Resolution Effects and Deconvolution of Diffraction Data

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SciSoft coffee seminar, 14h00 Friday 19 April 2013, ESRF

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General expression for diffraction

For a monochromatic incident beam of energy E_i, a diffraction measurement simply integrates the double differential scattering cross-section over all possible energy exchanges $\hbar\omega = E_i - E_f$ between the neutron (or x-ray) and the N atoms of the sample, in general at constant scattering angle 2θ:

$$\left.\frac{d\sigma}{d\Omega}\right|_{meas} = \int_{-\infty}^{E_i} d(\hbar\omega)\,\frac{d^2\sigma}{d\Omega\; dE_f}\,\varepsilon(E_f)\;,$$

where $\varepsilon(E_f)$ is the detector efficiency, and

$$\frac{d^2\sigma}{d\Omega\; dE_f} = \frac{\sigma}{4\pi}\,\frac{k_f}{k_i}\,N\,S(\mathbf{q},\omega)$$

can refer to either the coherent or incoherent scattering case, for which $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f$ is the wavevector transfer. The finite incident energy E_i leads to a non-zero "snapshot time" $\tau_{snapshot} \sim \hbar/E_i$ during which a neutron (or x-ray) probes the sample's structure within its coherent volume.

Static approximation

When the incident energy E_i exceeds the maximum possible energy transfer $\hbar\omega_{\max}$ between the scattered quantum and the excitations in the sample, and for $\varepsilon(E_\mathrm{f}) = 1$, it is perfectly valid to use the *static approximation* for diffraction:

$$\frac{d\sigma}{d\Omega}(\mathbf{q}) = \overline{\left\langle \left| \sum_i^N b_i \, e^{i\mathbf{q}\cdot\mathbf{r}_i} \right|^2 \right\rangle} = \left\langle \sum_{i,j}^N \overline{b_i b_j^*} \, e^{i\mathbf{q}\cdot\mathbf{r}_{ij}} \right\rangle ,$$

where b_i is the scattering length of the i^{th} atom at position $\mathbf{r}_i$, and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. The $<>$ represent a thermal average and the horizontal bars an ensemble average over the different possible coherence volumes within the sample, each having a particular assignment of scattering lengths in the case of neutron diffraction. Note that scattering lengths are q-dependent in the case of x-ray diffraction.

When $E_\mathrm{i} < \hbar\omega_{\max}$, as is often the case for neutron diffraction, the non-satisfaction of the static approximation requires inelasticity corrections to be made to the measured diffraction patterns.

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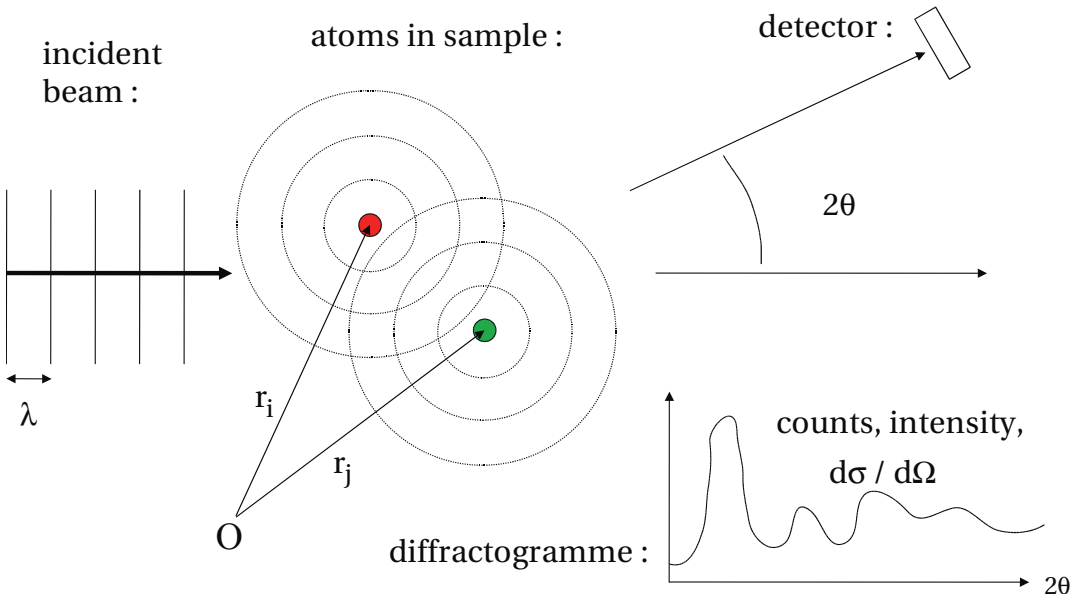
Schematic of a diffraction measurement (mono-λ)



The spherical waves of scattering amplitude interfere at the detector.

