Structural characterization of amorphous materials using x-ray scattering

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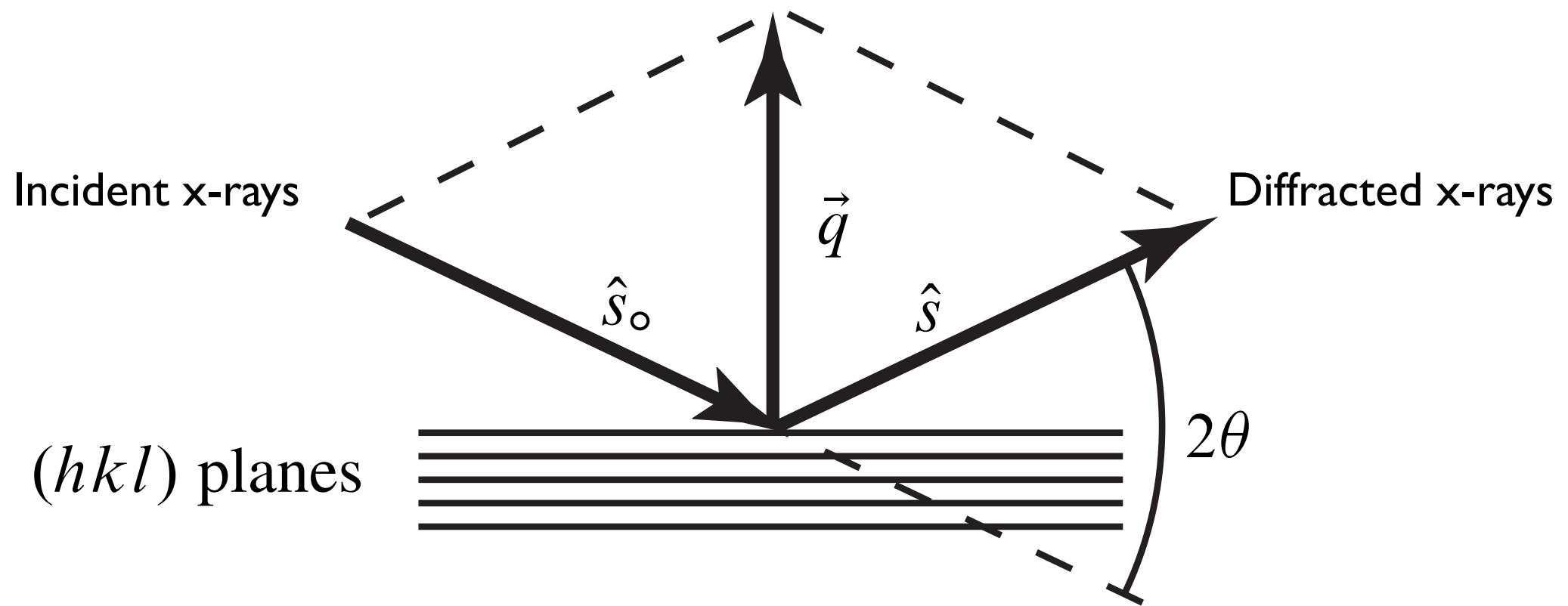*Johns Hopkins University, Baltimore, Maryland*

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Outline

1. How is scattering from amorphous materials different from diffraction from crystalline materials?

2. A gentle introduction to the theory of scattering from amorphous materials, and the structural information you get.

3. The path to enlightenment: From raw data to real-space structure

4. Experimental techniques and considerations

5. Resonant scattering

6. Resources

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X-ray diffraction (crystalline materials)

Incident x-rays

Diffracted x-rays

$\vec{q}$

$\hat{s}_\circ$

$\hat{s}$

2θ

(hkl) planes

Scattering vector: $\qquad \vec{q} \equiv \dfrac{2\pi}{\lambda} \left(\hat{s} - \hat{s}_\circ \right)$

Bragg's Law: $\qquad |\vec{q}| = \dfrac{4\pi \sin\theta}{\lambda} = \dfrac{2\pi}{d_{hkl}}$

Example: Mixed amorphous + crystalline structure

Composite consisting of ~4 vol. % Ta particles in Zr-based metallic glass matrix
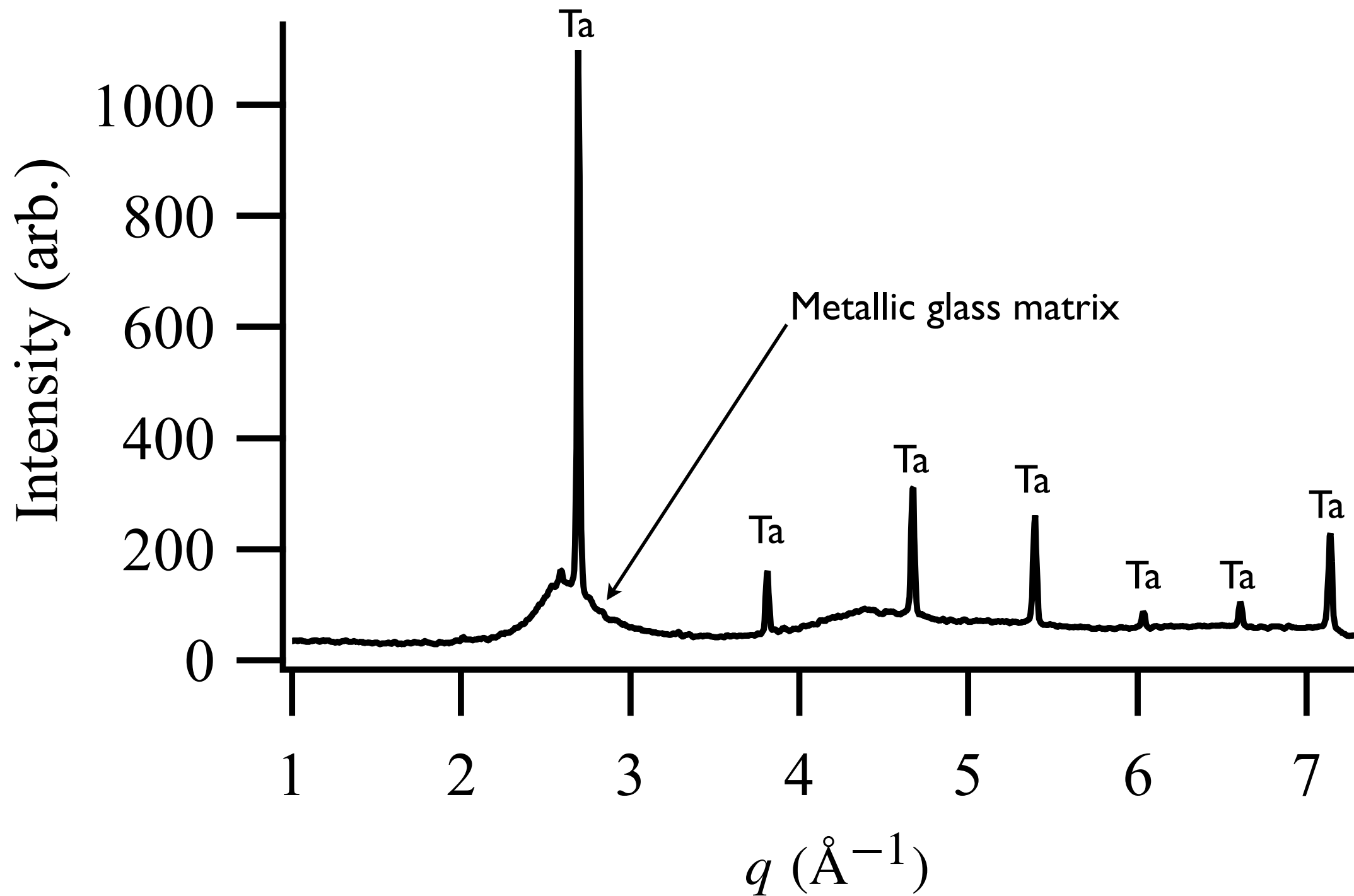
Crystalline	Amorphous
Scattering is strong (intense peaks)	Scattering is weak
Scattering concentrated into a few sharp diffraction peaks	Scattering spread throughout reciprocal space (all values of q)
Data easily interpreted using simple equations	Detailed analysis required to obtain real-space information

Amorphous scattering theory I

Scattered amplitude from a single atom:

$$A_n = f_n \exp(-i\vec{q} \cdot \vec{r}_n)$$

$f_n =$ Atomic scattering factor

$\vec{r}_n =$ Position of nth atom

Scattered intensity from n atoms (arbitrarily arranged):

$$I_{\mathrm{eu}}(\vec{q}) = \left(\sum_n A_n\right)\left(\sum_m A_m^*\right)$$

$$= \left(\sum_n f_n \exp(-i\vec{q} \cdot \vec{r}_n)\right)\left(\sum_m f_m^* \exp(i\vec{q} \cdot \vec{r}_m)\right)$$

$$= \sum_m \sum_n f_m^* f_n \exp(i\vec{q} \cdot \vec{r}_{nm})$$

$\vec{r}_{nm} =$ Vector joining nth and mth atoms

Amorphous scattering theory II

Assume that the material is isotropic (so we can average over all orientations of r_{nm}) to obtain the Debye scattering equation:

$$I_{\text{eu}}(q) = \sum_m \sum_n f_m^* f_n \frac{\sin q\, r_{nm}}{q\, r_{nm}}$$

This applies to any assemblage of identical scattering units (*e.g.* molecules) so long as they scatter independently and are randomly oriented.

Example: Ehrenfest relation

Amorphous case is too hard; instead, consider scattering from diatomic gas:
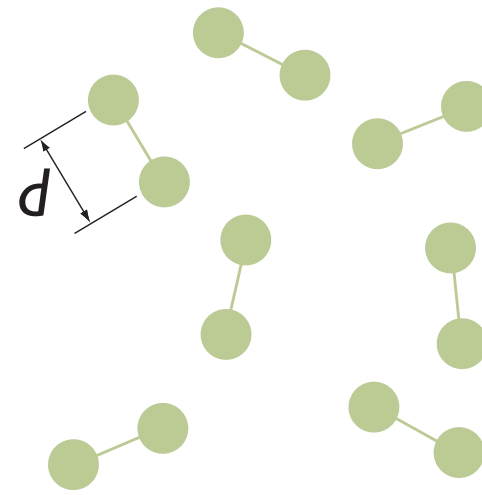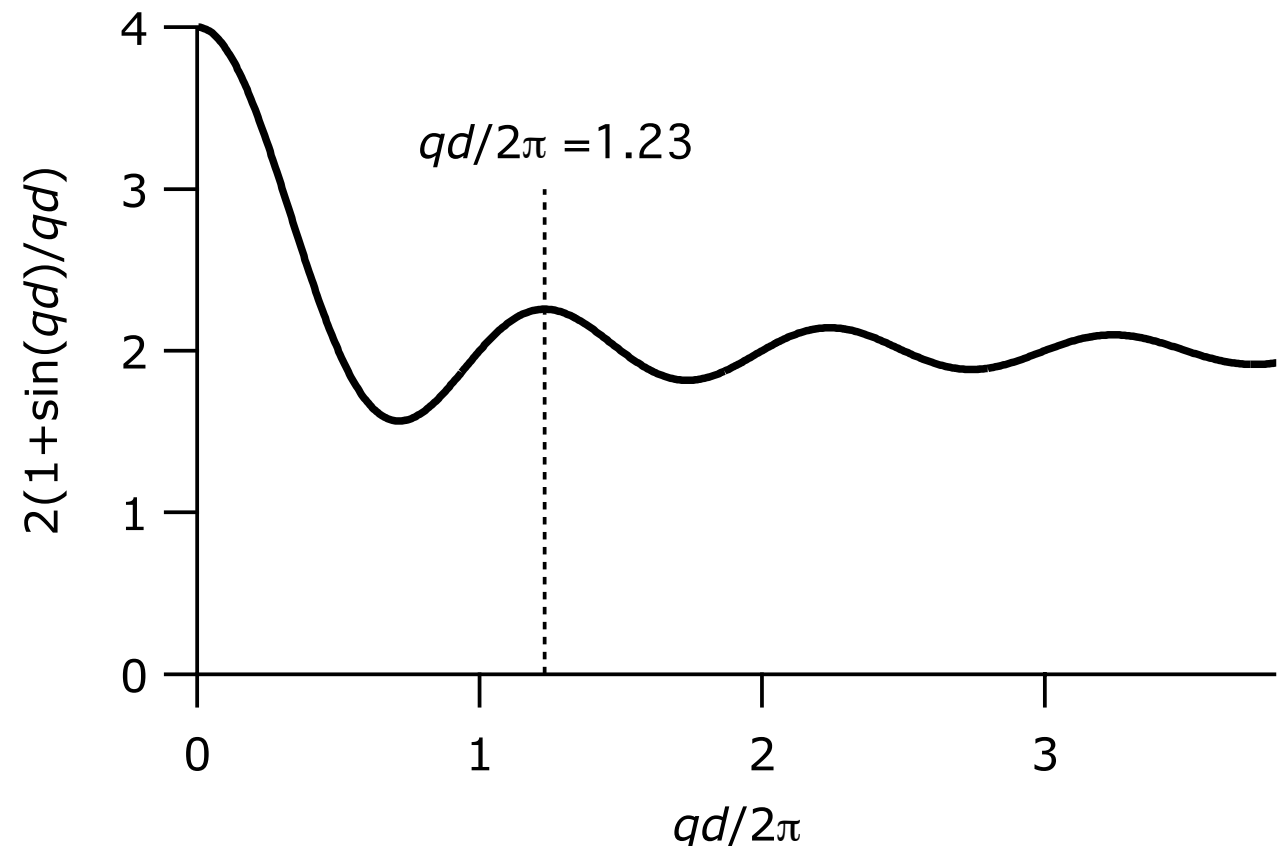
If the molecules scatter independently, then:

$$I(q) \propto \sum_m \sum_n f_m f_n \frac{\sin q r_{mn}}{q r_{mn}} = 2f^2 \left(1 + \frac{\sin qd}{qd} \right)$$

If the atoms are point scatters, then f is independent of q and the scattering has a maximum at

$$q_{\max} = \frac{1.23(2\pi)}{d}$$

P. Ehrenfest *Proc. Amsterdam Acad.* **17**, 1184 (1915)
A. Guinier *X-Ray Diffraction* (Dover, 1994), pp. 72-74.

Amorphous scattering theory III

Define a new quantity, the structure factor, $S(q)$:

$$S(q) \equiv \frac{I_{\mathrm{eu}}(q)}{N \langle f(q) \rangle^2} \qquad N = \text{number of atoms}$$
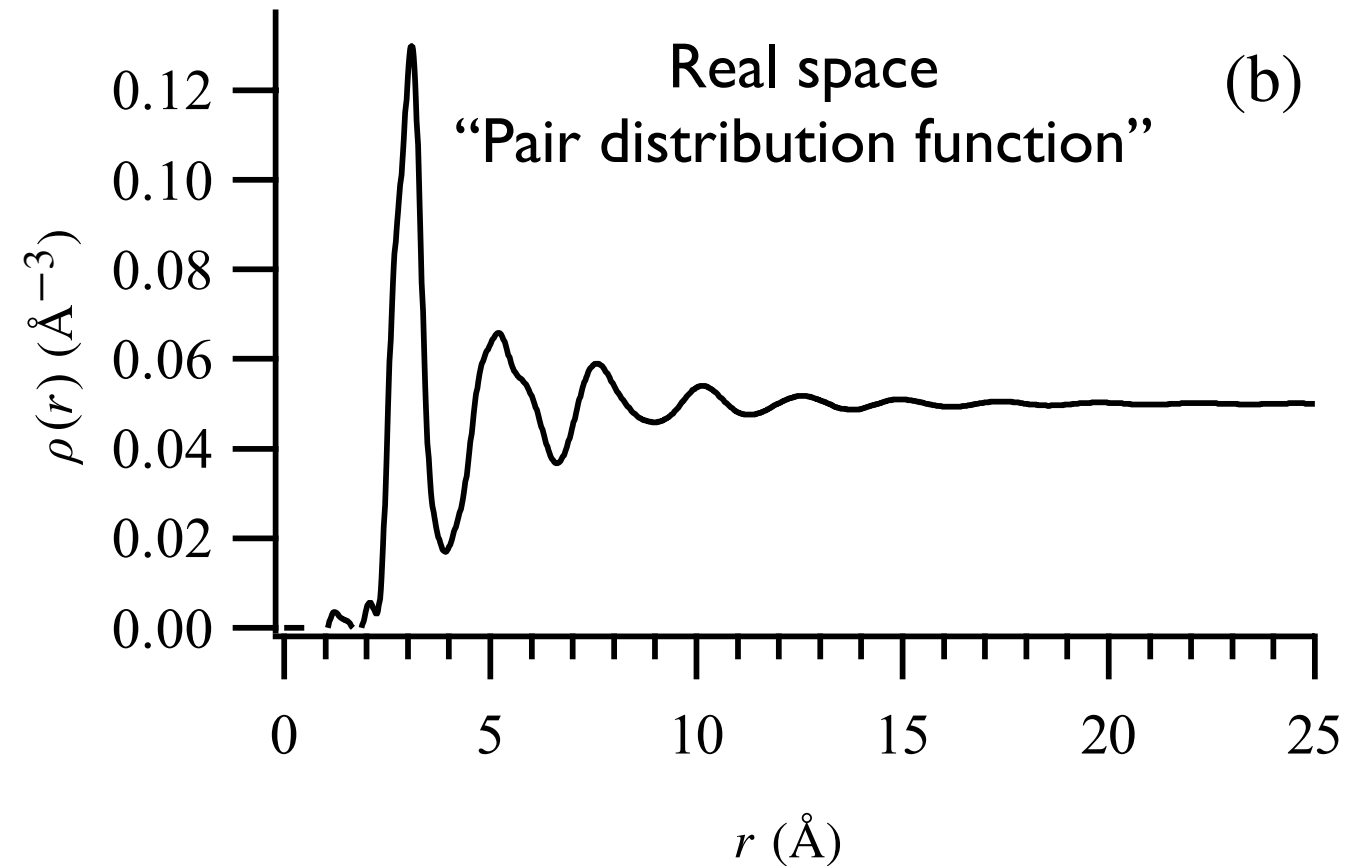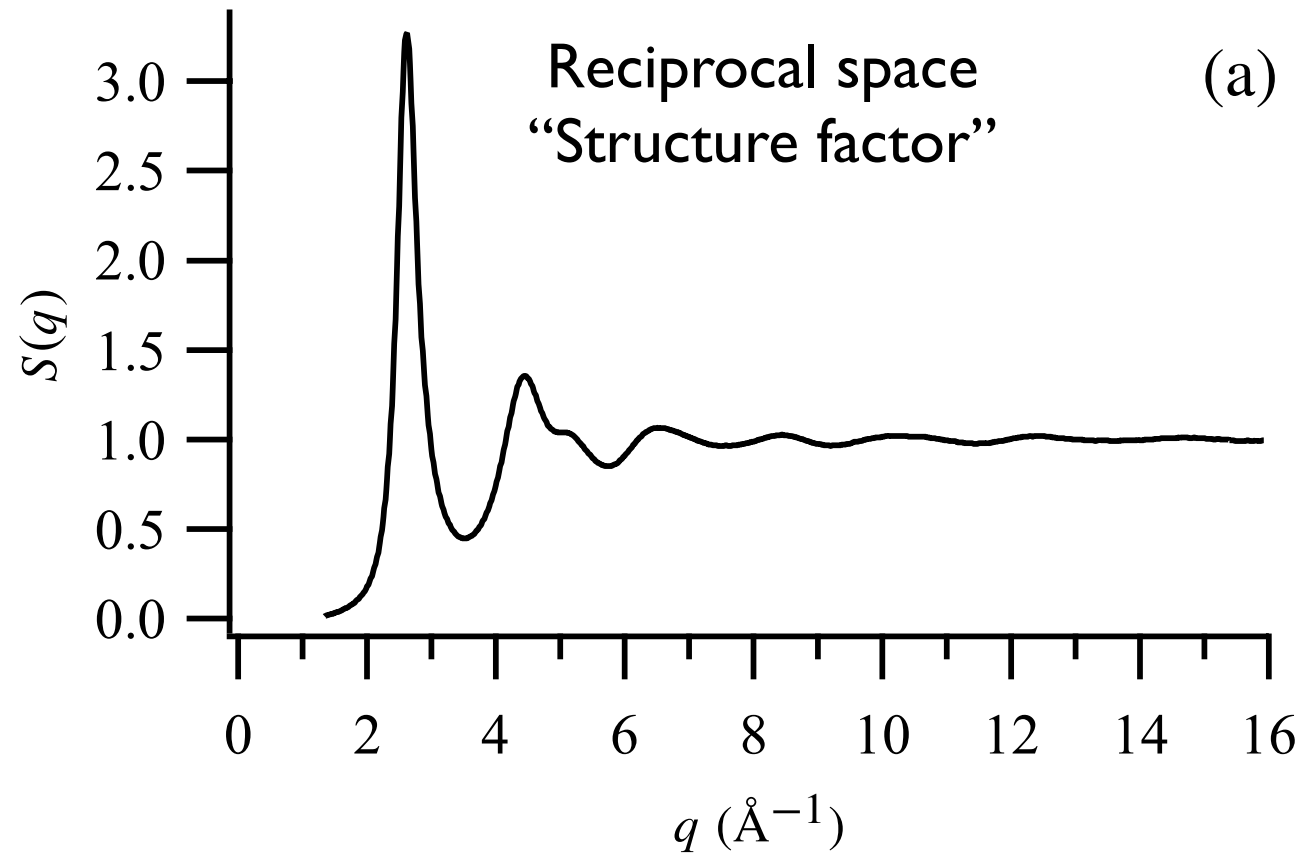
$S(q)$ is related to the real-space structure, the pair distribution function $\rho(r)$, by a Fourier transform:

