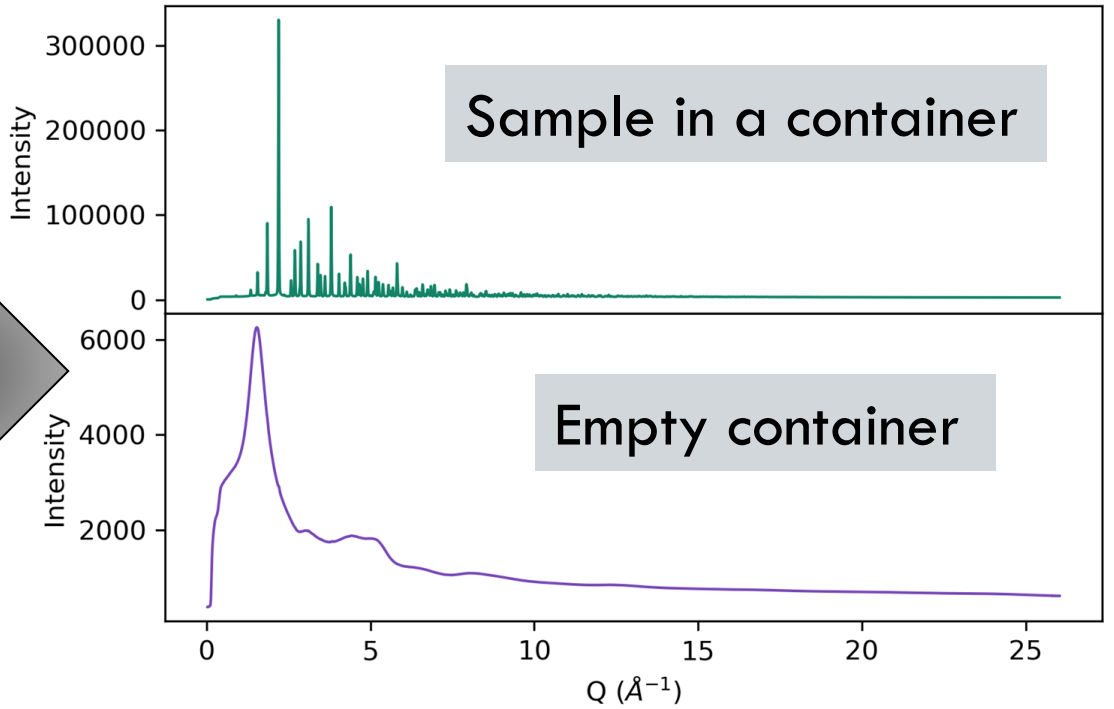




(2.5x speed)