Case of a monoatomic sample (only one Z)

In neutron scattering, a monoatomic sample can have a distribution of scattering lengths b_i, but there is no correlation between b_i and the structural environment of $\mathbf{r}_i$. The ensemble average over coherence volumes then leads to an expression involving a $\mathbf{q}$-dependent coherent term and an isotropic incoherent term:

$$\frac{1}{N}\left[\frac{d\sigma}{d\Omega}(\mathbf{q})\right] = \overline{b}^2 S(\mathbf{q}) + (\overline{b^2} - \overline{b}^2)$$

where the sample's average scattering length $\overline{b} = b_{\rm coh}$, and where $(\overline{b^2} - \overline{b}^2) = var(b)$ is simply the variance of scattering lengths throughout the sample. The alternative expression:

$$\frac{1}{N}\left[\frac{d\sigma}{d\Omega}(\mathbf{q})\right] = \overline{b}^2 \left[S(\mathbf{q}) - 1\right] + \overline{b^2}$$

comprises a "distinct" term (interference between different atoms) and a "self" term (self-interference from individual atoms).

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Case of a monoatomic sample (cont'd)

The *static structure factor* (dimensionless) is then given by

$$S(\mathbf{q}) = \frac{1}{N}\left\langle \sum_{i,j}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_{ij}} \right\rangle$$

and reduces to

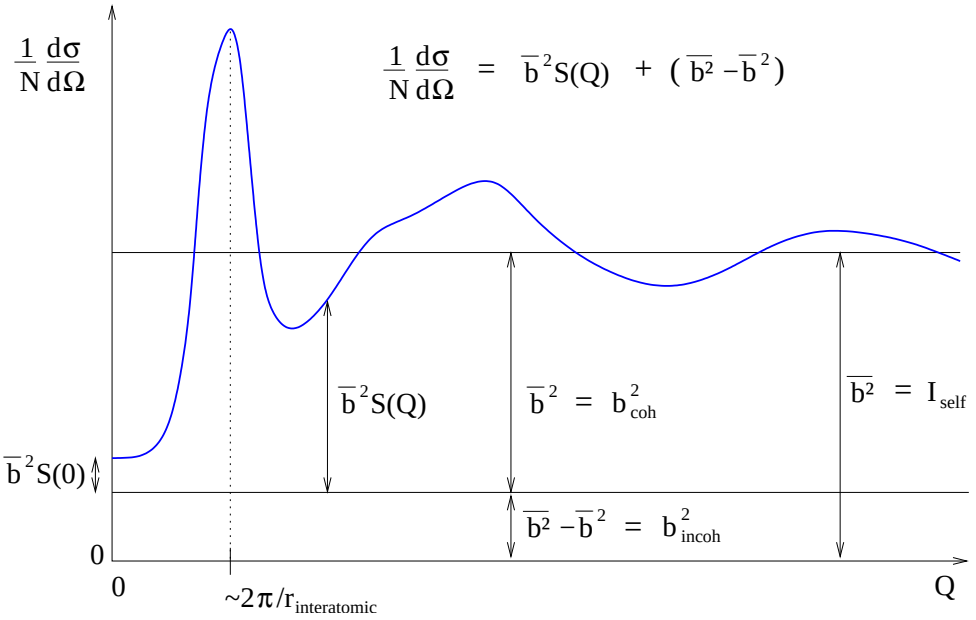
$$S(q) = \frac{1}{N}\left\langle \sum_{i,j}^{N} \frac{\sin(qr_{ij})}{(qr_{ij})} \right\rangle$$

in the case of conical Debye-Scherrer diffraction from an isotropic sample (*e.g.* powder, polycrystal, liquid, glass) for which

$$q = |\mathbf{q}| = \frac{4\pi}{\lambda}\sin\theta$$

and 2θ is the diffraction angle with respect to to the incident beam.

$S(q)$ for a monoatomic glass/liquid



Absence of long-range order leads to broad peaks in the diffraction pattern of a glass/liquid, and in the case of an ergodic system such as a liquid or gas, there also exists a useful thermodynamic limit: $S(q \to 0) = \rho_0 \chi_T k_B T$ where ρ_0 is the total atomic number density and χ_T is the isothermal compressibility.