$$\rho(r) - \rho_\circ = \frac{1}{8\pi^3} \int_0^\infty 4\pi q^2 \left(S(q) - 1 \right) \frac{\sin qr}{qr} \, dq$$

$$\rho_\circ = \text{average atomic density}$$

Note the limits on the integral!
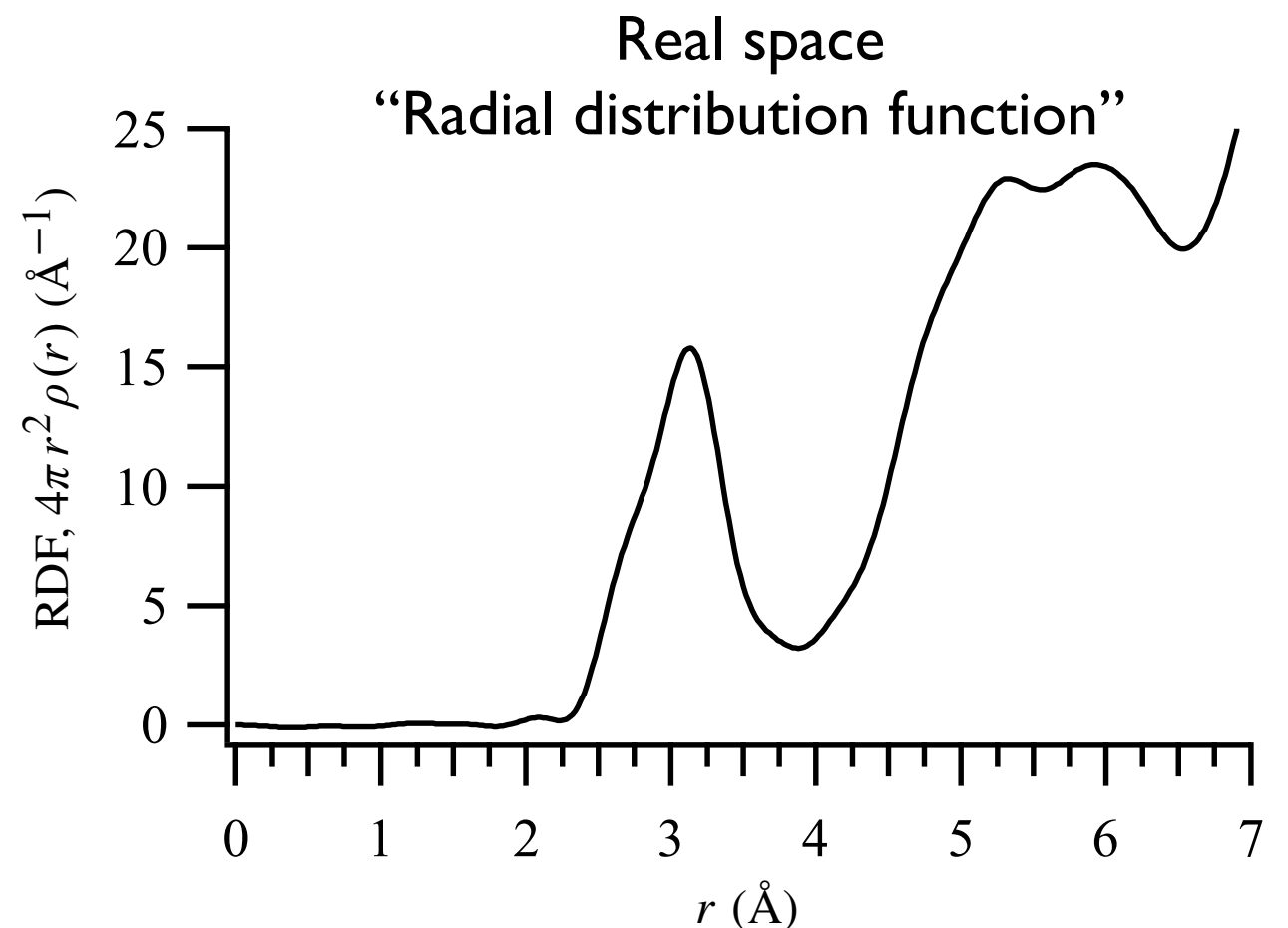
Data in reciprocal space and real space

Reciprocal space "Structure factor" (a)

$S(q)$ vs q (Å^{-1})

Real space "Pair distribution function" (b)

$\rho(r)$ (Å^{-3}) vs r (Å)

$$S(q) = \frac{I(q)}{N\langle f(q)\rangle^2}$$

$$\rho(r) - \rho_\circ = \frac{1}{8\pi^3}\int_0^\infty 4\pi q^2 \left(S(q) - 1\right)\frac{\sin qr}{qr}dq$$
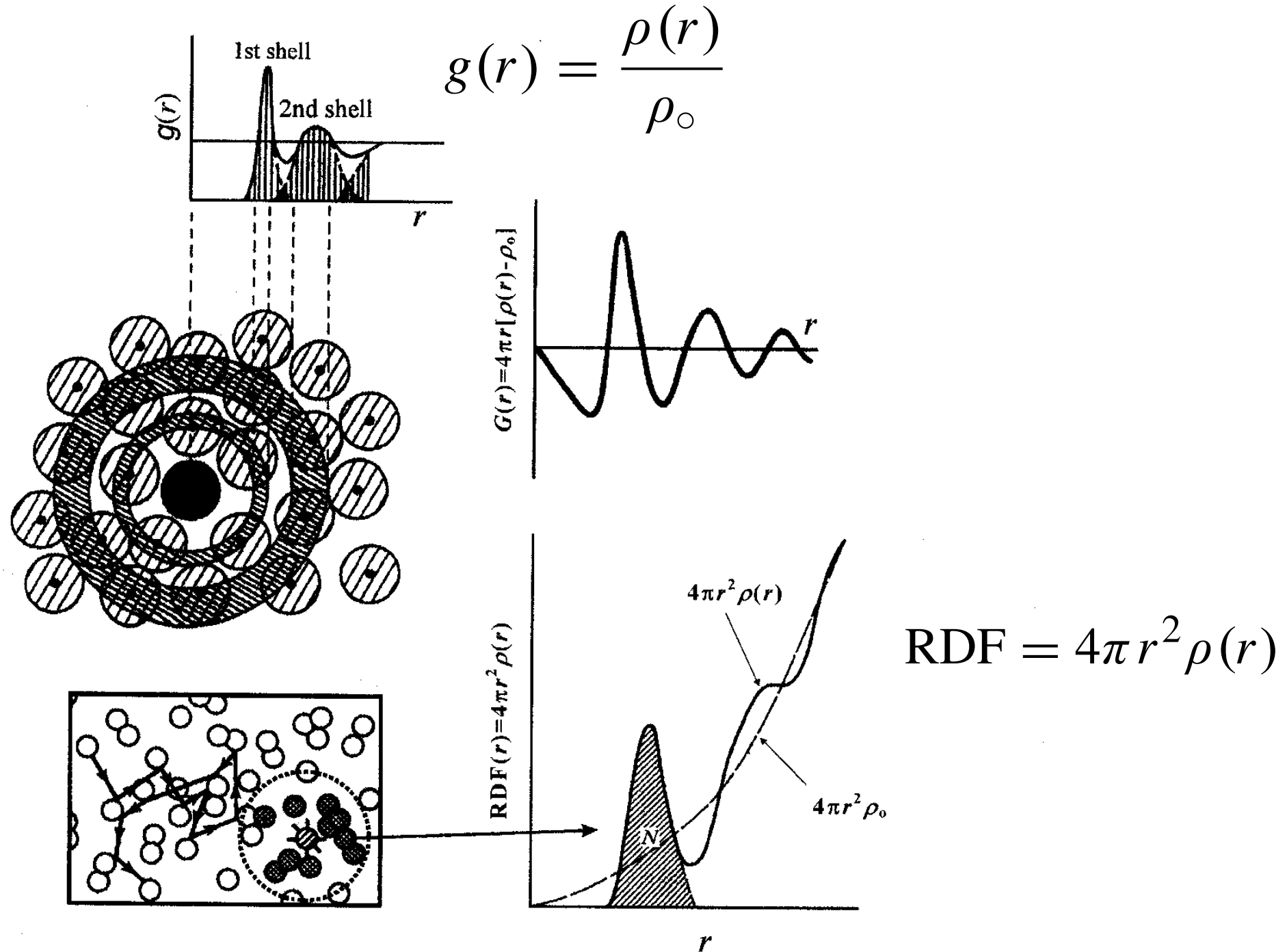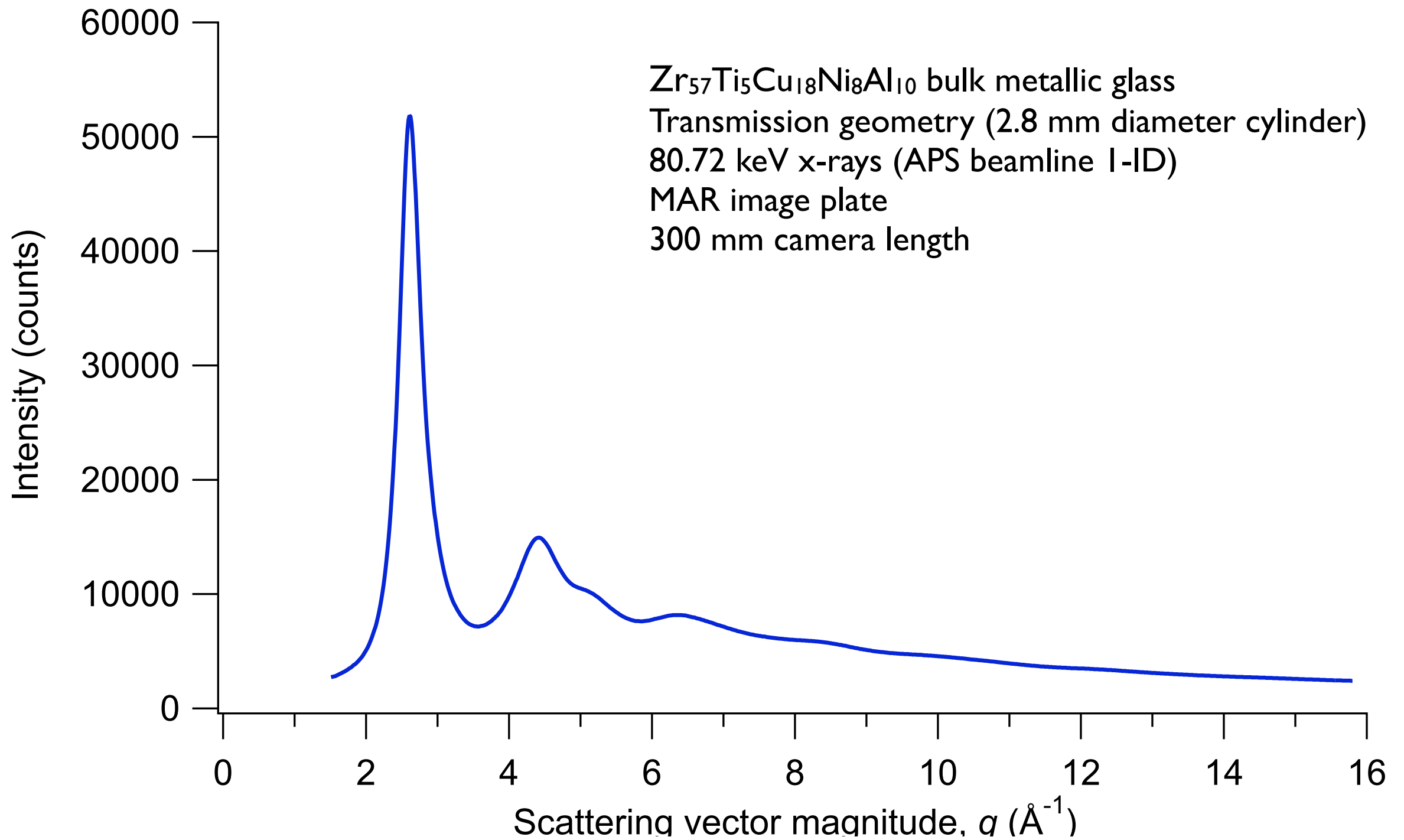
$$\text{RDF} = 4\pi r^2 \rho(r)$$

$$g(r) = \frac{\rho(r)}{\rho_\circ}$$

Real space "Radial distribution function"

RDF, $4\pi r^2 \rho(r)$ (Å^{-1}) vs r (Å)

Physical interpretation of real-space functions

$$S(q) = \frac{I(q)}{N\langle f(q)\rangle^2}$$

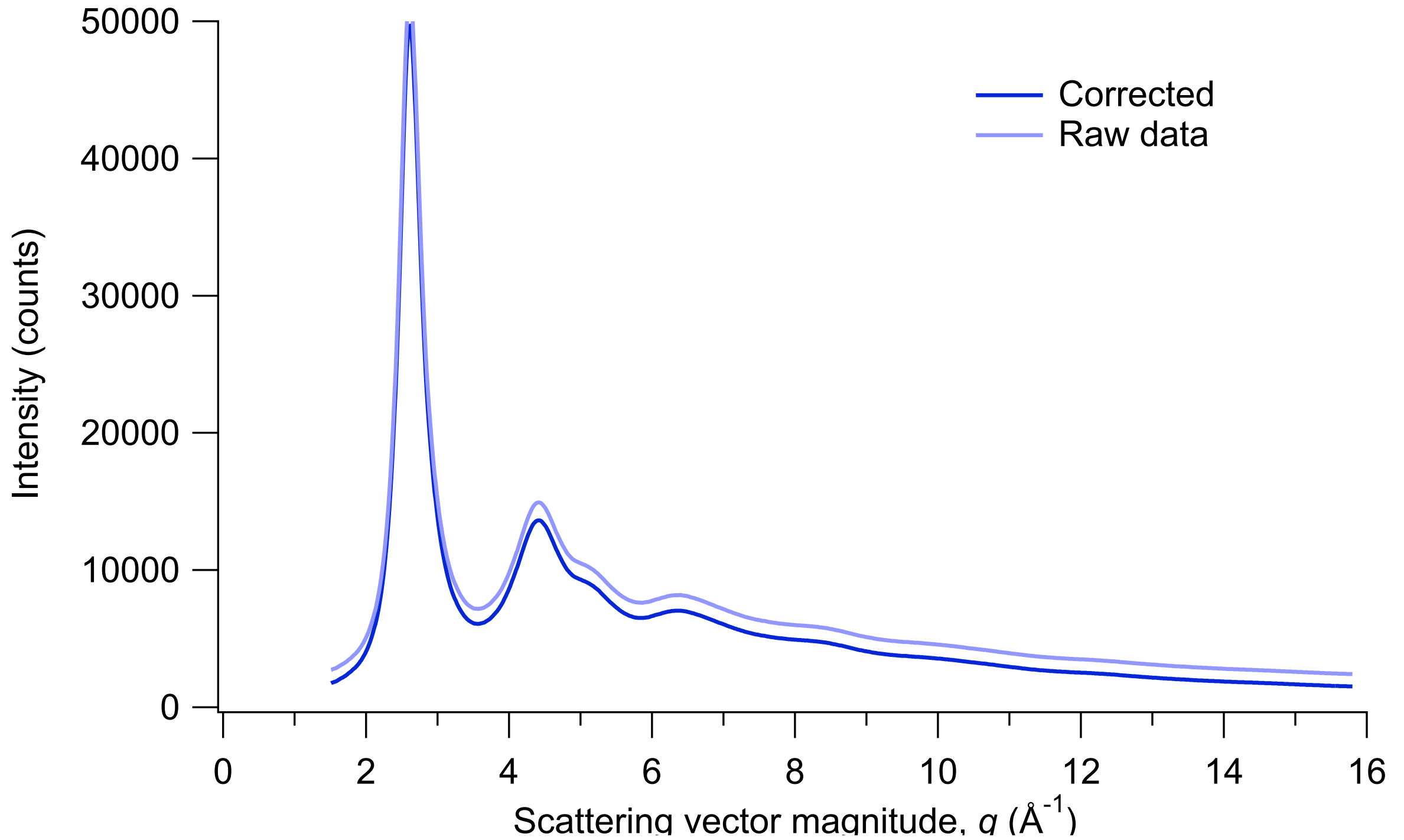$$\rho(r) - \rho_\circ = \frac{1}{8\pi^3} \int_0^\infty 4\pi q^2 \left(S(q) - 1\right) \frac{\sin qr}{qr} dq$$

$$g(r) = \frac{\rho(r)}{\rho_\circ}$$

$$RDF = 4\pi r^2 \rho(r)$$

Fig. 2.1. Schematic of a snapshot of the atomic distribution and its RDF in a non-crystalline system

