Data Preparation for Empirical Potential Structure Refinement

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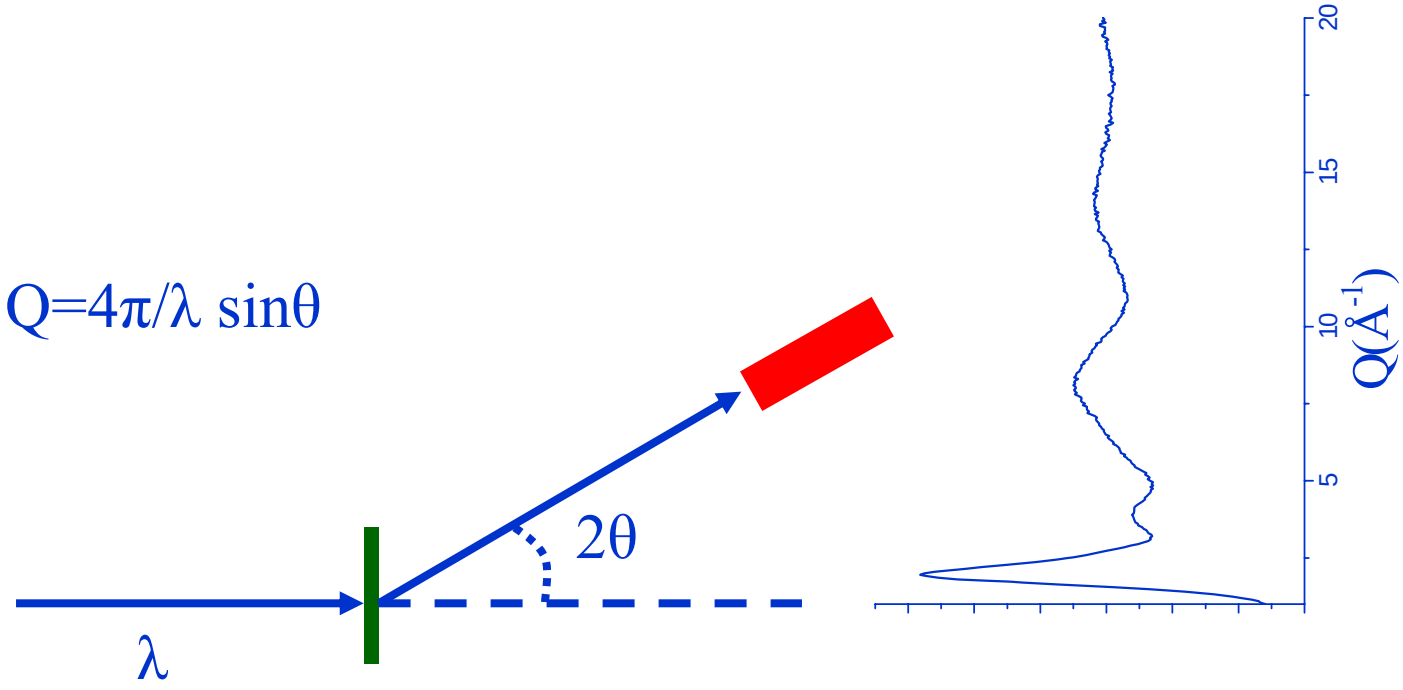
Schematic of a diffraction experiment



An EPSR model can only be as reliable as the experimental data against which it is refined!

The data to be modelled should be corrected for:

(1) Background scattering contributions (container/instrument)
(2) Absorption
(3) Multiple scattering
(4) Inelastic scattering (neutron) or Compton scattering (X-ray)
(5) Polarization (X-ray)
(6) Detector efficiencies, dead time etc.