Real-space functions (monoatomic case)

Fourier transform gives the *pair-distribution function* $g(r)$ which is proportional to the probability of finding an atom at a distance r from another atom taken as the origin:

$$g(r) - 1 = \frac{1}{2\pi^2 r \rho_o} \int_0^\infty q\,[S(q) - 1] \sin(qr)\, dq$$

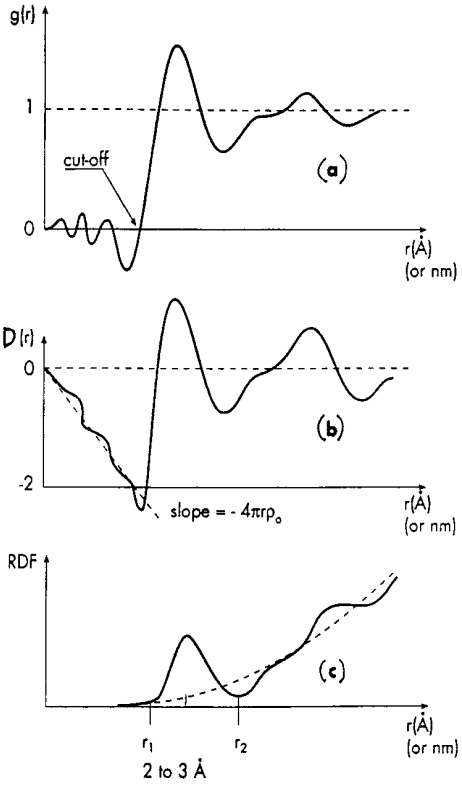
in addition to the density function $D(r)$ used for "PDF analysis":

$$\mathrm{PDF}(r) = D(r) = 4\pi r \rho_o\,[g(r) - 1]$$

as well as the radial distribution function $\mathrm{RDF}(r)$:

$$\mathrm{RDF}(r) = 4\pi r^2 \rho_o\, g(r)$$

whose integration yields atomic coordination numbers.



Disorder can mean more information, not less

For a monoatomic fluid at temperature T in the low-density limit, a mean-field theory relates $g(r)$, obtainable from diffraction, to the interatomic pair potential:

$$u(r) = -k_B T \ln[g(r)],$$

from which follows the interatomic force $\mathbf{F}(r) = -\vec{\mathrm{grad}}[u(r)]$, and thereby v_{sound}, etc. For realistic densities, an iterative procedure leads to an effective pair potential $u_{\mathrm{eff}}(r)$ (*e.g.* EPSR analysis).

In effect, the distribution of interatomic distances given by $g(r)$ in a liquid or glass "probes" the shape of $u(r)$, since energetically unfavorable distances will be more rare than favorable ones. By contrast, diffraction measurements on a crystalline sample cannot give information about $u(r)$ without recourse to modelling.

Note that the above expression also implies that $g(r)$, the structure measured via diffraction, is independent of atomic mass.

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Total scattering versus Bragg peak refinement

Refinement (*e.g.* Rietveld) of Bragg peak intensities ignores both the elastic ($\omega = 0$) diffuse scattering between peaks due to static disorder as well as the inelastic scattering due to dynamic disorder, and therefore provides only a space-time average picture of the sample's structure.

By comparison, making use of all the measured intensity $d\sigma/d\Omega$ in a "total scattering" data analysis provides (ensemble-averaged) information on the local quasi-instantaneous structure in the sample. *Recall that a liquid has no perfectly elastic scattering intensity.*

Note also that for an incident flux Φ and a detector cell of solid angle $d\Omega$, the measured intensity (cps) from an isotropic sample

$$I(q) = \Phi \, \frac{d\sigma}{d\Omega}(q) \, d\Omega$$

is a function of q *only*. An increase in incident wavelength λ will therefore increase the angular *widths* of Bragg peaks in 2θ, and thus their *integrated* intensities, but *not* their peak intensities. However, when powder diffraction is resolution-limited (which is generally the case), the measured Bragg peak intensities do seem to increase with increasing λ.