T. C. Hufnagel, Johns Hopkins University   Figure from Y. Waseda, *Anomalous X-Ray Scattering for Materials Characterization* (Springer, 2002)

Data reduction 1: Raw data

Zr$_{57}$Ti$_5$Cu$_{18}$Ni$_8$Al$_{10}$ bulk metallic glass
Transmission geometry (2.8 mm diameter cylinder)
80.72 keV x-rays (APS beamline 1-ID)
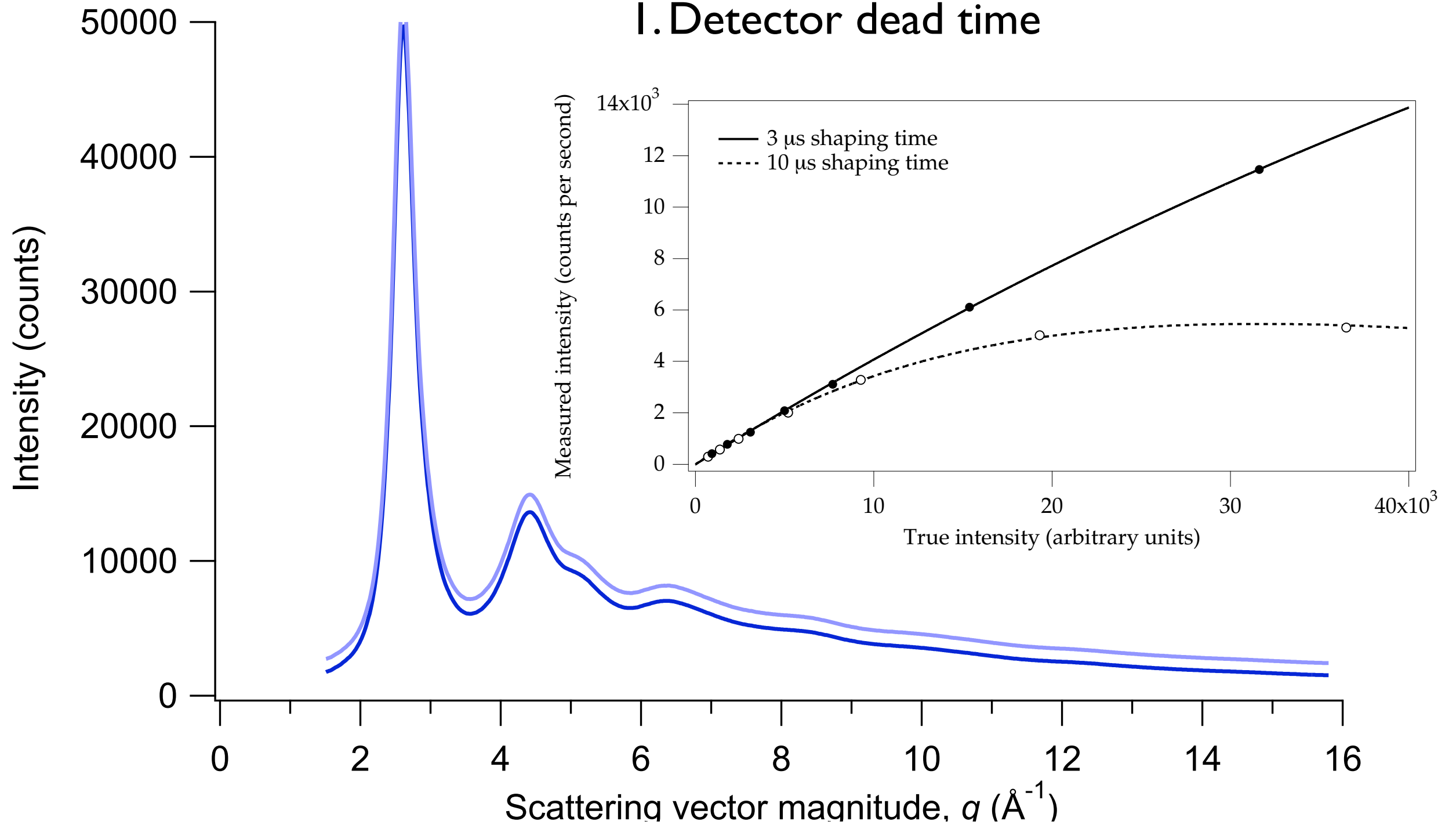MAR image plate
300 mm camera length
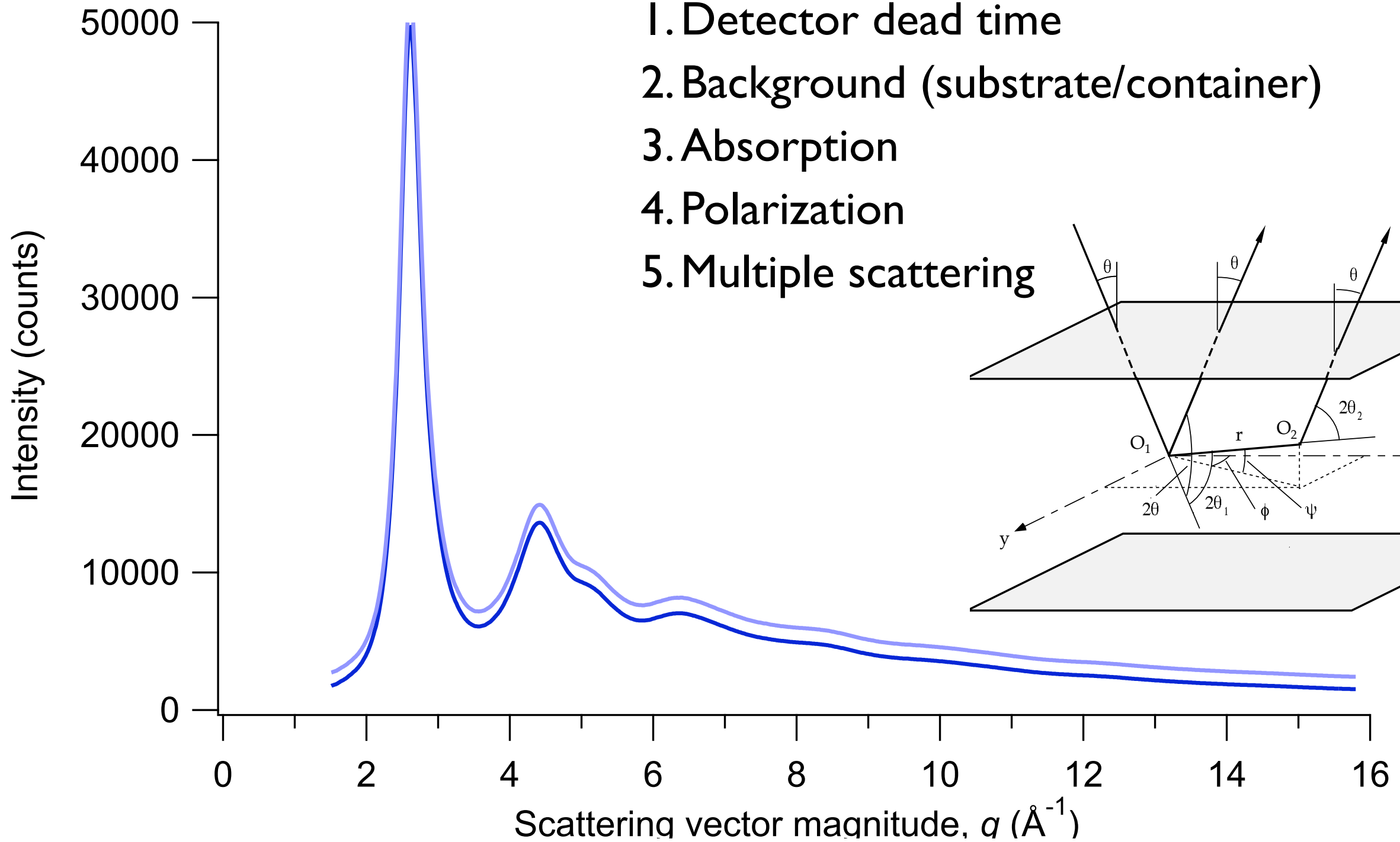
Data reduction 11: Apply corrections

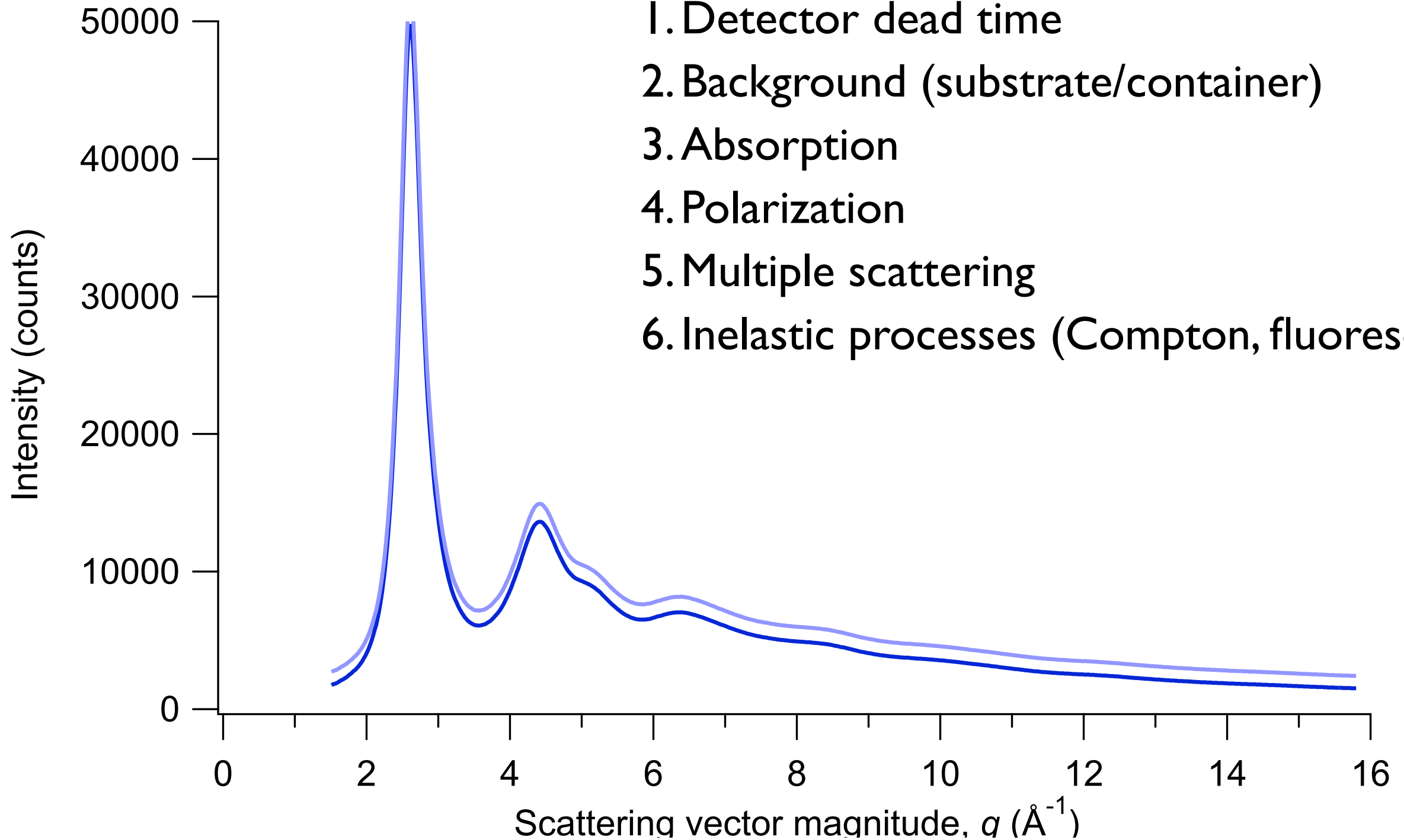# Data reduction II: Apply corrections
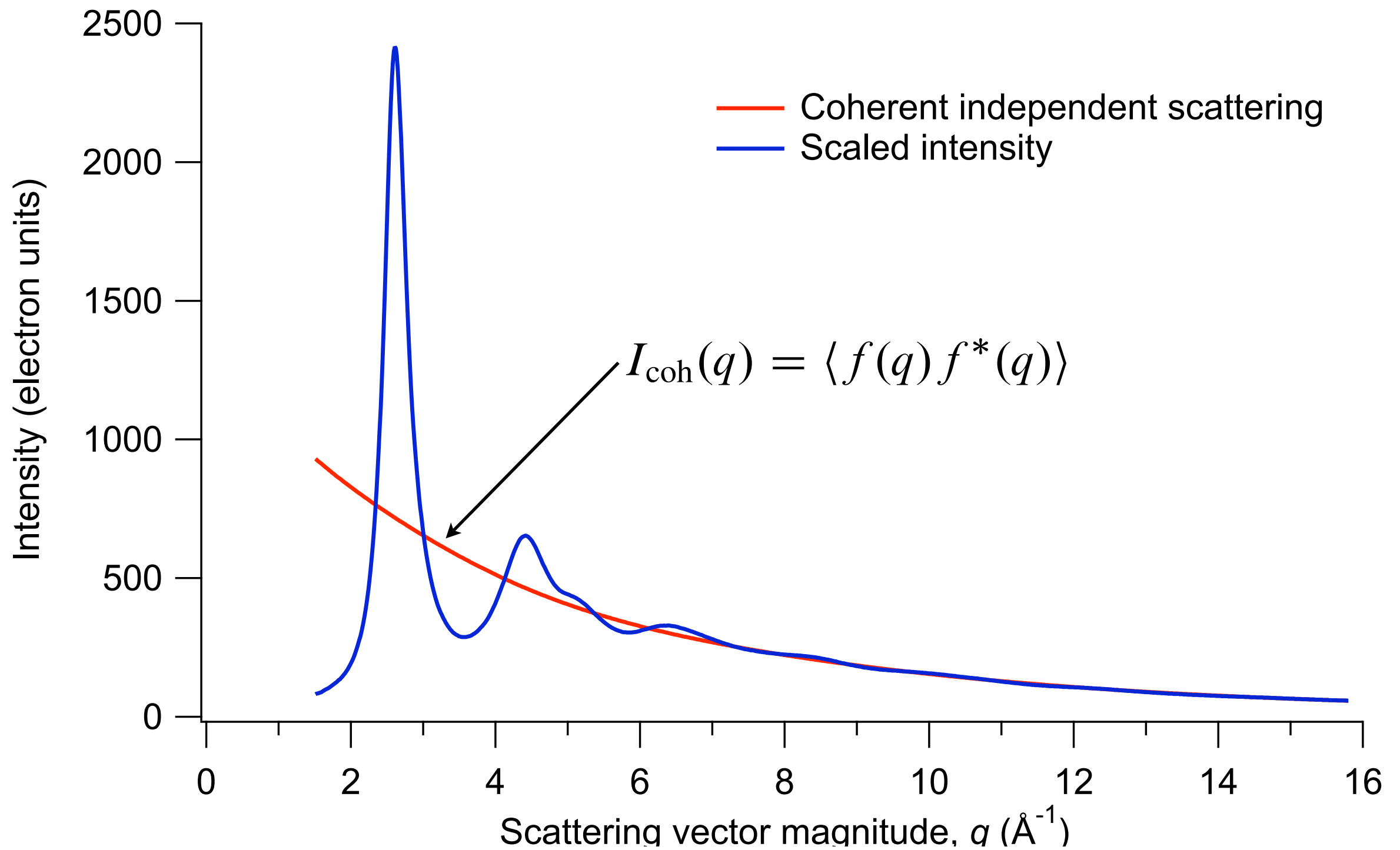
1. Detector dead time

Data reduction II: Apply corrections

1. Detector dead time
2. Background (substrate/container)
3. Absorption
4. Polarization
5. Multiple scattering

Data reduction II: Apply corrections

1. Detector dead time
2. Background (substrate/container)
3. Absorption
4. Polarization
5. Multiple scattering
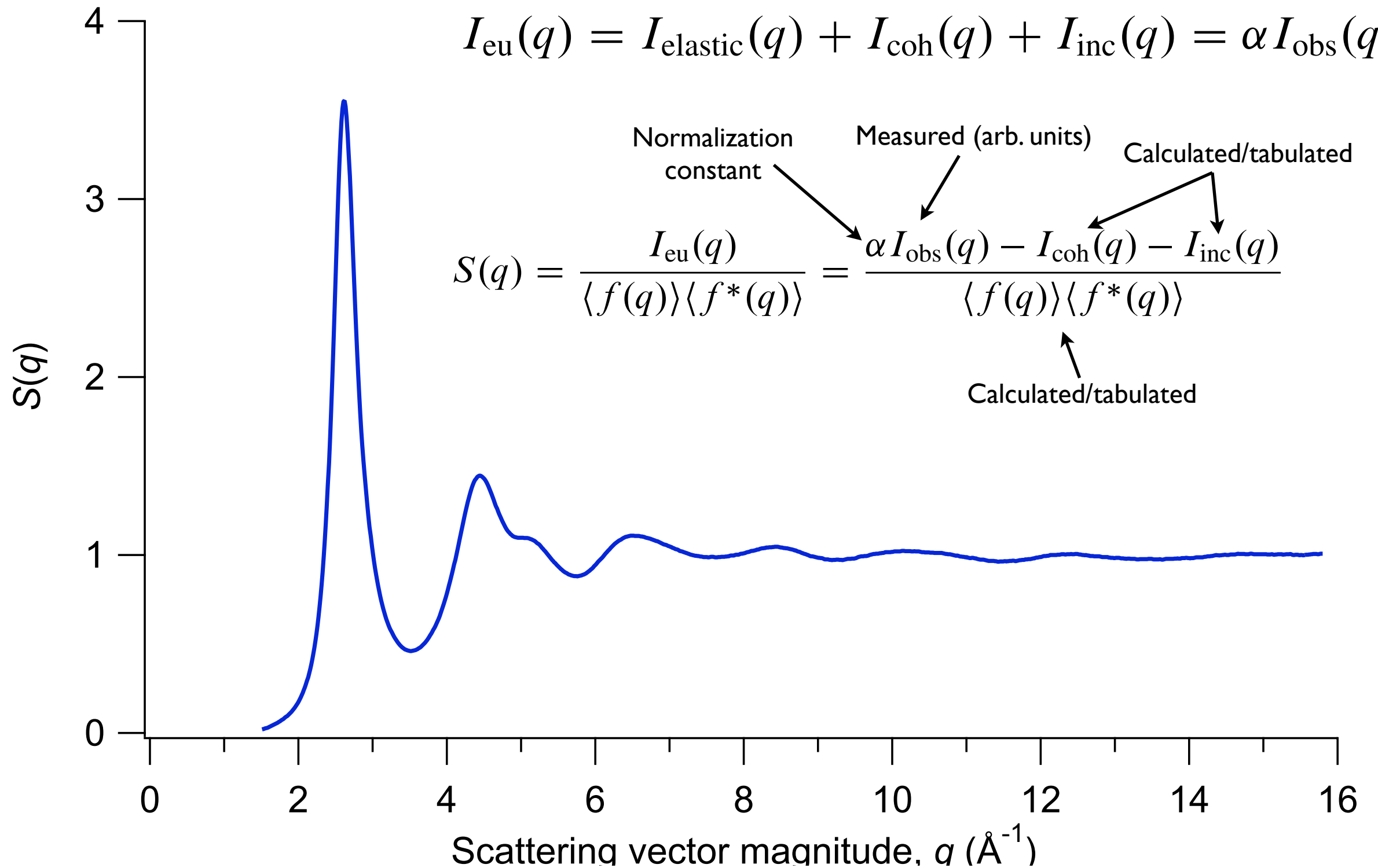6. Inelastic processes (Compton, fluorescence)