And ideally should be

(7) CAREFULLY NORMALISED

The neutron diffraction experiment

Total Structure Factor

Atomic concentrations and scattering lengths

$$F(Q) = \sum_{\alpha\beta} c_\alpha c_\beta b_\alpha b_\beta S_{\alpha\beta}(Q)$$

Partial Structure Factors

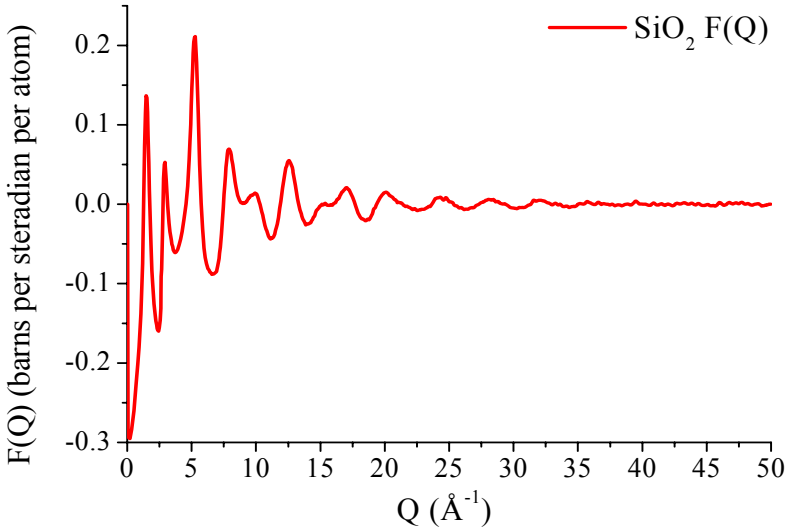
$$S_{\alpha\beta}(Q) - 1 = 4\pi\rho \int_0^\infty r^2 \left[g_{\alpha\beta}(r) - 1 \right] \frac{\sin(Qr)}{Qr} dr$$