Case of a polyatomic sample (several Z)

In a polyatomic system, the chemical affinities of n different atomic species Z_α necessarily leads to a correlation at atomic sites $\mathbf{r}_i$ between the structural environment and the average scattering length $\overline{b}_\alpha$. This correlation prevents a proper definition of a dimensionless $S(q)$, but the scattered intensity can still be expressed as the sum of a distinct term (the interference function $F(q)$) and a total self-scattering term:

$$\frac{1}{N}\left[\frac{d\sigma}{d\Omega}(q)\right] = \sum_{\alpha,\beta}^{n} c_\alpha c_\beta \overline{b}_\alpha \overline{b}^*_\beta \left[S_{\alpha\beta}(q) - 1\right] + \sum_{\alpha}^{n} c_\alpha \overline{b^2}_\alpha \ ,$$

where c_α is the fraction or concentration of atomic species Z_α, and the *partial* structure factor (PSF) $S_{\alpha\beta}(q)$ is the Fourier transform of the *partial* pair-distribution function (PPDF) $g_{\alpha\beta}(r)$, which is in turn proportional to the probability of finding an atom of type Z_α at a distance r from an atom of type Z_β taken as the origin:

$$g_{\alpha\beta}(r) - 1 = \frac{1}{2\pi^2 r \rho_o} \int_0^\infty q \left[S_{\alpha\beta}(q) - 1\right] \sin(qr)\, dq \ .$$

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Neutron Diffraction with Isotope Substitution (NDIS)

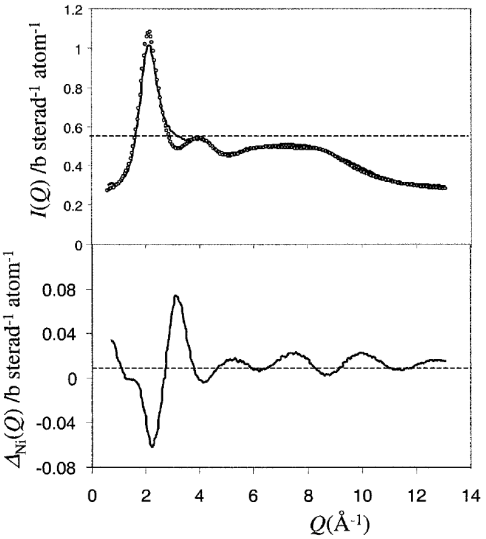
The technique of Neutron Diffraction with Isotopic Substitution (NDIS) is a powerful method for determining PSFs. It takes advantage of the distribution in isotopes of one or several elements Z_α in the sample, in order to modify $\overline{b}_\alpha$. One must therefore prepare several samples that are chemically identical but of different isotopic distribution. Each sample will give a different diffractogramme $d\sigma/d\Omega$.

Subtraction of two such diffractogrammes cancels the contributions of certain atomic pairs in the sample, yielding thereby a "first-difference function" whose Fourier transform contains information on the local environment of the isotopically substituted species only.

For a binary system ($n = 2$) there are 3 partial structure factors: S_{11}, S_{22} et $S_{12} = S_{21}$, and therefore 3 NDIS samples are sufficient for a complete PSF determination.

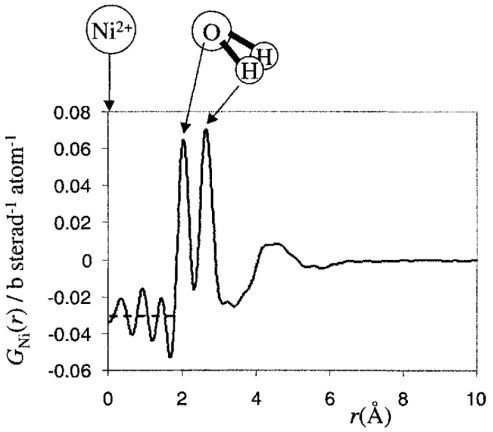
For more information on NDIS techniques, see *e.g.* the review paper: *H.E. Fischer,* et al*, Rep. Prog. Phys.* **69** *(2006) 233–299 (***95** *citations).*

NDIS example: First-difference function



Total structure factors (top) for D_2O solutions of $^{62}NiCl_2$ versus $^{nat}NiCl_2$. Subtraction (bottom) gives a "first-difference" $\Delta_{Ni}(q)$ retaining only those partial structure factors for atomic pairs including a Ni atom.

(D.H. Powell, JDN11 proceedings)



Fourier transformation leads to a first-difference pair-distribution function $G_{Ni}(r)$ showing the distribution of atoms with respect to a Ni atom at the origin. Assuming identical atomic environments for ^{62}Ni and ^{nat}Ni, NDIS thus reveals this local structure.