Data reduction III: Normalize to e⁻ units

$$I_{\mathrm{coh}}(q) = \langle f(q) f^*(q) \rangle$$

Legend:
- Coherent independent scattering
- Scaled intensity

Y-axis: Intensity (electron units)

X-axis: Scattering vector magnitude, q (Å⁻¹)

Data reduction IV: Normalization, $S(q)$

$$I_{\mathrm{eu}}(q) = I_{\mathrm{elastic}}(q) + I_{\mathrm{coh}}(q) + I_{\mathrm{inc}}(q) = \alpha I_{\mathrm{obs}}(q)$$

Normalization constant

Measured (arb. units)

Calculated/tabulated

$$S(q) = \frac{I_{\mathrm{eu}}(q)}{\langle f(q)\rangle\langle f^*(q)\rangle} = \frac{\alpha I_{\mathrm{obs}}(q) - I_{\mathrm{coh}}(q) - I_{\mathrm{inc}}(q)}{\langle f(q)\rangle\langle f^*(q)\rangle}$$

Calculated/tabulated

S(q) vs. Scattering vector magnitude, q (Å^{-1})
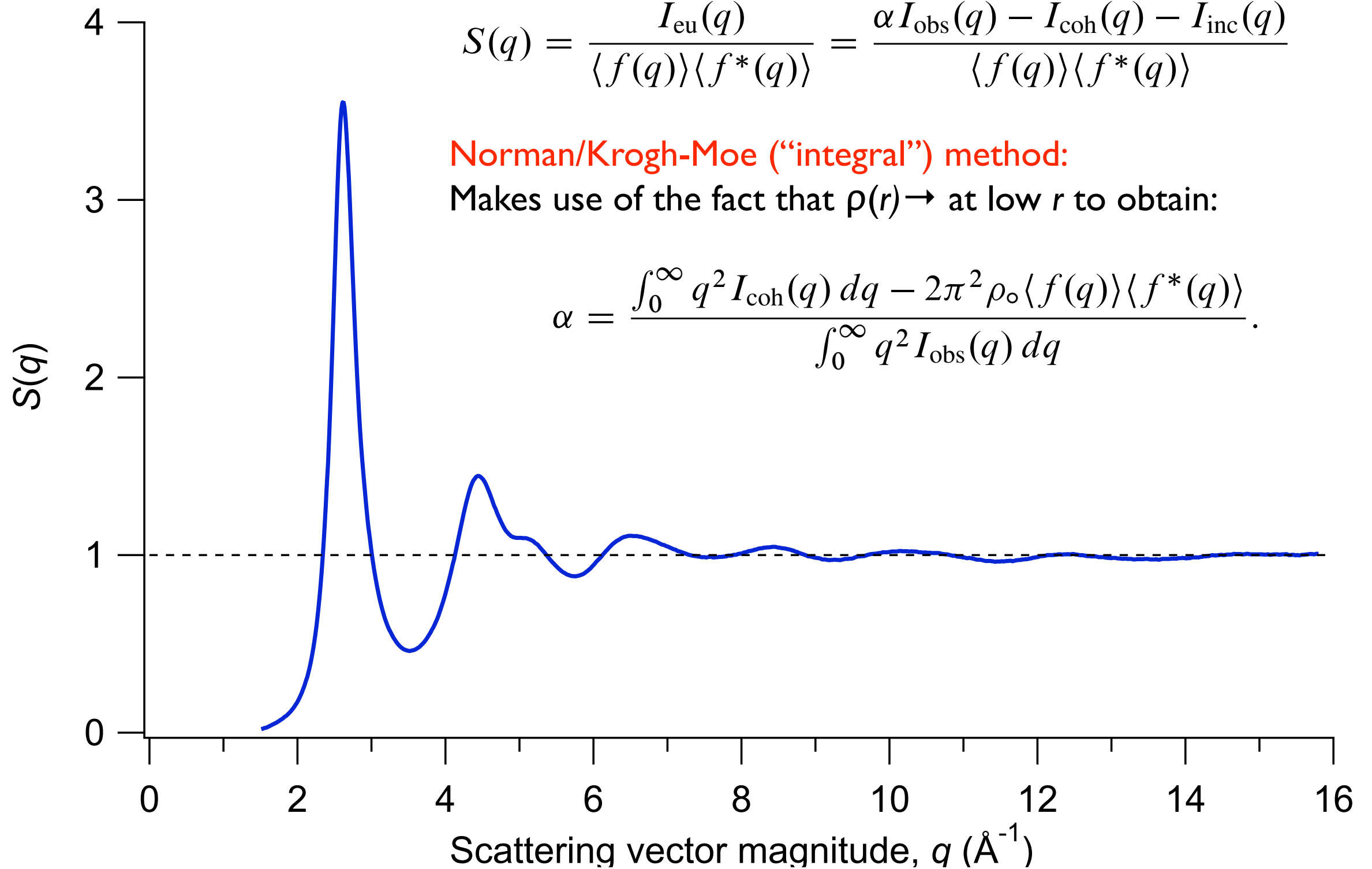
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Data reduction IV: Normalization, $S(q)$

$$S(q) = \frac{I_{\text{eu}}(q)}{\langle f(q) \rangle \langle f^*(q) \rangle} = \frac{\alpha I_{\text{obs}}(q) - I_{\text{coh}}(q) - I_{\text{inc}}(q)}{\langle f(q) \rangle \langle f^*(q) \rangle}$$
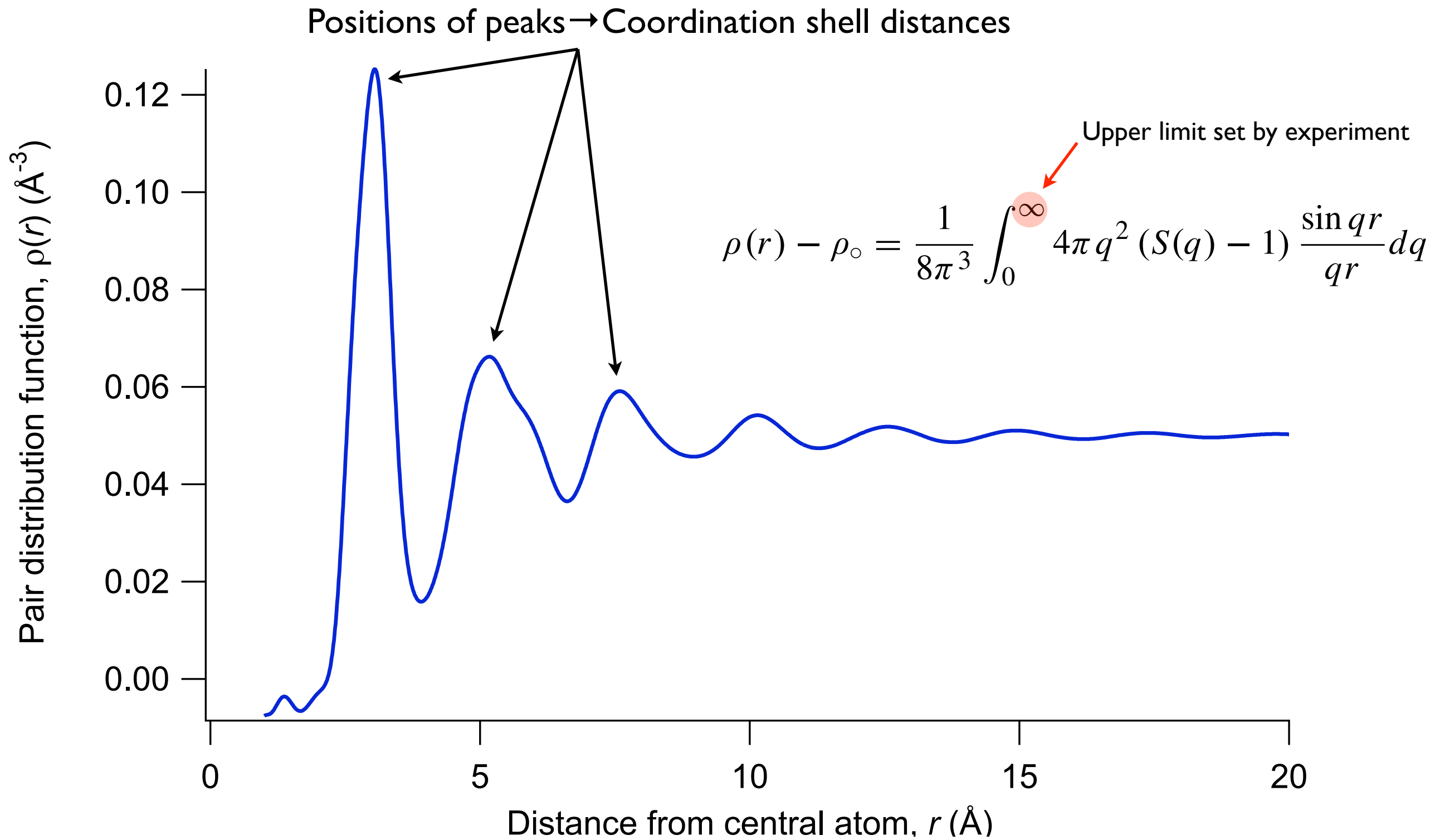
Warren's "large angle" method: $I_{\text{eu}}(q)$ should oscillate about the independent coherent scattering at large q.

Oscillating about $S(q)=1$ is equivalent to oscillating about $\langle f(q) f^*(q) \rangle$
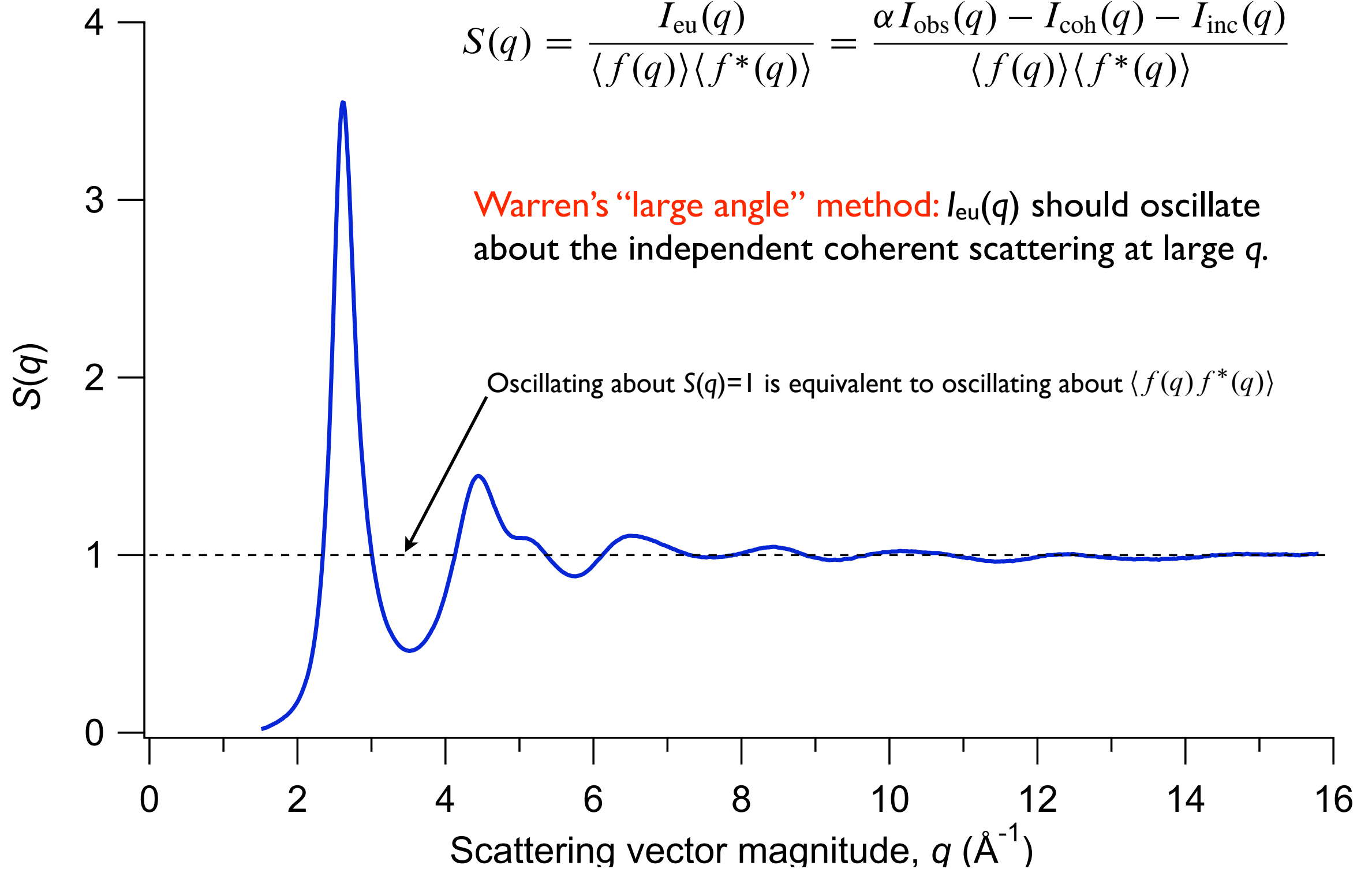
Data reduction IV: Normalization, $S(q)$

$$S(q) = \frac{I_{eu}(q)}{\langle f(q) \rangle \langle f^*(q) \rangle} = \frac{\alpha I_{obs}(q) - I_{coh}(q) - I_{inc}(q)}{\langle f(q) \rangle \langle f^*(q) \rangle}$$

Norman/Krogh-Moe ("integral") method:

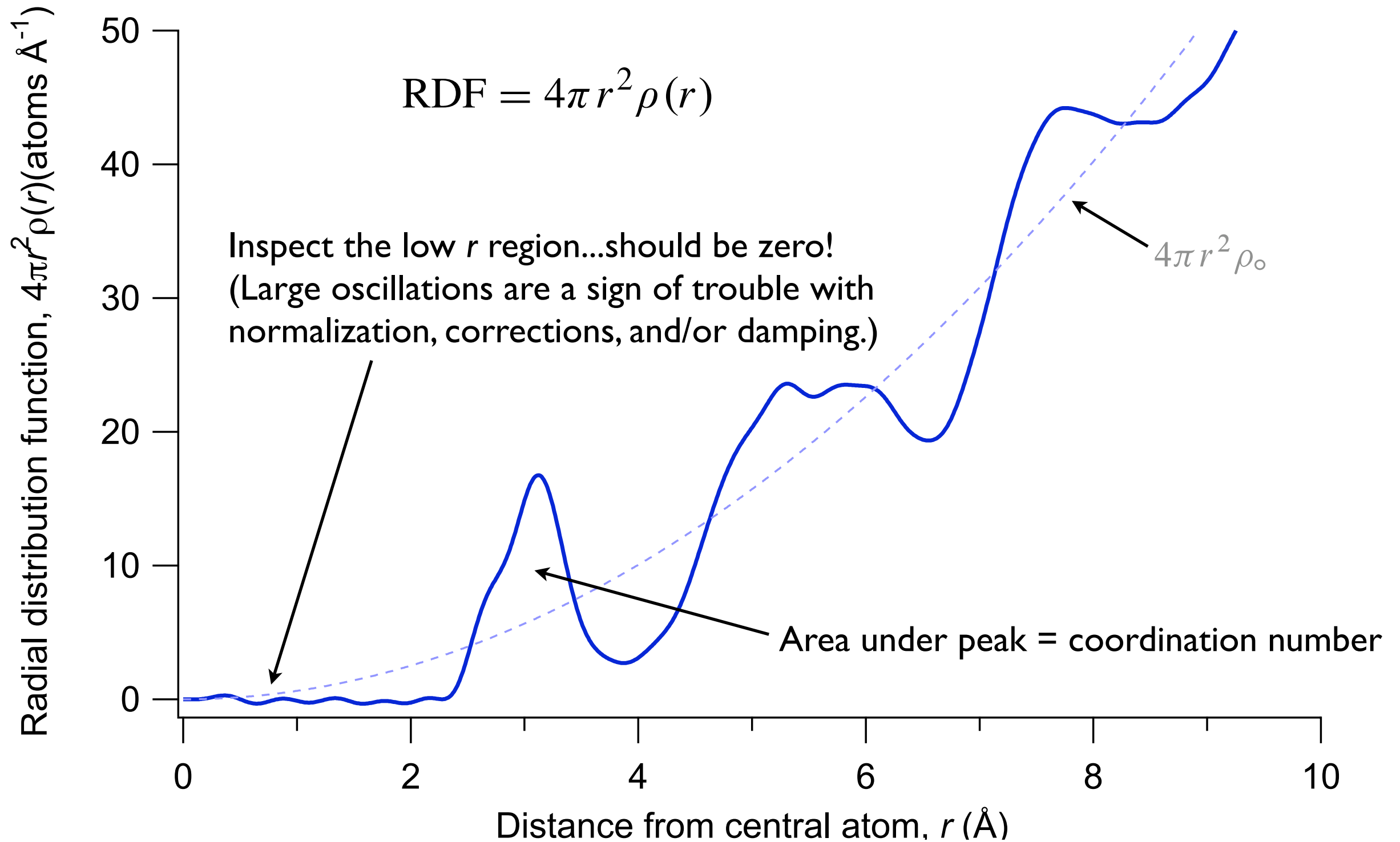Makes use of the fact that $\rho(r) \rightarrow$ at low r to obtain:

$$\alpha = \frac{\int_0^\infty q^2 I_{coh}(q)\, dq - 2\pi^2 \rho_\circ \langle f(q) \rangle \langle f^*(q) \rangle}{\int_0^\infty q^2 I_{obs}(q)\, dq}.$$
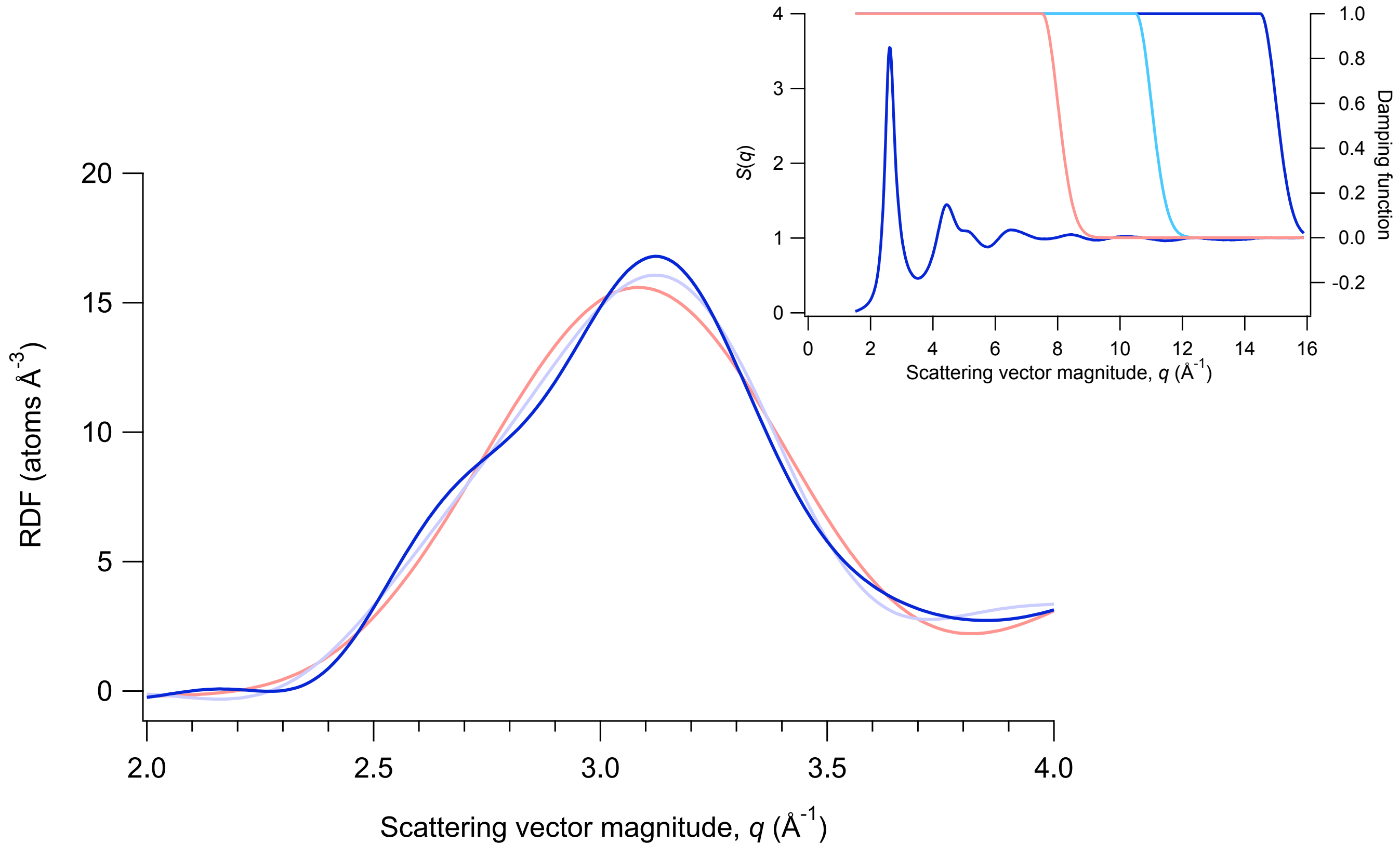

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N. Norman, *Acta Crystallogr.* **10**, 370 (1957)
J. Krogh-Moe, *Acta Crystallogr.* **9**, 951 (1956)

Data reduction V: Real-space functions

Positions of peaks → Coordination shell distances

Upper limit set by experiment

$$\rho(r) - \rho_{\circ} = \frac{1}{8\pi^3} \int_0^{\infty} 4\pi q^2 \left(S(q) - 1 \right) \frac{\sin qr}{qr} dq$$

Pair distribution function, $\rho(r)$ (Å^{-3})

Distance from central atom, r (Å)

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Data reduction V: Real-space functions

$$\mathrm{RDF} = 4\pi r^2 \rho(r)$$

Inspect the low r region...should be zero!
(Large oscillations are a sign of trouble with normalization, corrections, and/or damping.)

$4\pi r^2 \rho_\circ$

Area under peak = coordination number

Radial distribution function, $4\pi r^2 \rho(r)$ (atoms Å^{-1})

Distance from central atom, r (Å)

Damping and the high q limit

More on damping and Fourier transform

The Nyquist theorem puts a limit on the real space resolution:

$$\Delta r = \pi/q_{\max} \ (\simeq 0.2 \text{ Å for these data})$$
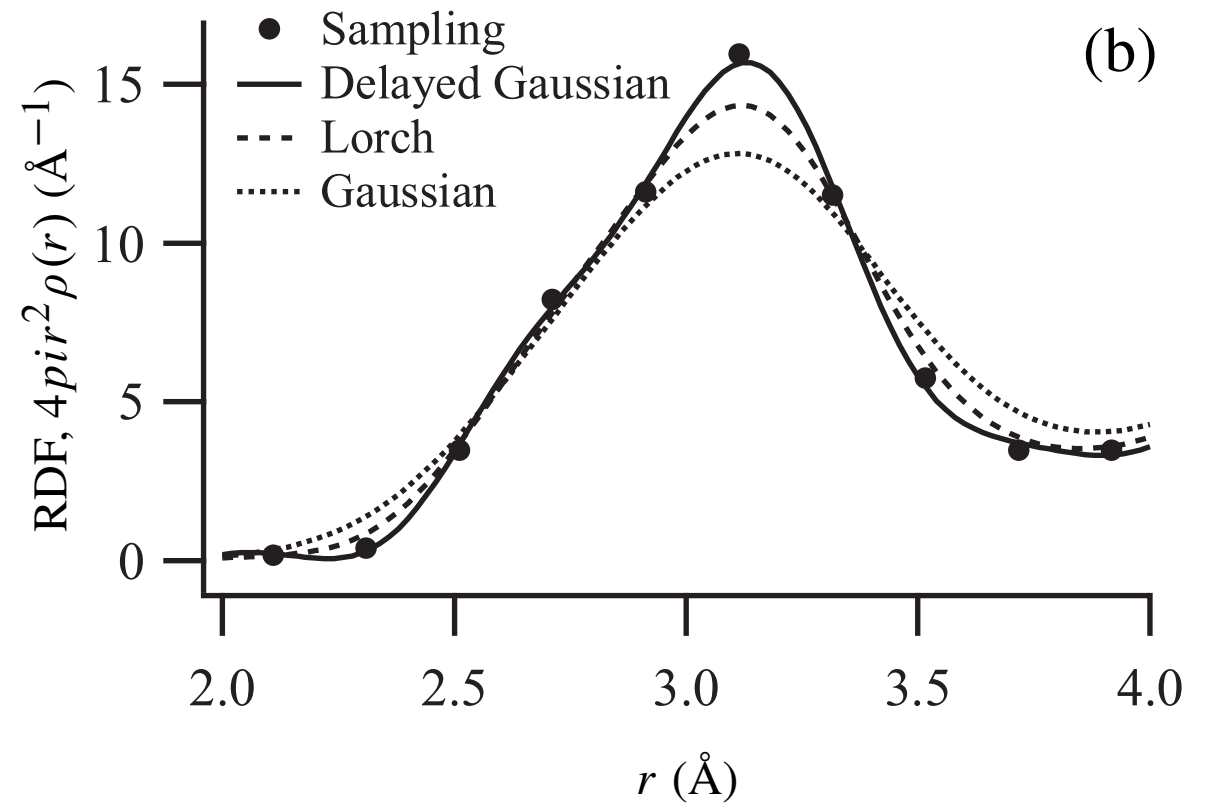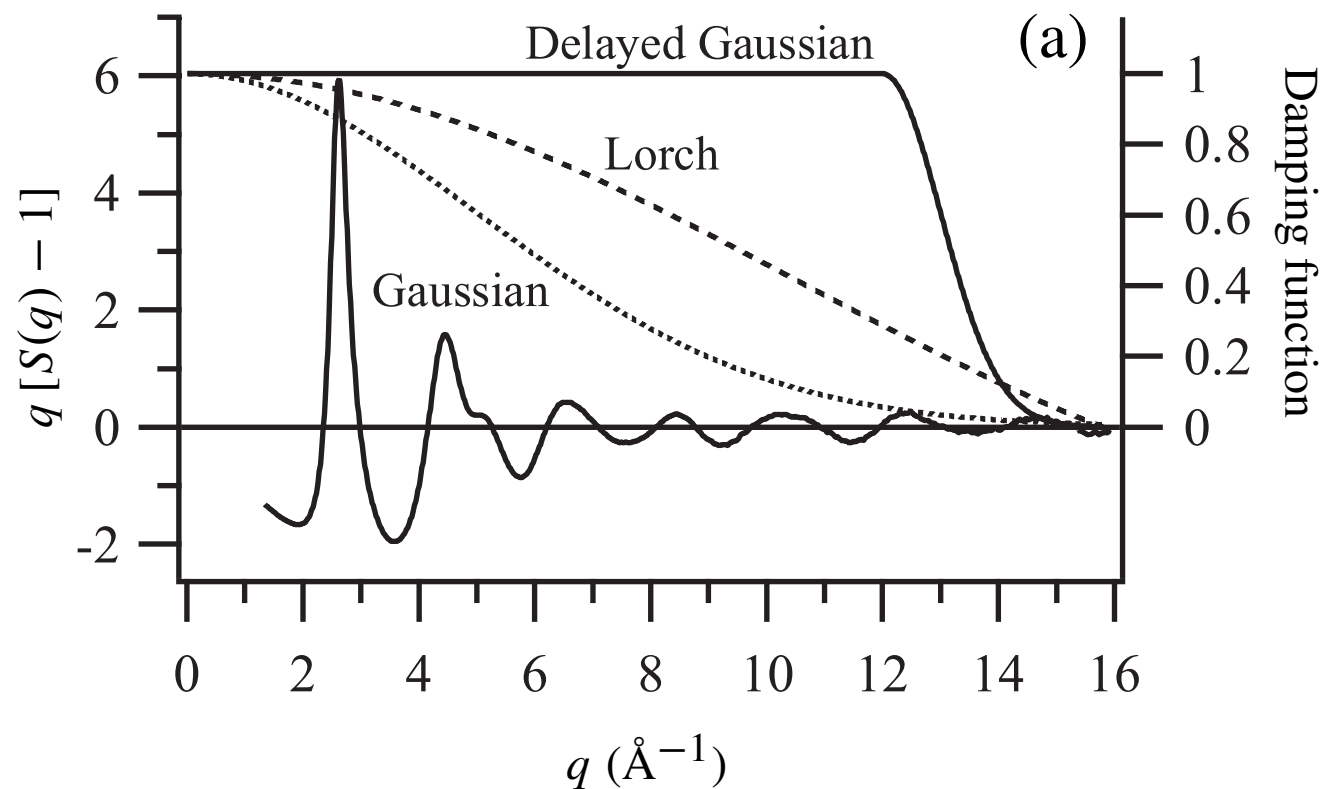
R. Lovell, G. R. Mitchell, and A. H. Windle. *Acta Crystallogr. Sec. A*, **35**, 598–603 (1979)
T. C. Hufnagel, R. T. Ott, and J. Almer. *MRS Symp. Proc.* **913**, Z18-01 (2006)

Extracting MRO information from the RDF

Write the RDF as:

$$\frac{\rho(r)}{4\pi r^2} - 1 = g(r) - 1 = \frac{A}{r}\exp\left(-\frac{r}{\lambda}\right)\sin\left(\frac{2\pi r}{D} + \phi\right)$$

Exponential decay "envelope"
in terms of a screening length, λ

Oscillations due
to short-range order
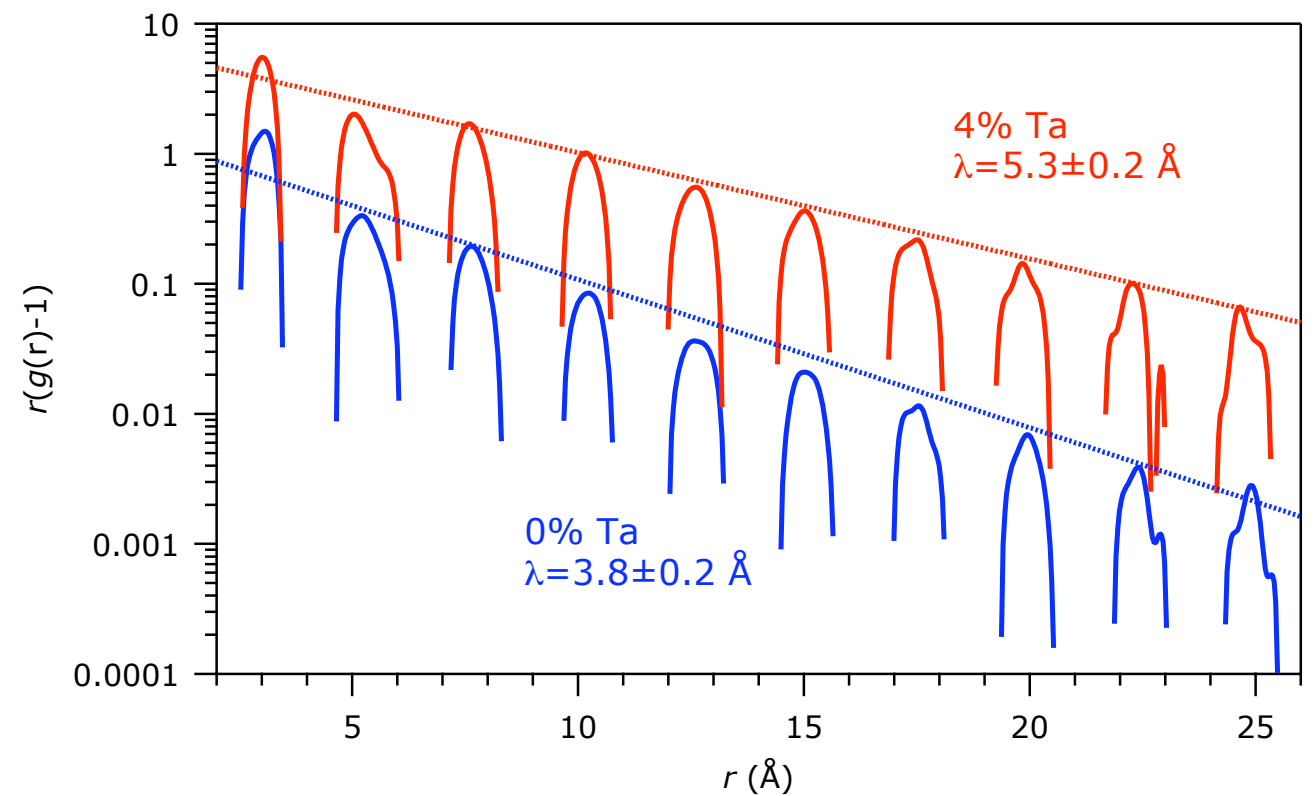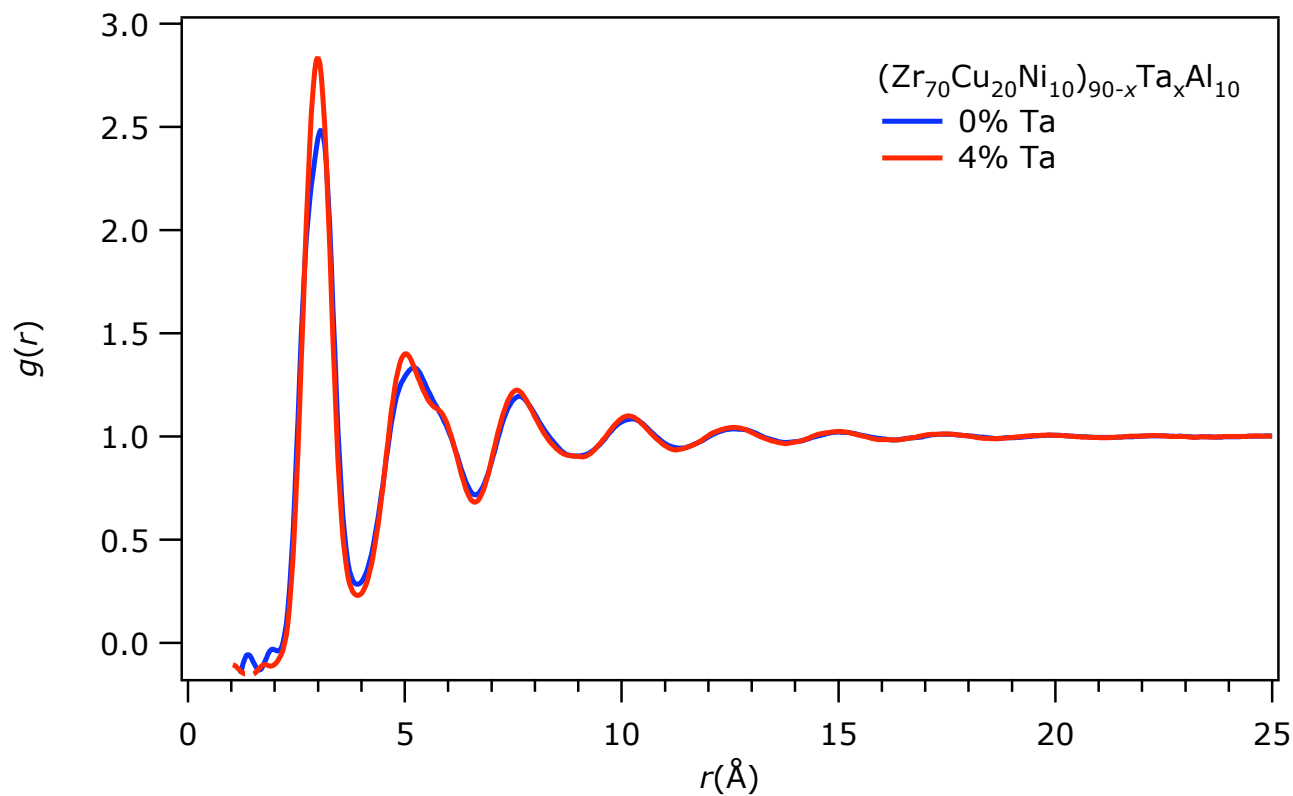
$(Zr_{70}Cu_{20}Ni_{10})_{90-x}Ta_xAl_{10}$
— 0% Ta
— 4% Ta