DATA PROCESSING





- 2D image is automatically masked and integrated into 1D data

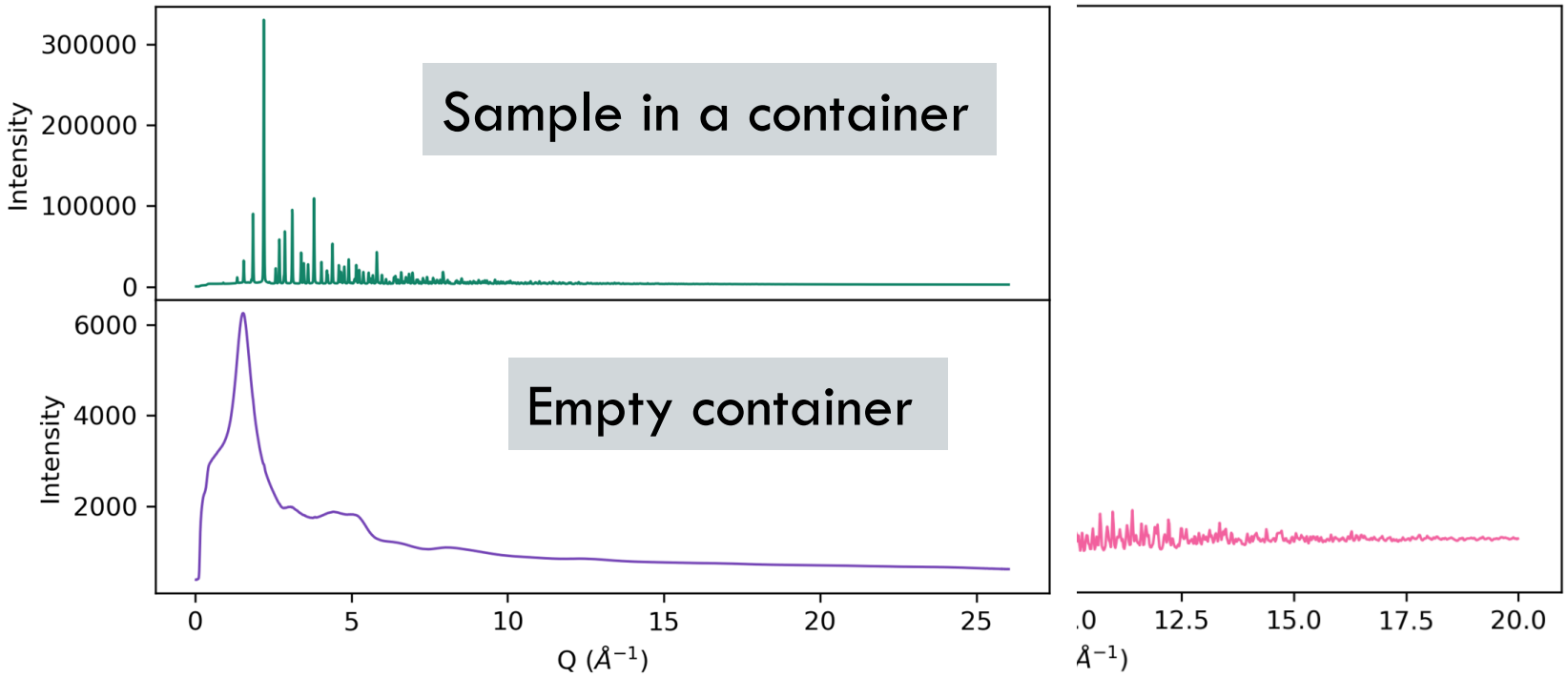
DATA PROCESSING

Information you need:

- Composition
- Density
- Q-range

Example processing programmes:

- Gudrun
- PDFGetX3



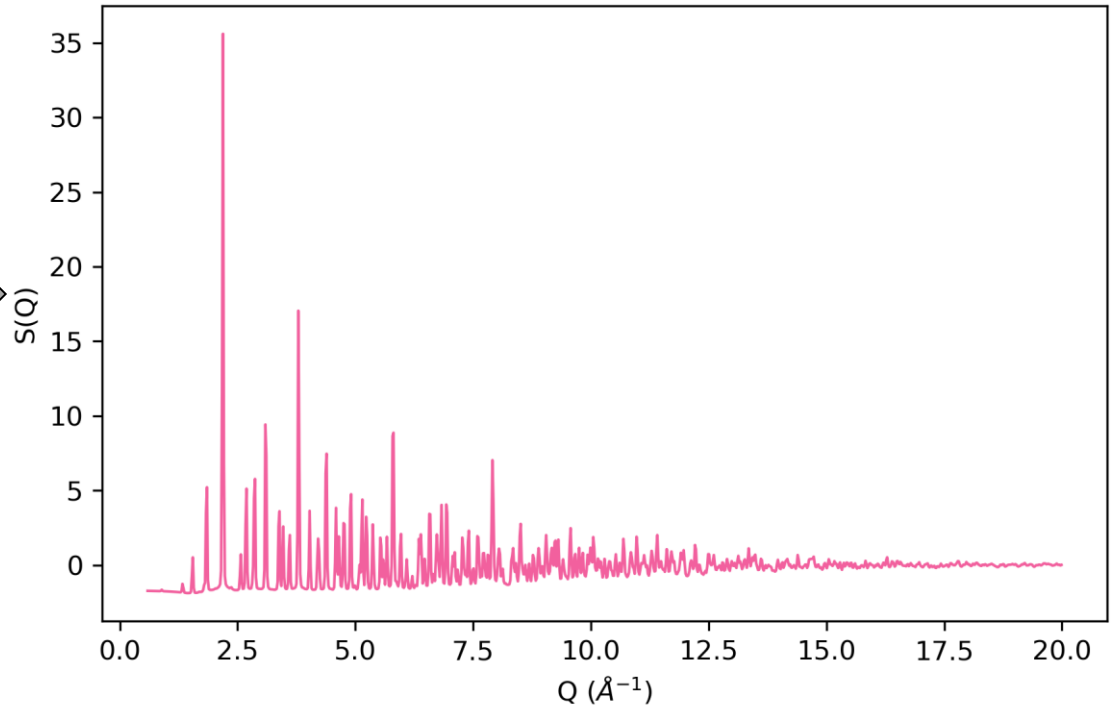
- Subtract the empty container and calculate the total scattering function (S(Q))