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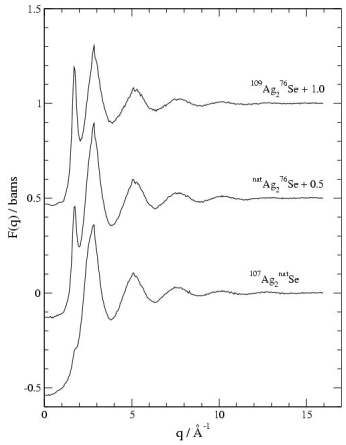
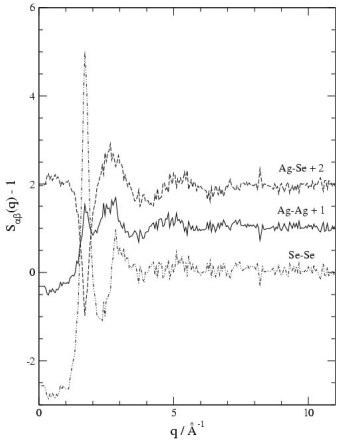
NDIS example: Complete PSF determination

molten Ag_2Se (ILL) :

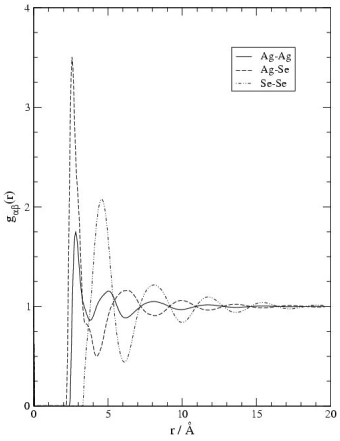
< *Barnes et al., J. Phys. Condens. Matter 9 (1997) 6195* >



3 dσ/dΩ



3 partial S(q)'s



3 partial g(r)'s

The anti-phase correlations in the partial $g_{\alpha\beta}(r)$ extend to large r, indicating a relatively strong charge ordering consistent with maintaining electroneutrality in this ionic binary liquid, whose local structure is found to resemble that of the high-temperature crystal phase.

PDF analysis: FT of a powder diffraction pattern

Basic idea: Disordered, nano-structured or reduced-dimensional crystals often lack sufficient long-range order to produce sharp diffraction peaks. It can then be advantageous to sacrifice q-space resolution by using short wavelengths to provide a high $q_{\max}$ and thus better r-space resolution $\Delta r = 3.79/q_{\max}$ after Fourier Transform (FT) of the diffraction pattern $S(q)$ or $F(q)$.

The resulting Pair-Distribution Function PDF(r) is the distribution of relative interatomic distances with respect to an average atom at the origin (*i.e.* an ensemble of quasi-instantaneous local structures $\neq$ the time+space averaged structure from Rietveld).

q-space resolution Δq leads to an envelope that modulates and limits the spatial extent of the PDF(r) via $r_{\max} = (5.55/2)/\Delta q$.

NB: The PDF(r) is not the output of structural refinement, and is therefore a *model-independent* result that can of course then be used as input for structural modelling/simulation in r-space.

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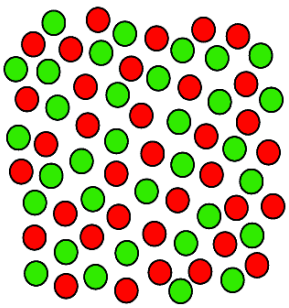
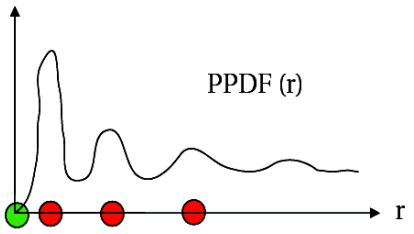
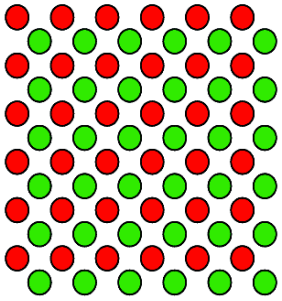
Atomic distributions in glass/liquid versus crystal

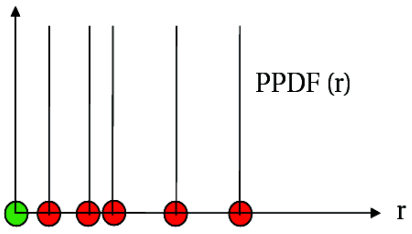
Liquid/Glass :





Crystal :