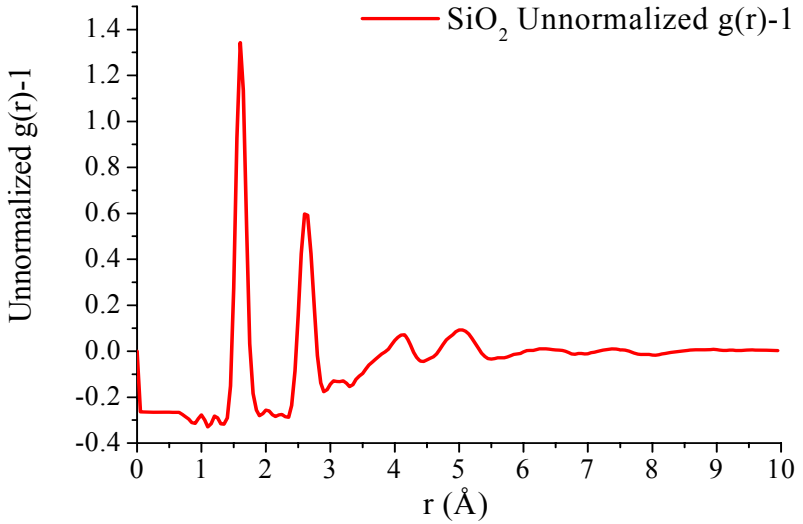
Atomic density

Partial Pair Distribution Functions

From neutron F(Q) to normalized structure factors

$$S(Q)-1=\frac{F(Q)}{\sum_{i=1}^{n}(c_i b_i)^2}$$





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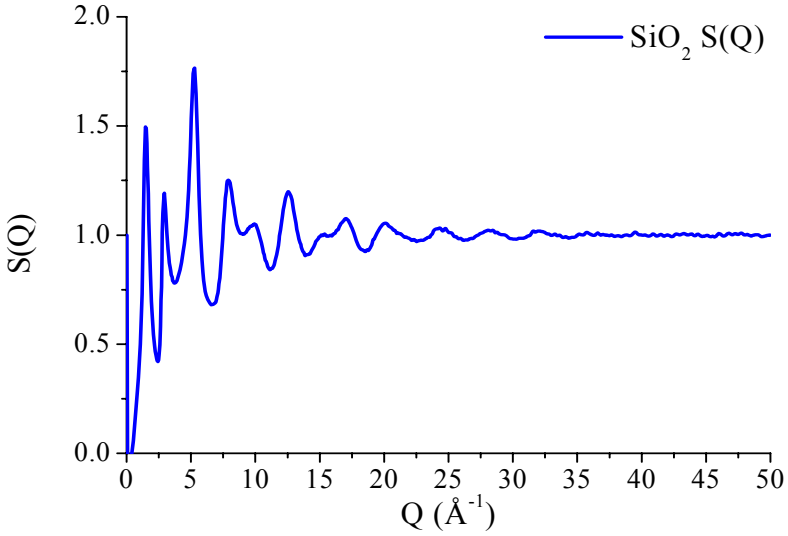
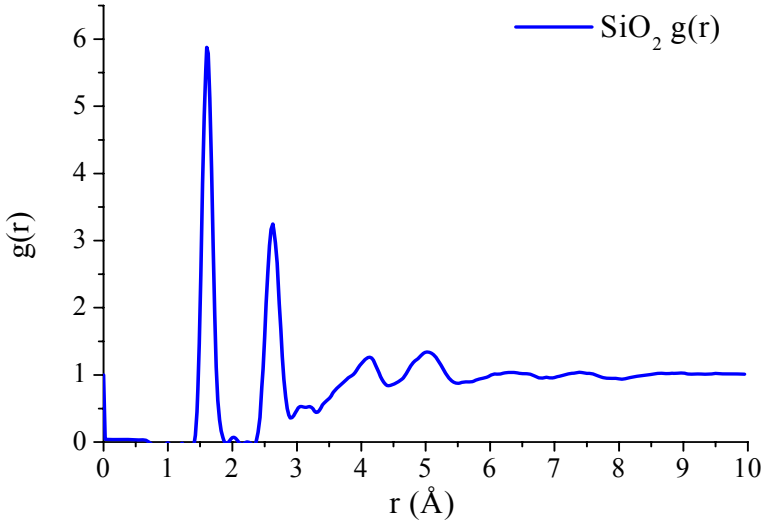
From neutron F(Q) to normalized structure factors

$$S(Q)-1=\frac{F(Q)}{\sum_{i=1}^{n}(c_i b_i)^2}$$





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The X-ray diffraction experiment

Total Structure Factor

Atomic concentrations and scattering form factors

$$F(Q) = \sum_{\alpha\beta} c_\alpha c_\beta f_\alpha(Q) f_\beta(Q) S_{\alpha\beta}(Q)$$