4% Ta
$\lambda=5.3\pm0.2$ Å

0% Ta
$\lambda=3.8\pm0.2$ Å

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Experimental geometries and detectors

Step scanning

- Excellent energy resolution possible (with the right detector)
- Slow scanning (hours)
- May be count-rate (dead time) limited

Focusing graphite monochromator

Position-sensitive x-ray detector

Beam slits

Detector slits

X-ray beam from monochromator

Sample

Ion chamber (incident beam monitor)

Evacuated enclosure
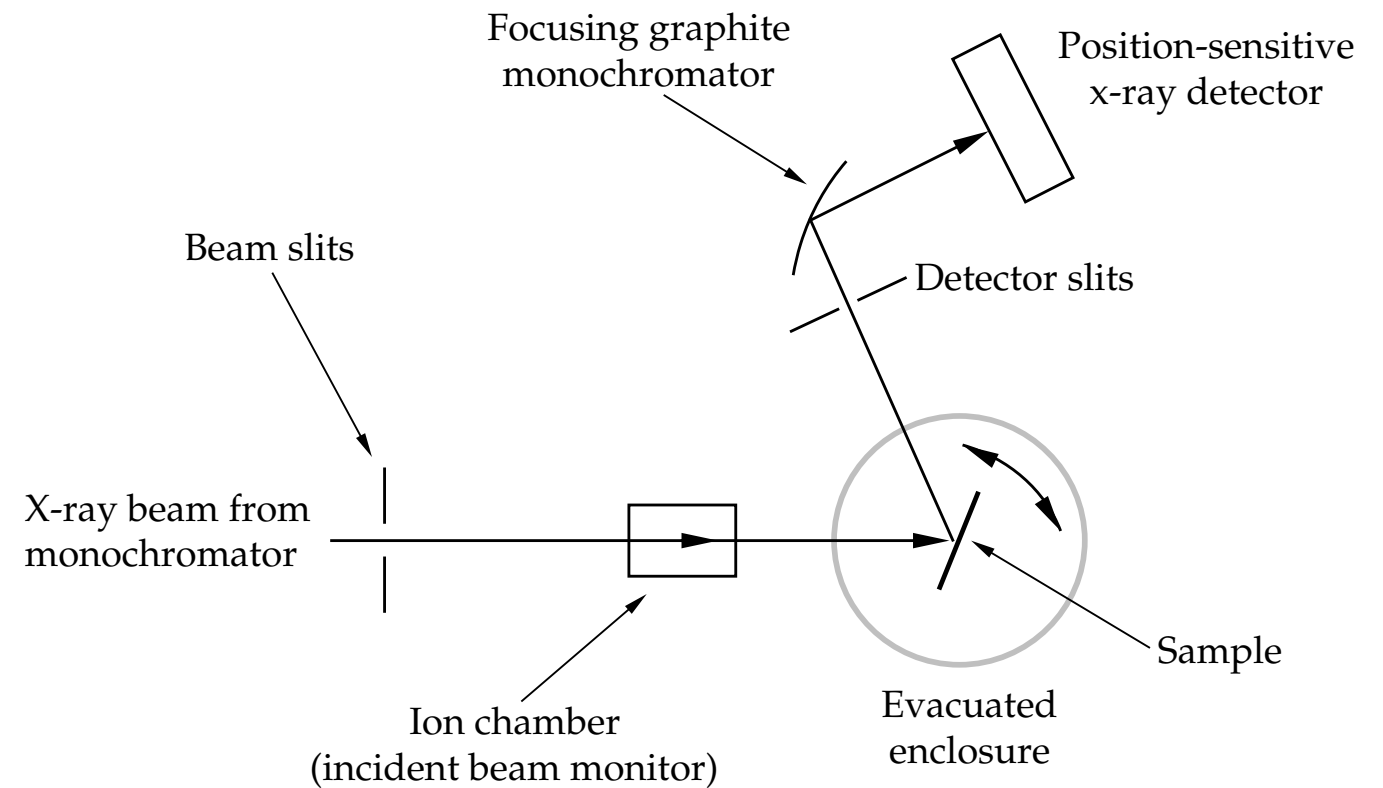
Area detector

- Excellent signal-to-noise ratio
- Very fast "scans" (seconds)
- Measure q in multiple orientations simultaneously (anisotropic specimens)
- Poor energy resolution
- Limited angular range

$\vec{q}_{||}$

Image plate

$\vec{q}_{\perp}$

Specimen
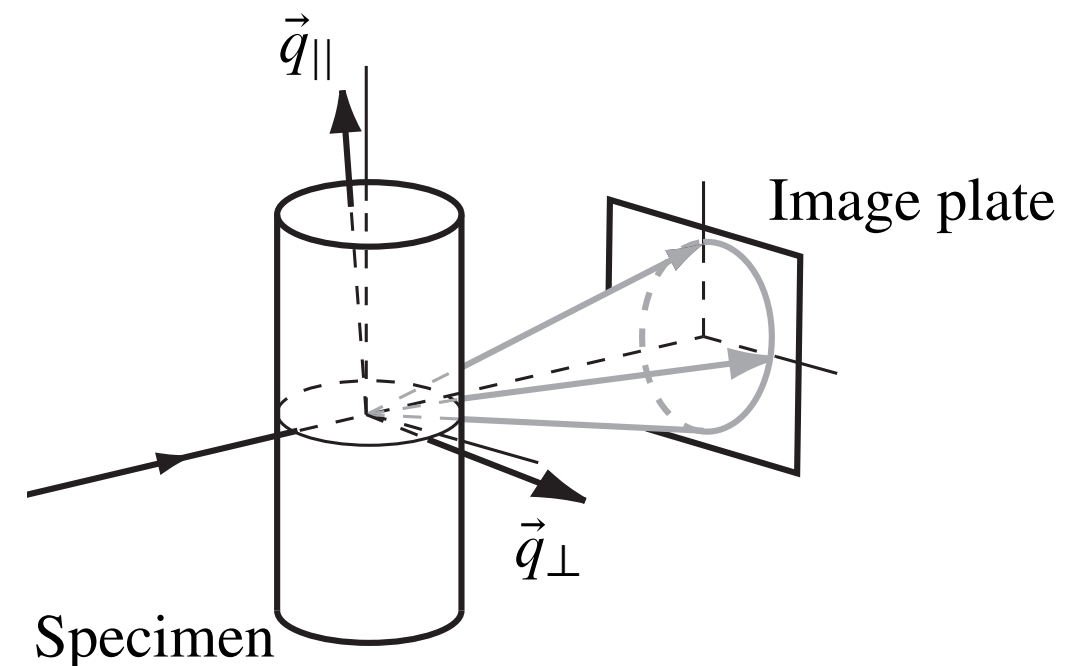
Data collection considerations

- Need to measure *I(q)* to the largest *q* possible:

$$q_{\mathrm{max}} = \frac{4\pi}{\lambda} = \frac{4\pi E}{hc} \qquad \longrightarrow \qquad q_{\mathrm{max}}(\text{Å}^{-1}) \approx E(\mathrm{keV})$$

- The elastic, single-scattering intensity *I(q)* must be separated from all other sources of intensity. (This usually involves both experimental design and data analysis.)

- High signal-to-noise is essential at all values of *q*, especially at high *q*:

$$\rho(r) - \rho_{\circ} = \frac{1}{8\pi^3} \int_0^{\infty} 4\pi q^2 \, (S(q) - 1) \, \frac{\sin qr}{qr} dq$$

Anomalous dispersion of x-rays

Write the atomic scattering factor for x-rays as

$$f(q,E) = f_\circ(q) + f'(q,E) + if''(q,E)$$

Energy-independent atomic form factor

Energy-dependent anomalous scattering factors

$f(q,E)$ is unique for each element:
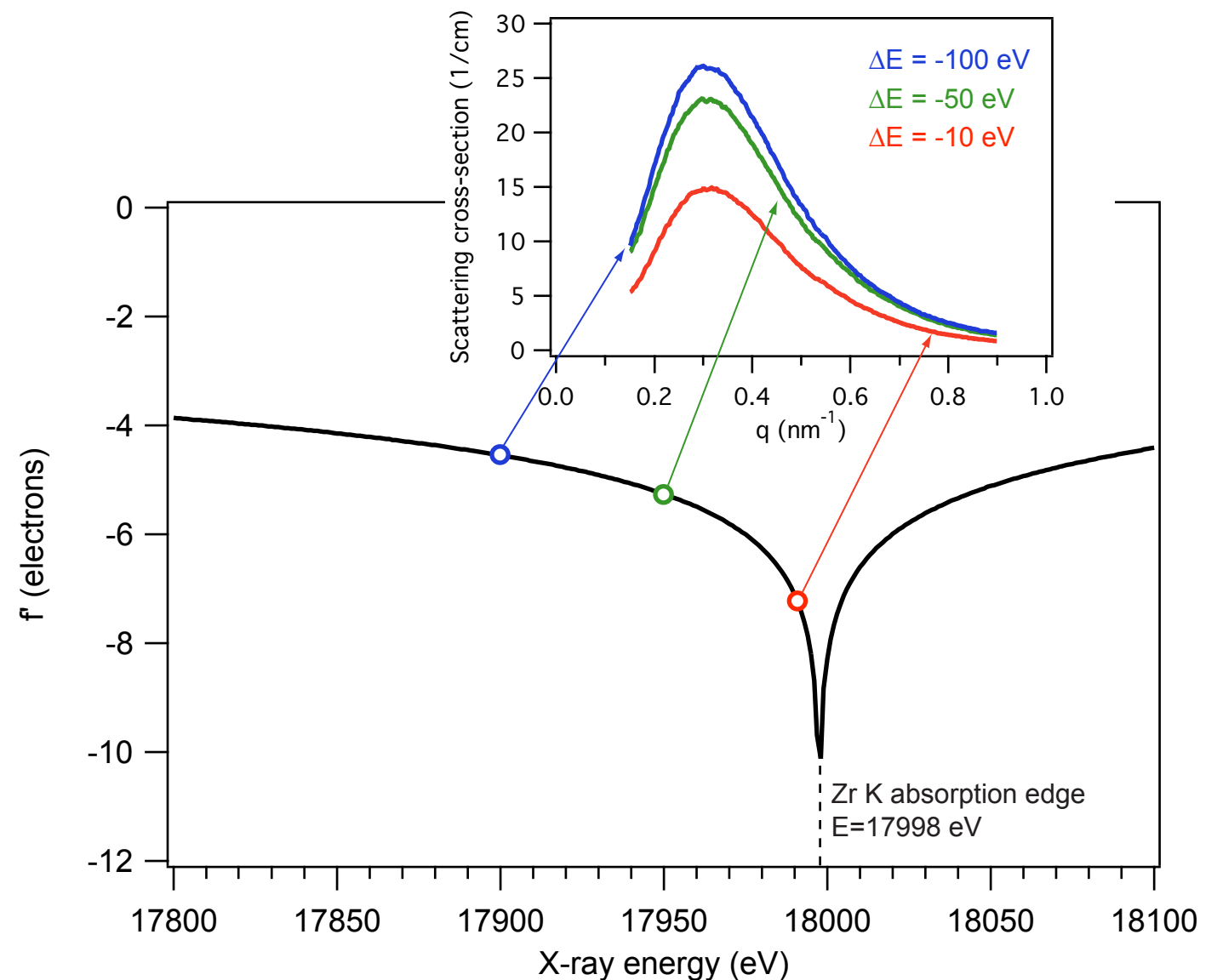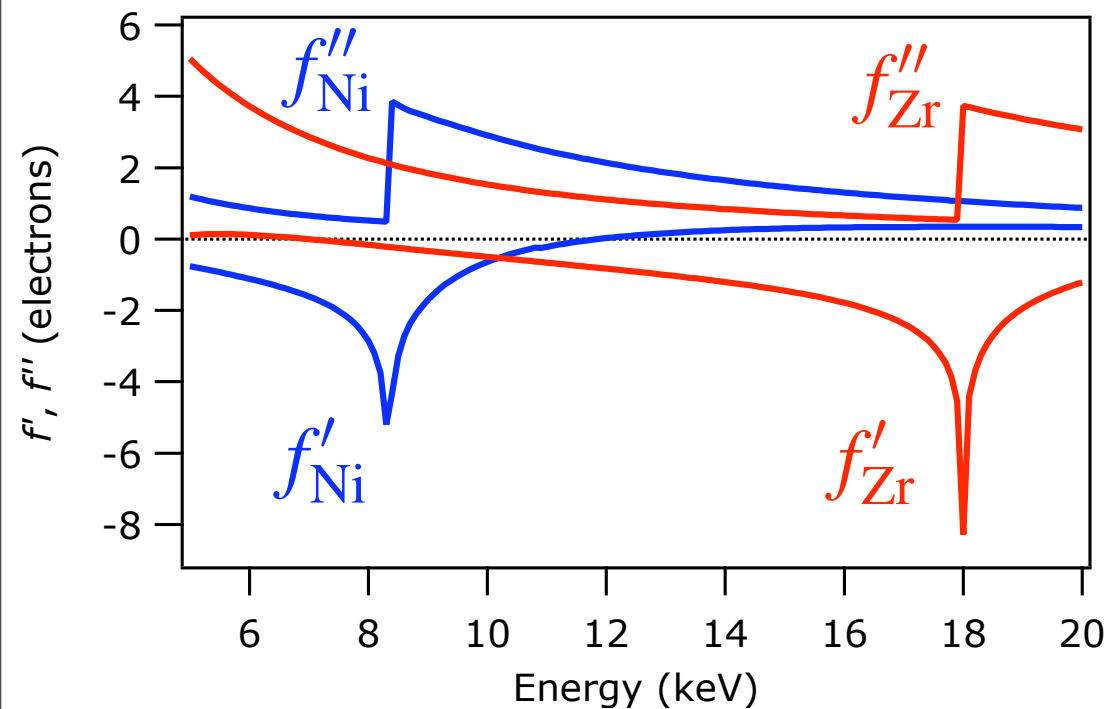
Energy resolution is critical
Position-Sensitive Detector Output

19.985 keV

intensity (cts/monitor cts)

elastic

$K_\beta RR$

$K_\alpha RR$

k (1/Å)

energy

x 10^4

ΔE^{Mo}_{RR} = 394 eV
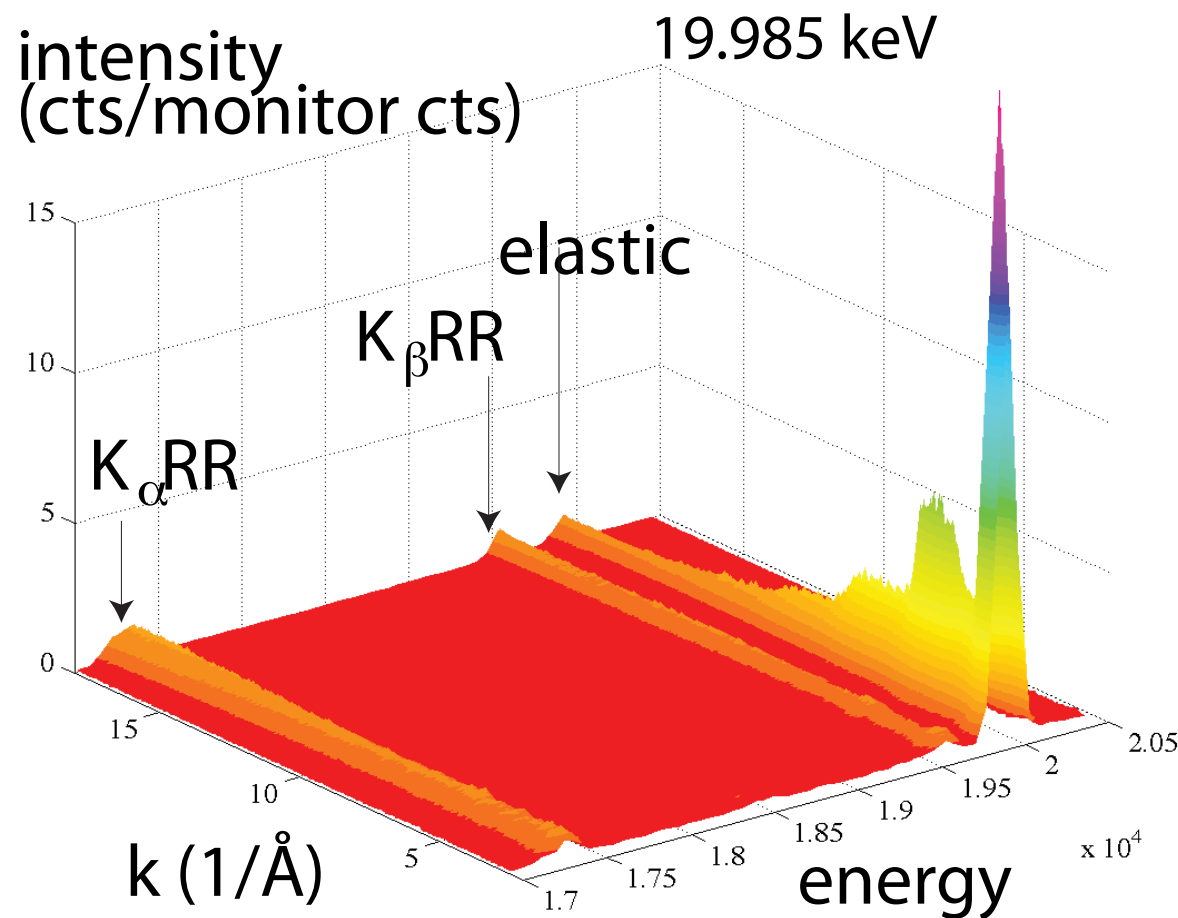
ΔE^{Ge}_{RR} = 121 eV

Complete spectrum allows experimental removal of inelastic contributions from Compton and resonant Raman scattering

Compton scattering nominally eliminated down to ~3 Å^{-1} below Ge edge and ~5 Å$^-$ below Mo edge.

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H. Ishii and S. Brennan (unpublished)

Partial pair distribution function analysis

Amorphous $NiZr_2$ studied by combined resonant x-ray scattering and Reverse Monte Carlo simulations.