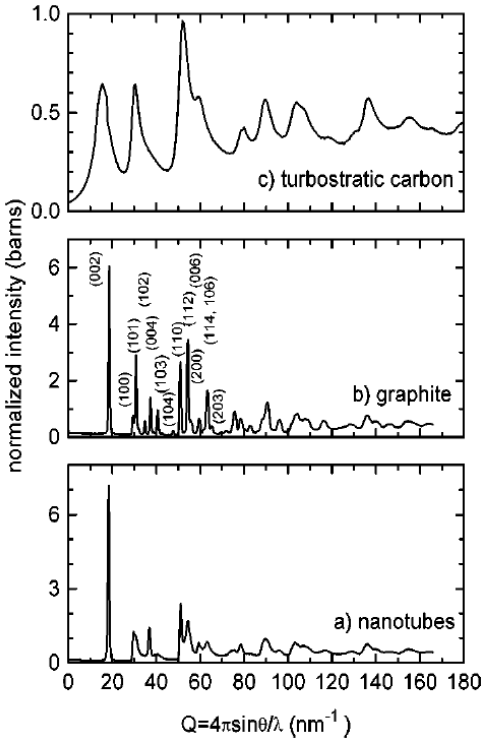




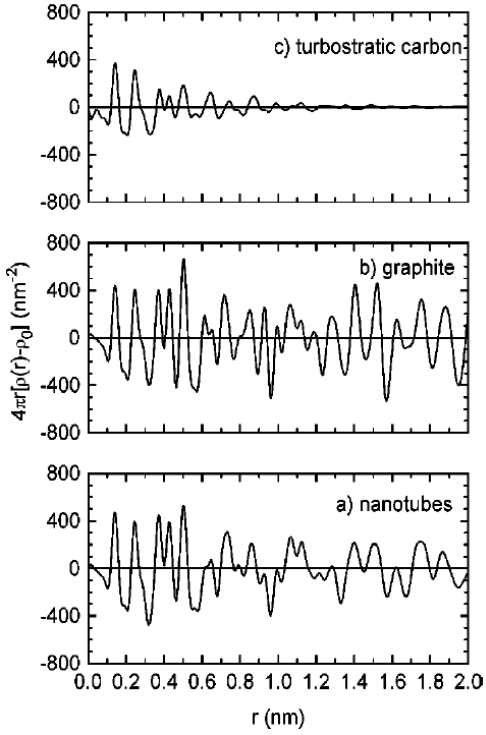
These *partial* PDFs or PPDFs (*e.g.* from NDIS) represent an ensemble of quasi-instantaneous spatial correlations between red and green atoms: more specifically $g_{RG}(r)$ which is proportional to the average probability of finding a Red atom at a distance r from a Green atom.

Early application of PDF analysis: Carbon at D4b

q-space:



r-space:



A. Burian, J.C. Dore, H.E. Fischer and J. Sloan, Phys. Rev. B **59** *(1999) 1665–8 (***49** *citations).*

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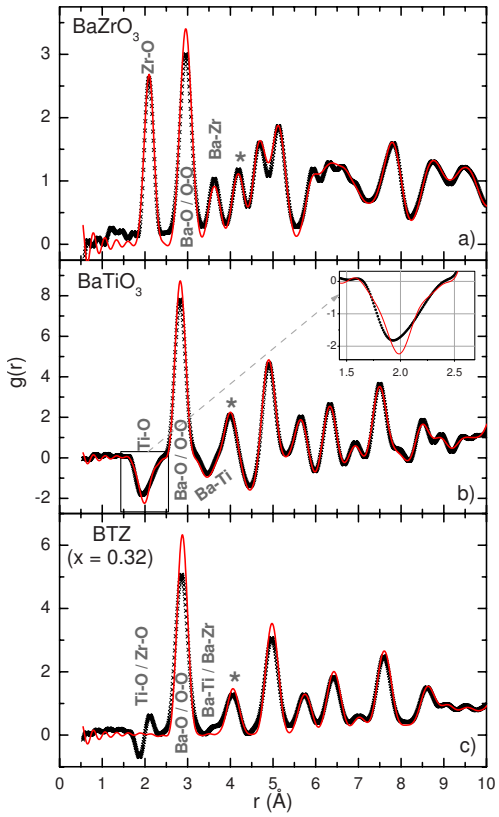
Local structure in $BaTi_{1-x}Zr_xO_3$ relaxors

Bragg peak refinement shows that $BaTi_{1-x}Zr_xO_3$'s crystallographic structure is ABO_3 cubic perovskite for $x = 1$ and over the relaxor ferroelectric range ($0.25 \leq x \leq 0.5$) which includes the null-alloy composition $x = 0.32$. As charge disorder is minimized by the isovalent substitution Ti^{4+}/Zr^{4+}, it can be hypothesized that the long-range ferroelectric order is impeded by local structural distortions resulting from the large difference in the two cationic radii.

$\Rightarrow$ PDF analysis using D4c ($\lambda = 0.5$ Å) gave unambiguous evidence that the Ti and Zr atoms do not occupy equivalent octahedral sites as expected from the crystallographic structure, but rather the Ti atoms are displaced along [111].