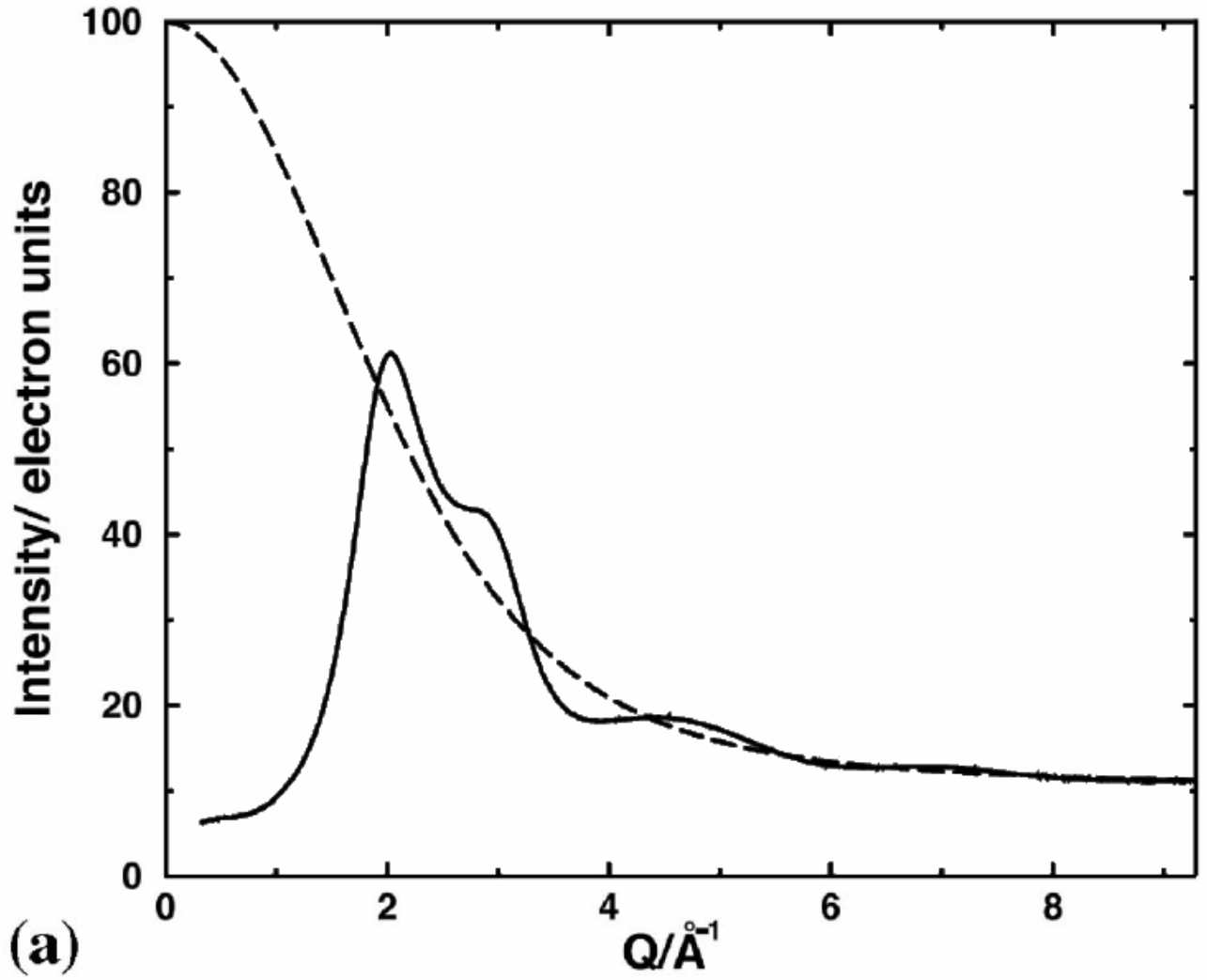
Partial Structure Factors

$$S_{\alpha\beta}(Q) - 1 = 4\pi\rho_e \int_0^\infty r^2 \left[g_{\alpha\beta}(r) - 1\right] \frac{\sin(Qr)}{Qr} dr$$

Electronic density

Partial Pair Distribution Functions

From X-ray intensities to normalized structure factors



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Mean Form Factor Squared Normalization Procedure

$$S_{X-ray}(Q) = \frac{\left[I_{eu}^{coherent}(Q) - \sum_{i=1}^{n} x_i f_i^2(Q) \right]}{\left[\sum_{i=1}^{n} x_i f(Q)_i \right]^2}$$

$S_{X\text{-}ray}(Q)$ is the normalized X-ray structure factor
x_i is the fraction of atoms of type i in the sample
f_i is the atomic scattering form factor for the atom type i
Q is the magnitude of the scattering vector

Single Atom Scattering Normalization Procedure

$$S_{X-ray}(Q) = \frac{\left[I_{eu}^{coherent}(Q) - \sum_{i=1}^{n} x_i f_i^2(Q) \right]}{\left[\sum_{i=1}^{n} x_i f^2(Q)_i \right]}$$

$S_{X\text{-}ray}(Q)$ is the normalized X-ray structure factor
x_i is the fraction of atoms of type i in the sample
f_i is the atomic scattering form factor for the atom type i
Q is the magnitude of the scattering vector

Modified Atomic Form Factors

J.M.Sorenson, G.Hura, R.M.Glaeser and T.Head-Gordon
Journal of Chemical Physics **113** (2000) 9149-9161

Essentially a mechanism to allow for charge transfer in molecular systems, such as from the hydrogen atoms to oxygen atom in water molecules.

$$f'(Q) = \left[1 + (\alpha)\exp\left(\frac{-Q^2}{2\delta^2}\right)\right] f(Q)$$

f' is the modified atomic scattering form factor
f is the free atom scattering form factor
α is a parameter controlling the magnitude of charge transfer
δ is a parameter controlling the extent of electron delocalization