Total structure factor $S(q)$ — Partial structure factors — Partial distribution functions
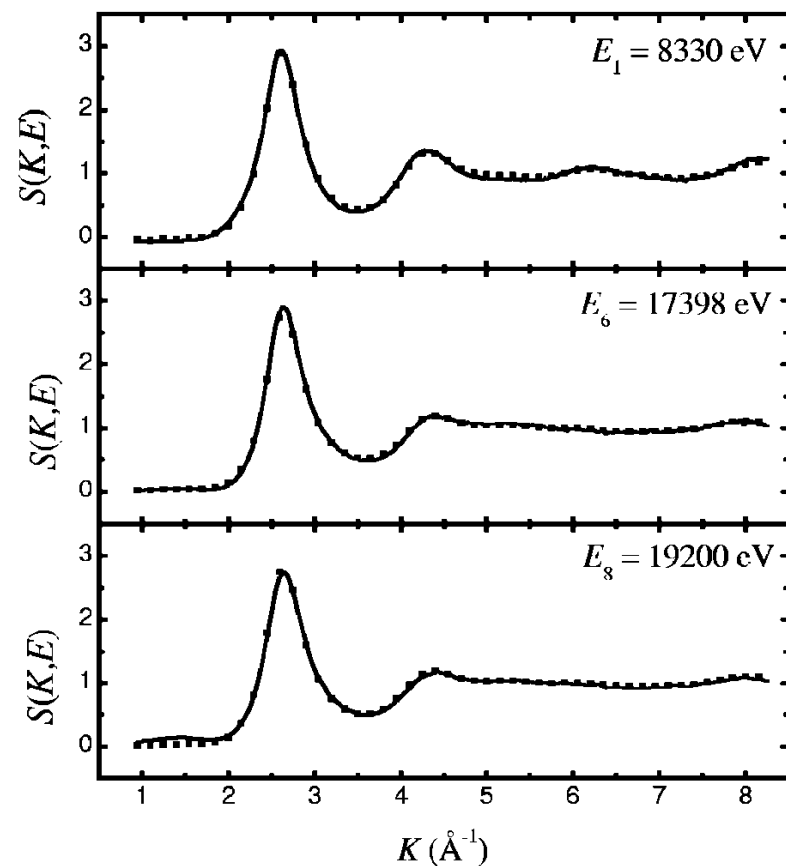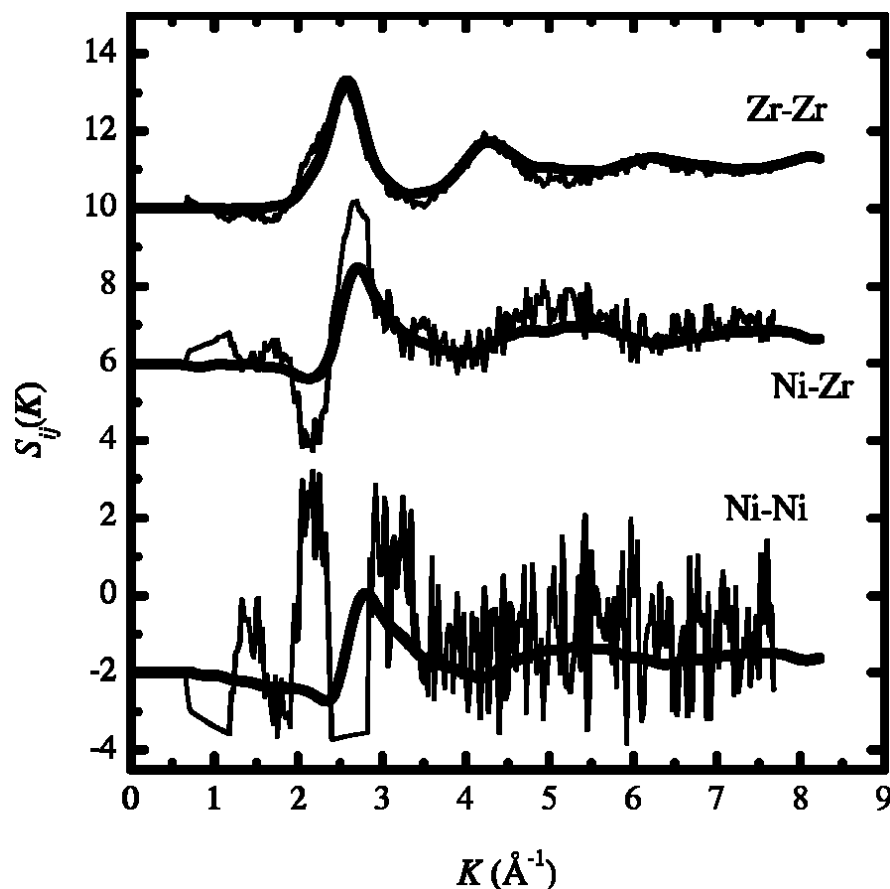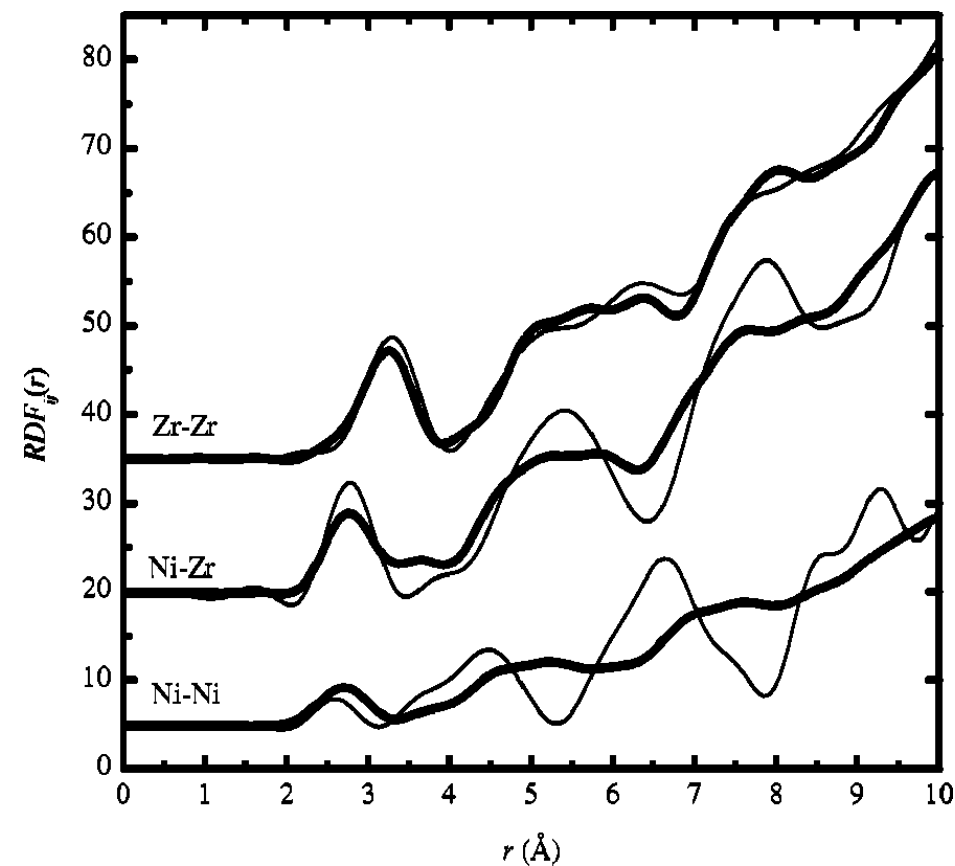
More complicated alloys are ... more complicated.

Resonant x-ray scattering on amorphous materials
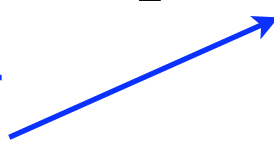
For a sample with *m* elements, the total scattered intensity is a weighted sum of *m(m+1)/2* partial structure factors:

$$I(q) = n \sum_\alpha \sum_\beta x_\alpha f_\alpha(q,E) f_\beta^*(q,E) S_{\alpha\beta}(q)$$

Because *f* (*q, E*) only varies rapidly with *E* near an absorption edge, we can make a differential measurement for an element of interest (*A* here):

$$\left(\frac{\partial I(q,E)}{\partial E} \right)_q = x_A \sum_\beta \frac{\partial}{\partial E} \left[f_A(q,E) f_\beta^*(q,E) + f_A^*(q,E) f_\beta(q,E) \right] S_{A\beta}(q)$$

Only pair correlations that involve atoms of type A contribute to the total scattering

For instance, we can make scattering measurements at two energies below an absorption edge, and take the difference. The resulting real-space information is a distribution function specific to the element of interest.

Resonant x-ray scattering from $(Zr_{70}Cu_{20}Ni_{10})_{90-x}Ta_xAl_{10}$
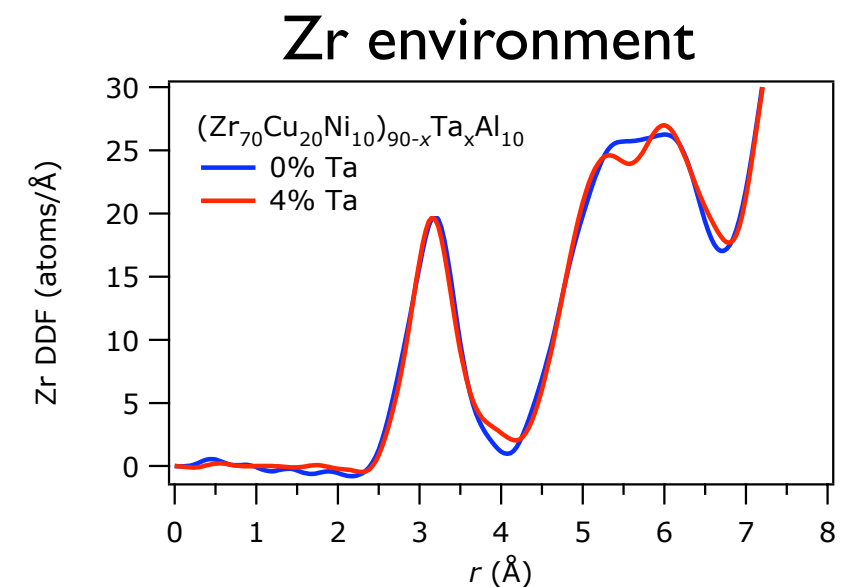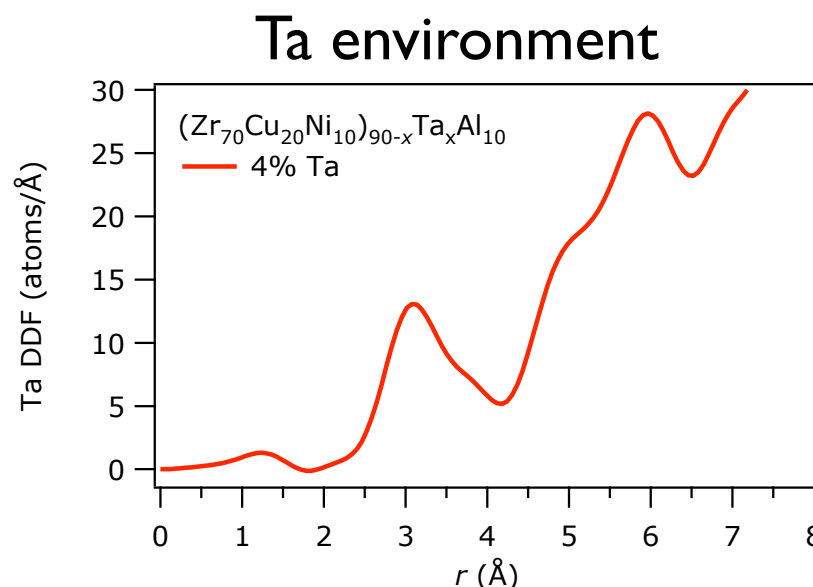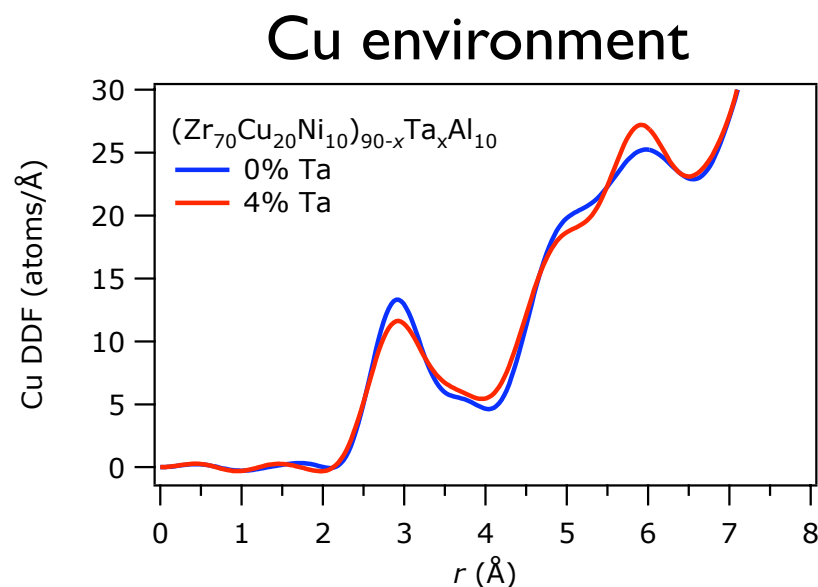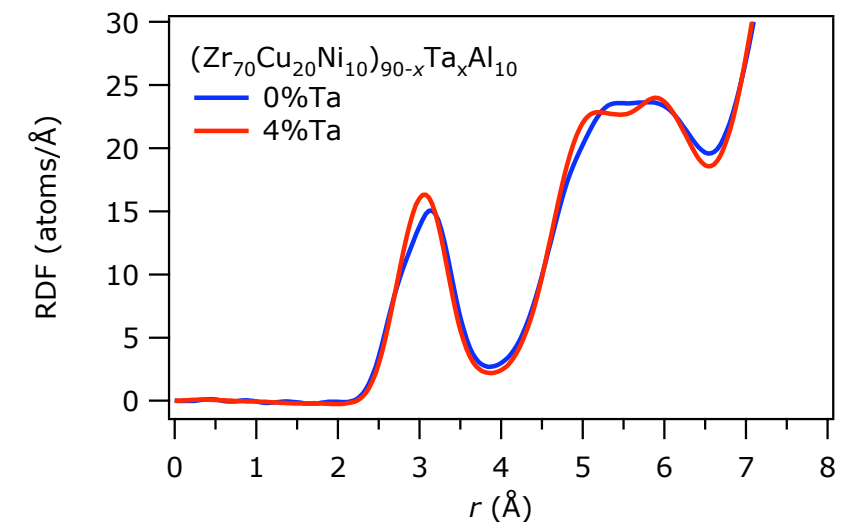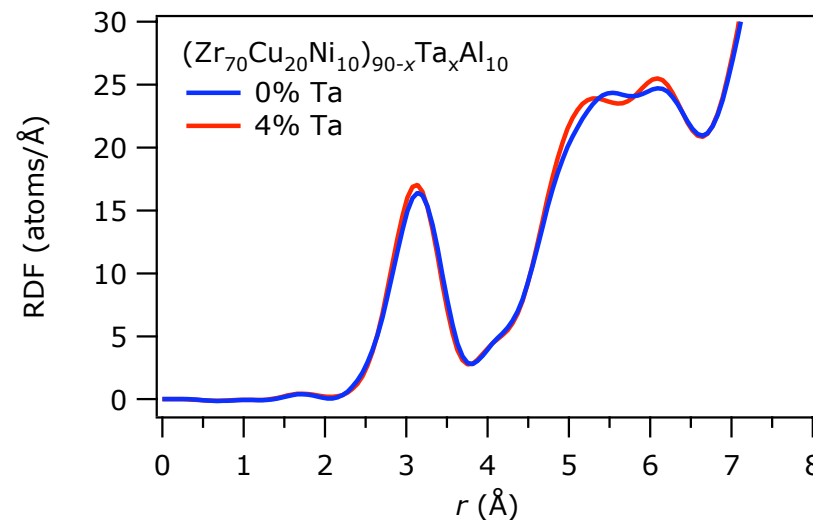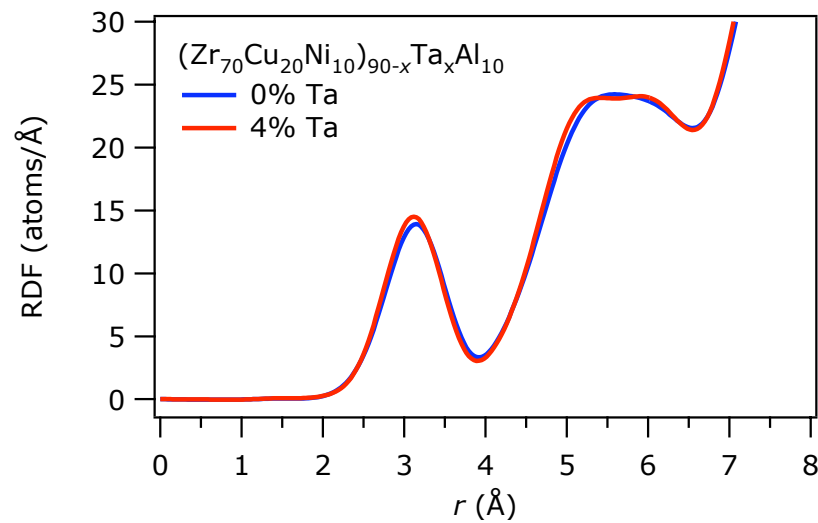
Lessons I've learned the hard way

1. Characterize the dead time of your detector at the x-ray energies you use, and over a large range of count rates.

2. Either exclude the Compton scattering experimentally, or count *all* of it (so you can calculate and subtract it later).

3. If doing a transmission experiment, measure the actual absorption of your specimen (μt product).

4. If possible, measure the fluorescence from the specimen separately from the elastic scattering. (This tells you a lot about potential alignment problems.)