DATA PROCESSING

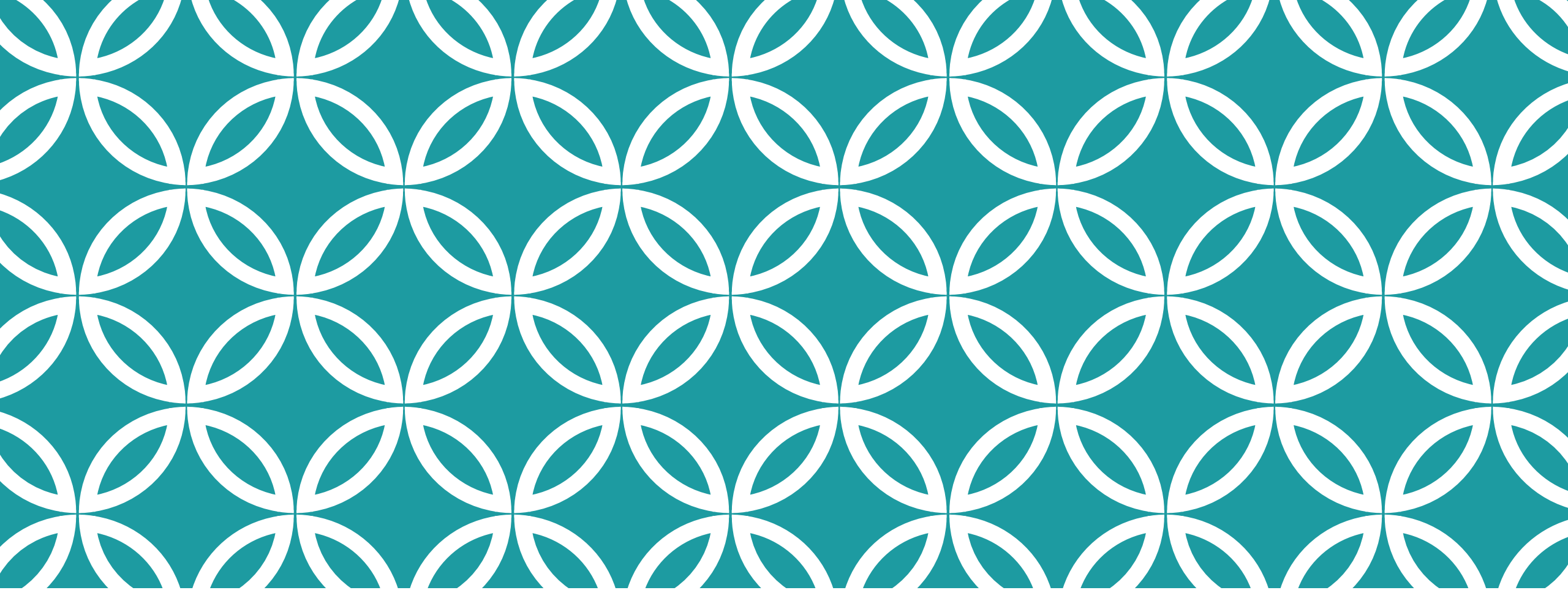
Example processing programmes:

- Gudrun
- PDFGetX3

Fourier Transform



- Fourier Transform of the total scattering gives the pair distribution function!