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Modified Atomic Form Factors

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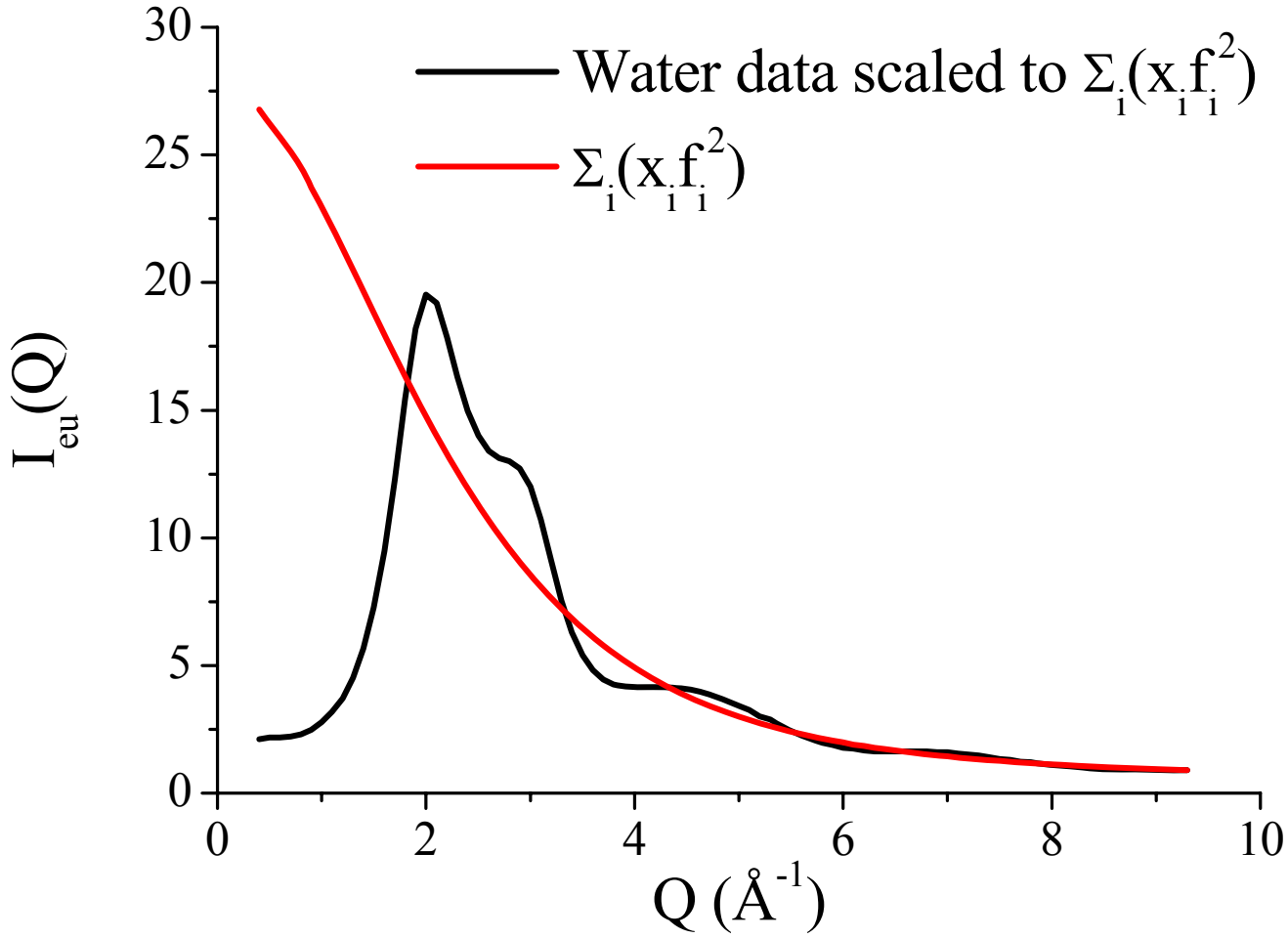
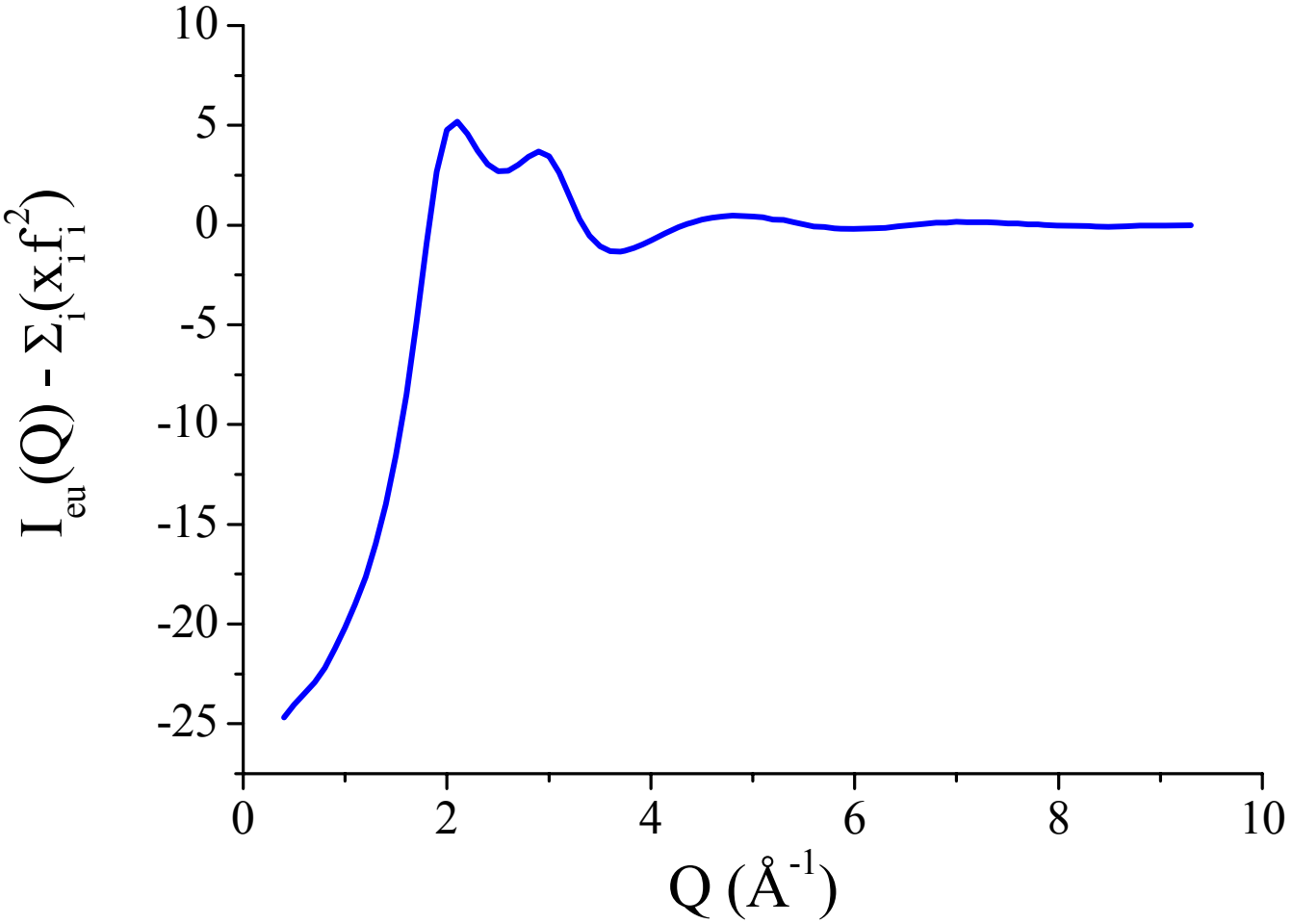
$$f'(Q) = \left[1 + (\alpha)\exp\left(\frac{-Q^2}{2\delta^2}\right)\right] f(Q)$$