5. Rather than doing a few lengthy scans, do many scans of short duration (to avoid systematic errors).

6. Do the data analysis in near-real time on the first few scans, to identify problems early.

What's important

1. Signal-to-noise ratio (particularly at high q)

2. Energy resolution on the scattered beam side (*critical* for resonant scattering)

3. Energy resolution on the incident beam side (resonant scattering only)

4. Minimizing background (anything that is not elastic scattering from your specimen)

What's not (within reason)

Resolution in q space; brightness (divergence)

"X-ray amorphous"
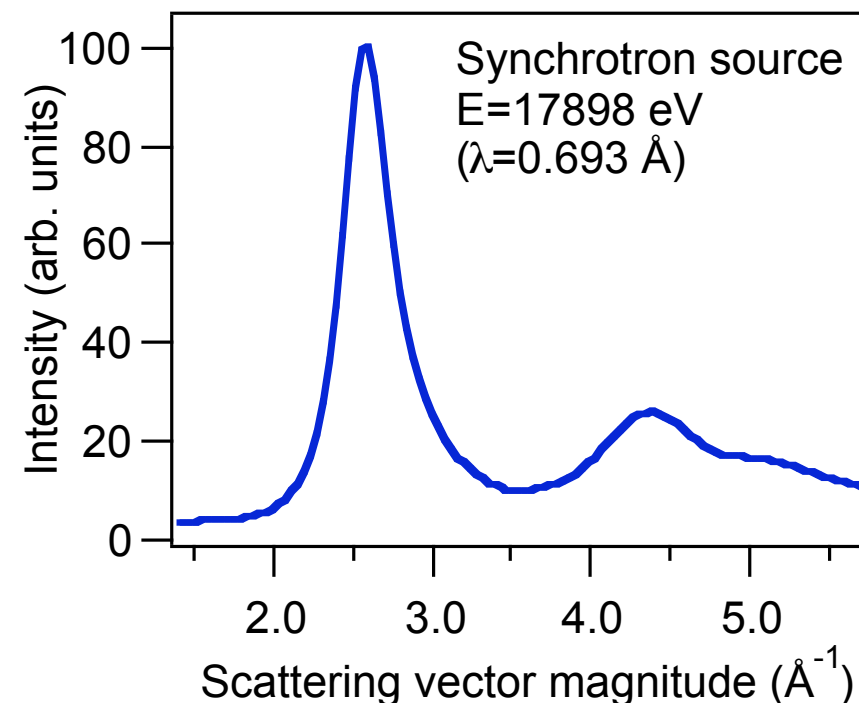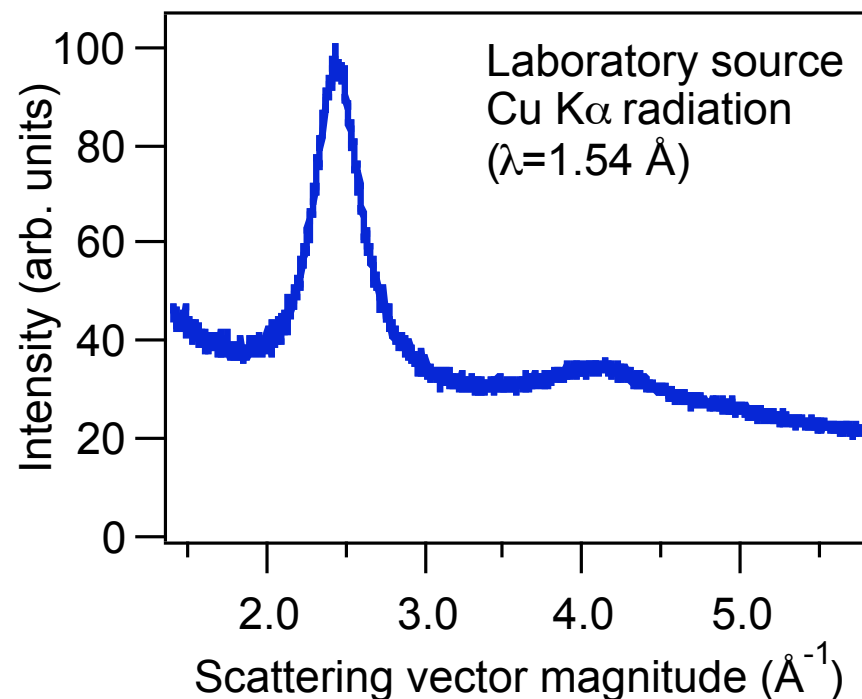
Is it amorphous?
- First peak symmetric
- Second peak at ~1.6-1.8 q_{max} (for a metallic glass)
- No other scattering features present
- Combine with other techniques (TEM, DSC)

Fundamental problem: All you get (from scattering) is the RDF, which is only sensitive to pair correlations.
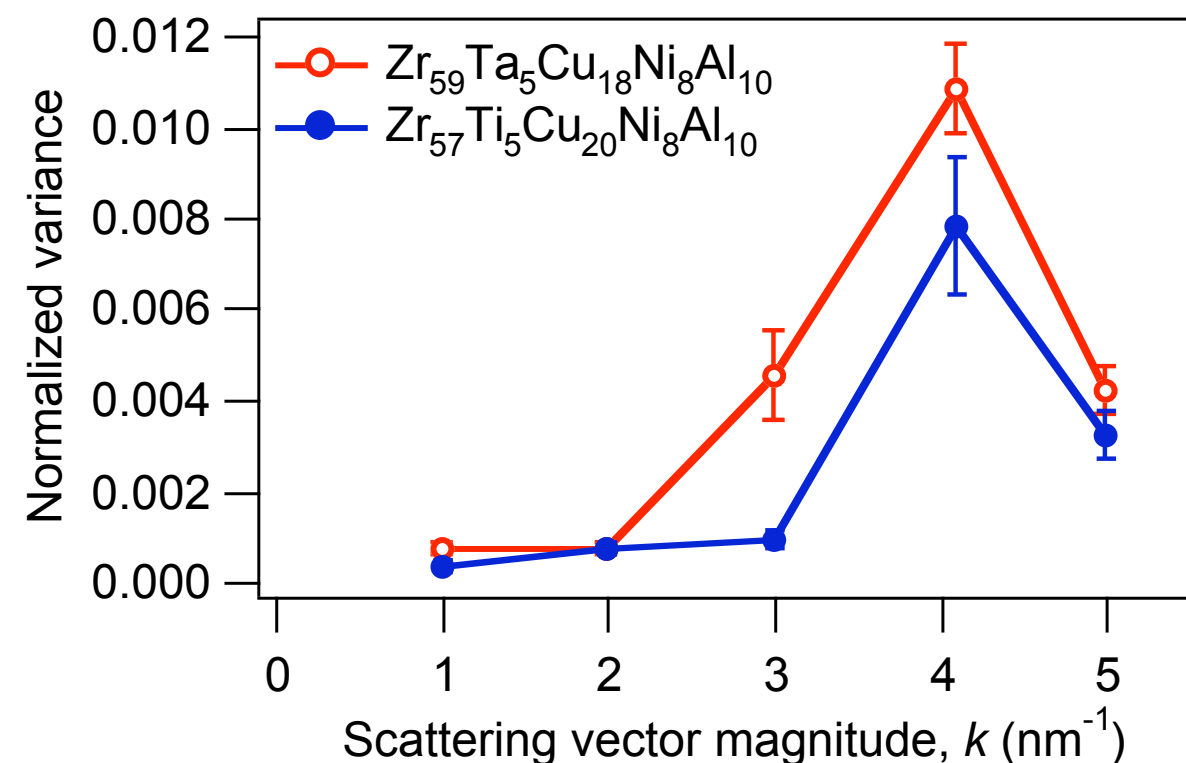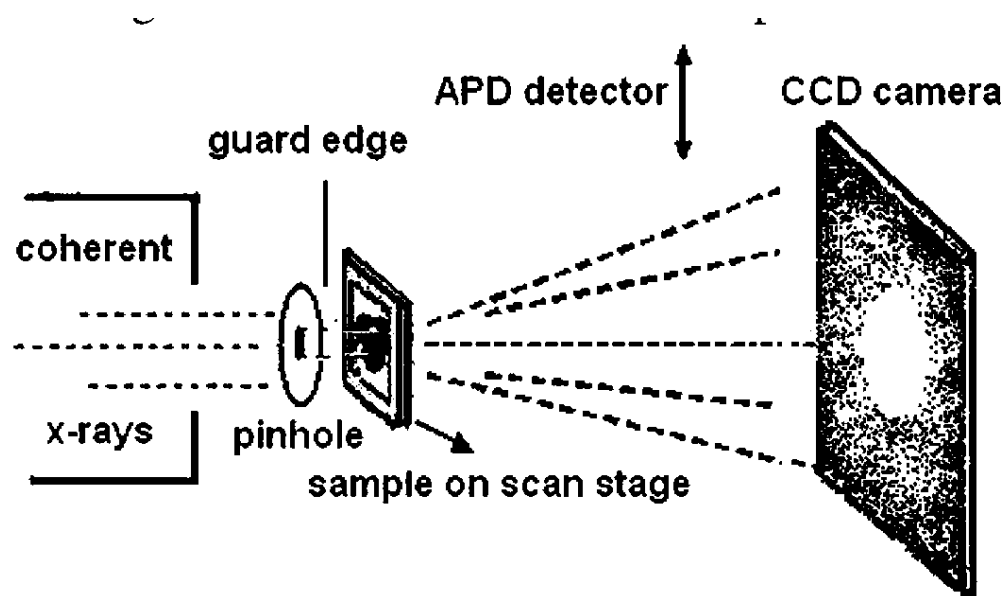
Beyond the RDF: Fluctuation microscopy
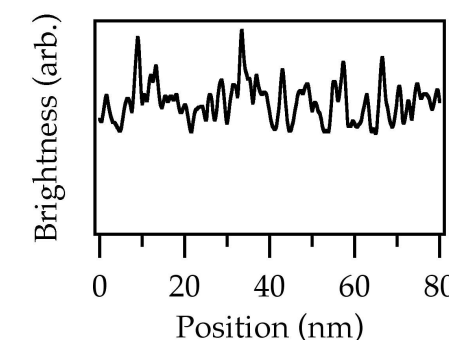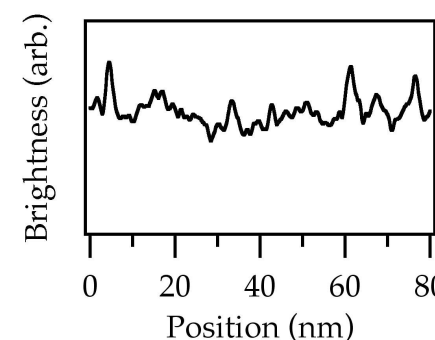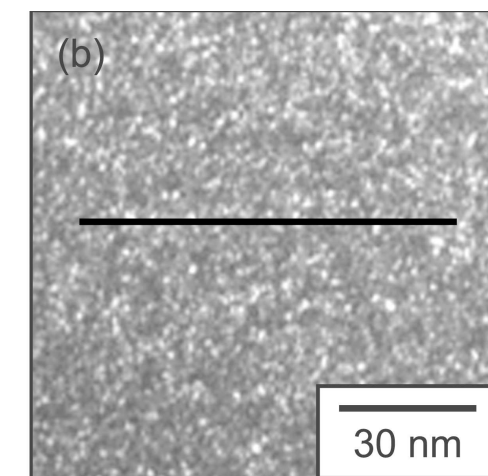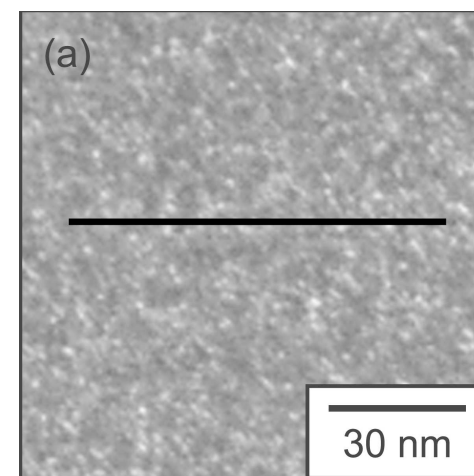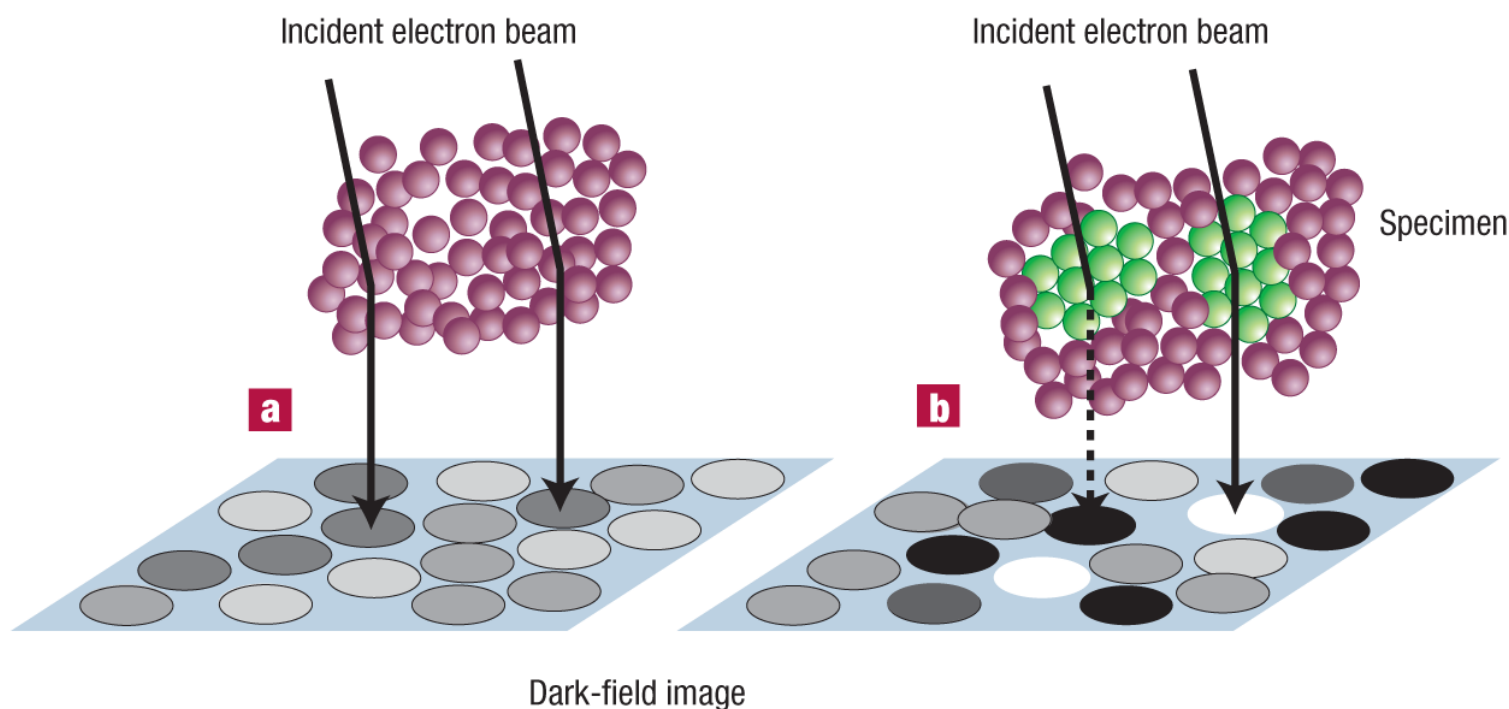
T. C. Hufnagel, *Nature Mat.* **3**, 666 (2004)
(figure adapted from P. M. Voyles)

$$V(\vec{k}, Q) = \frac{\langle I^2(\vec{r}, \vec{k}, Q)\rangle}{\langle I(\vec{r}, \vec{k}, Q)\rangle^2} - 1$$

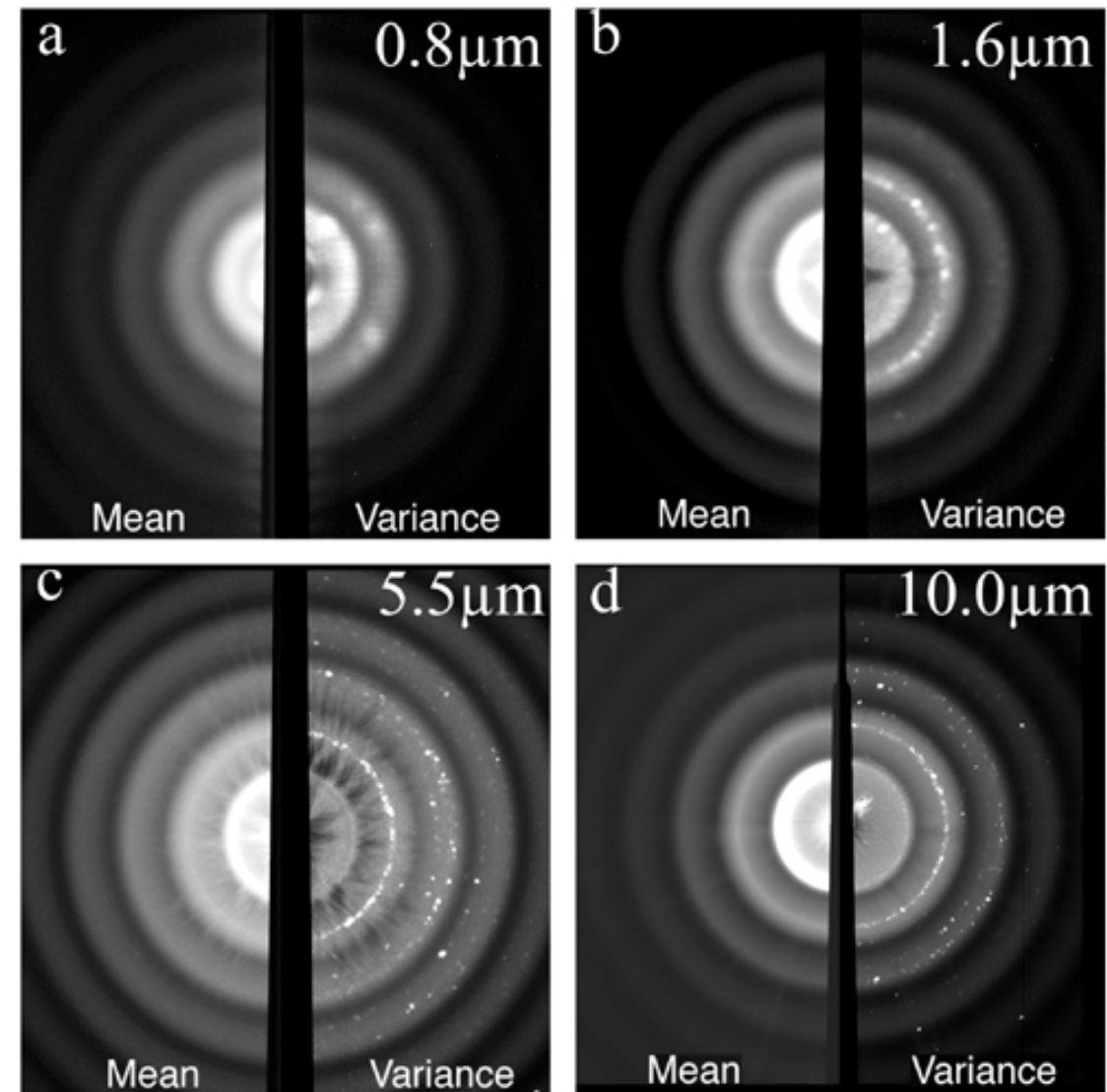The variance contains information about higher order (3- and 4-body) correlations

Fluctuation x-ray microscopy

Complement to FEM–great potential for looking at polymers, biologics, self-assembled materials

Future:
• Higher spatial resolution
• Harder x-rays
• Resonant scattering

7 μm thick layer of 277 nm latex spheres

$E = 1.83$ keV (6.77 Å)

L. Fan *et al.*, *MRS Symp. Proc.* **840**, QC6.7 (2005)

References and resources

- Books

    - B. E. Warren, *X-Ray Diffraction* (Dover, 1990)

    - T. Egami and S. Billinge, *Underneath the Bragg Peaks: Structural Analysis of Complex Materials* (Pergamon, 2003)

- Dissertations/SSRL reports from the Bienenstock group (Fuoss, Kortright, Ludwig, Wilson, Ishii...)

- Software

    - Matlab routines (http://ssrl.slac.stanford.edu/~bren/files/amorphous/)

    - Billinge group software (http://www.pa.msu.edu/ftp/pub/billinge/)