HOW TO ANALYSE PDF DATA

A Brief Overview

ANNA HERLIHY - POLYU SYNCHROTRON SUMMER SCHOOL

THERE ARE BROADLY THREE TYPES OF PDF ANALYSIS

Model-free Analysis

Peak fitting
Addition/Subtraction of data

Small Box Modelling

"Real-space Rietveld"
(Topas / PDFfit / PDFGui)

Big Box Modelling

Empirical Potential Structure Refinement
(Dissolve, EPSR)

Reverse Monte Carlo
(RMCProfile)

MODEL-FREE ANALYSIS

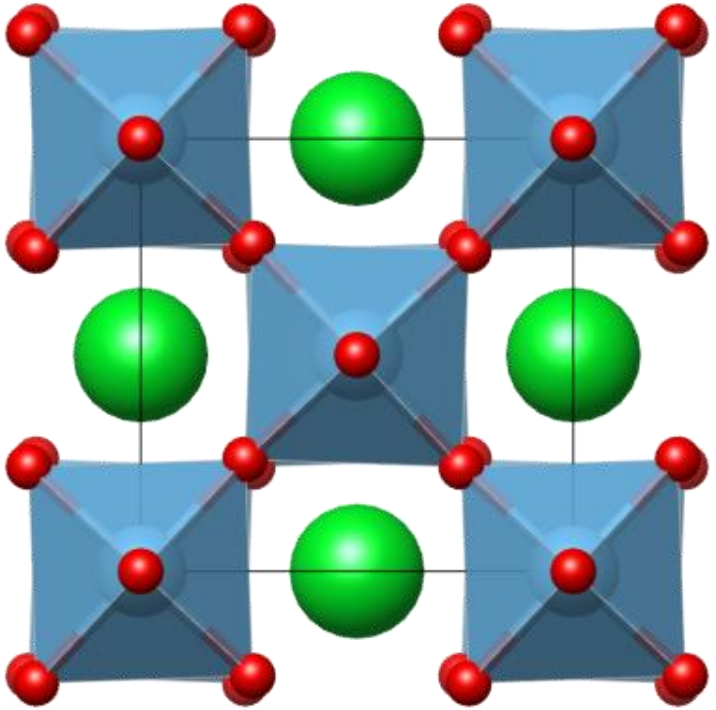
+ Very quick
+ No specialist software
+ Can access fundamental parameters of a material

– Limited in scope
– Does not always provide strong link back to atomic structure
– Is improved by having lots of PDFs on a system

SMALL BOX MODELLING

+ Quick
+ Low entry barrier
+ Domain sizes / nanoparticles straightforward

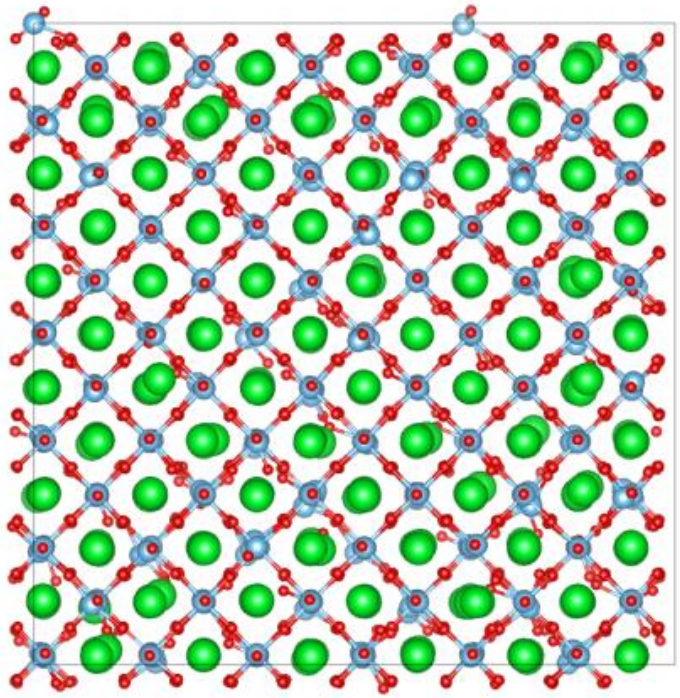
– Need starting model
– Need periodicity
– Is there a better model?



BIG BOX MODELLING

+ Arbitrary degrees/types of disorder
+ Simultaneous fits to real and reciprocal space
+ Interface with MD

– Bigger entry barrier
– Resource (time/effort) intensive
– Model uniqueness / need for restraints



NEXT:

X-ray PDF Measurements at Synchrotrons

Dr Dan Irving