Typical values for water are:
$\alpha(O) = +0.12$, $\alpha(H) = -0.48$ and $\delta(O) = \delta(H) = 2.2 Å^{-1}$

From X-ray intensities to normalized structure factor: the liquid water example



From X-ray intensities to normalized structure factor: the liquid water example



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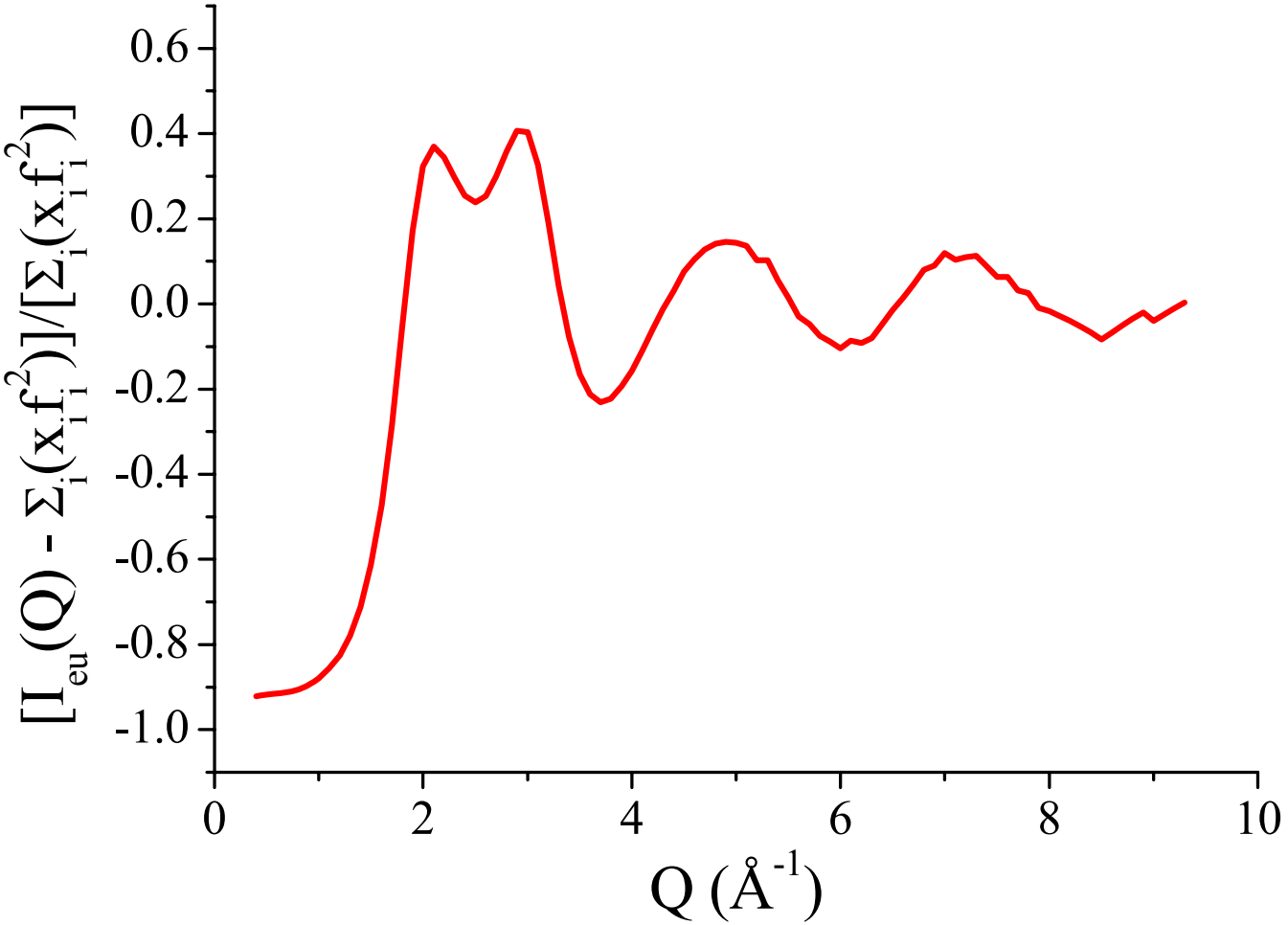
From X-ray intensities to normalized structure factor: the liquid water example



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