C. Laulhé, et al*, Phys. Rev. B* **79** *(2009) 064104 (***15** *citations).*

Basic principles of (de)convolution

The *convolution* of two functions $f(q)$ and $g(q)$ is given by:

$$f(q) \otimes g(q) = (f \otimes g)(q) = \int_{-\infty}^{\infty} f(q')\, g(q-q')\, dq'$$

where q' is the (dummy) variable of integration.

The *convolution theorem* states that the Fourier Transform (FT) of a convolution is the simply the product of the Fourier Transforms:

$$\mathrm{FT}[f(q) \otimes g(q)] = \mathrm{FT}(f(q))\,\mathrm{FT}(g(q)) = F(r)\; G(r)$$

so that a convolution in q-space gives a modulation in r-space, and vice-versa of course. Therefore deconvolution in q-space should be as simple as FT-ing to r-space, dividing two functions, and then FT-ing back to q-space. For example, if the measured diffraction pattern is $I(q) = f(q) \otimes g(q)$, where $g(q)$ is the real diffraction pattern and $f(q)$ is the known resolution function, then:

$$g(q) = \mathrm{FT}[\,\mathrm{FT}(I(q)) \,/\, \mathrm{FT}(f(q))\,] \quad .$$

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Some useful rules of thumb for Fourier Transforms

The FT of a Gaussian with standard deviation σ_q is also a Gaussian but with standard deviation $\sigma_r = 1/\sigma_q$. And since:

$$\mathrm{HWHM}_q = \mathrm{FWHM}_q/2 = \sqrt{\ln(4)}\;\sigma_q = 1.18\;\sigma_q$$

then the FT of a Gaussian of width FWHM_q is a Gaussian of width

$$\mathrm{FWHM}_r = 4\ln(4)/\mathrm{FWHM}_q = 5.55/\mathrm{FWHM}_q$$

and therefore *not* $2\pi/\mathrm{FWHM}_q$. A sharp resolution function of small FWHM_q for the diffraction data will therefore lead to a broad or gentle modulation of large FWHM_r for the $\mathrm{PDF}(r)$.

Note that for data of finite $q_{\max}$, the FT of the Heavyside step function is

$$sinc(r) = \sin(r)/r \quad \text{having} \quad \mathrm{FWHM}_r = 3.79/q_{\max}$$

so that the theoretical $\mathrm{PDF}(r)$ should be convolved with $sinc(r)$ before comparison to data. This is the source of the "low-r wiggles" in the FTs of diffraction data, which in fact exist around all sharp peaks in $\mathrm{PDF}(r)$.

Two problems for deconvolving diffraction data

Now take another look at the formula for convolution:

$$f(q) \otimes g(q) = (f \otimes g)(q) = \int_{-\infty}^{\infty} f(q')\, g(q - q')\, dq'$$

$\Rightarrow$ there are two problems in applying the convolution theorem

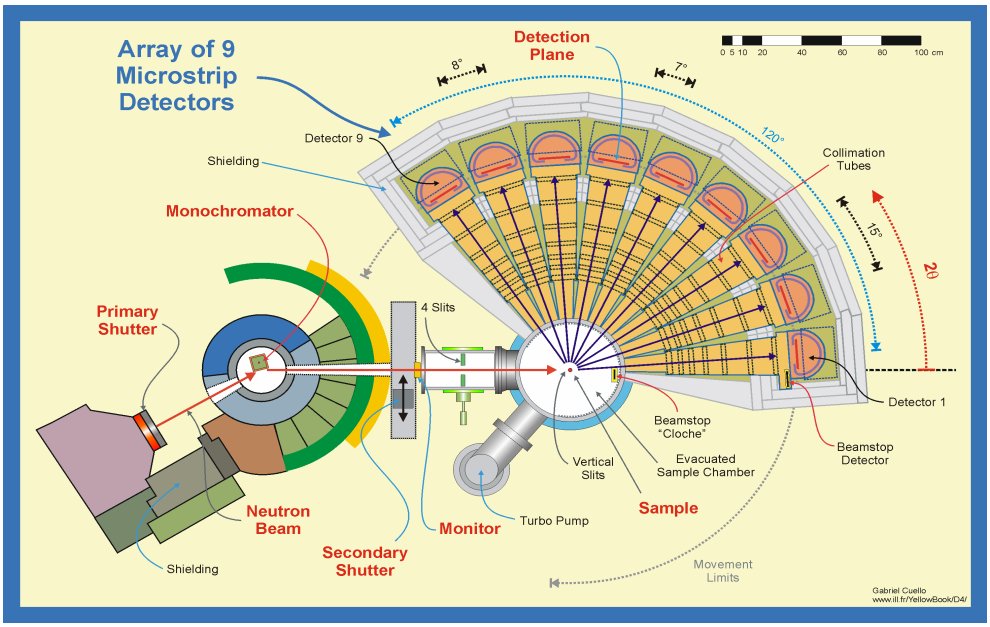
$$g(q) = \mathrm{FT}[\, \mathrm{FT}(I(q)) \,/\, \mathrm{FT}(f(q))\,]$$

to real diffraction data:

First problem: We need data of infinite q-range for $g(q)$ and hence for the measured $I(q)$, as well as an infinite q-range for perfect knowledge of the resolution function $f(q)$. None of this is possible in practice.

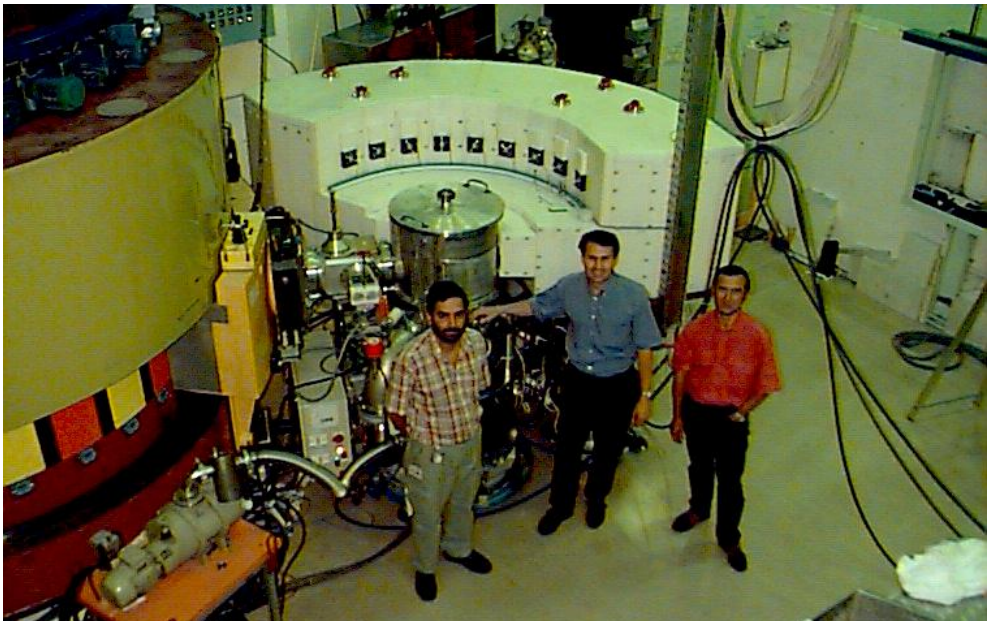
Second problem: The resolution function shape or profile $f(q')$ must be independent of the argument q of $g(q - q')$. In other words, the resolution function should have the same shape at all $q = 4\pi/\lambda \sin(\theta)$, where 2θ is the diffraction angle. We will see from Caglioti that the resolution function FWHM depends strongly on 2θ.

Schematic of the D4c neutron diffractometer (ILL)



Hot source: $0.3 < \lambda/\text{Å} < 1.05$, standard $\lambda = 0.5$ Å for $q_{\max} = 23.5$ Å^{-1}
Counting rate: 1,000,000 (*i.e.* 0.1 % stats) per 0.125° in 3 hours.
Overall detector stability: $\sigma = \pm\, 1 \times 10^{-4}$ over 3 days.
Low background sans parasitic peaks for all λ (0.5, 0.7 and 0.35 Å).
$\Rightarrow$ Champion of low-contrast ($\Delta b < 0.5$ fm) isotopic substitution expts.

D4c commissioning in May/June 2000



Big belljar for all sample environments (cryostat, furnace, special).
q-resolution: $\Delta q/q \lesssim 0.025$ for $2\theta > 15^\circ \Rightarrow \mathrm{FWHM}_r \approx 60$ Å.
r-resolution: for $\lambda = 0.5$ Å, $\Delta r = 3.79/(q_{\max} = 23.5\ \text{Å}^{-1}) = 0.16$ Å.
$\Rightarrow$ Increasing use for PDF-analysis (FT of powder diffraction pattern).

H.E. Fischer, et al*, Appl. Phys. A* **74** *(2002) S160–2 (***62** *citations).*

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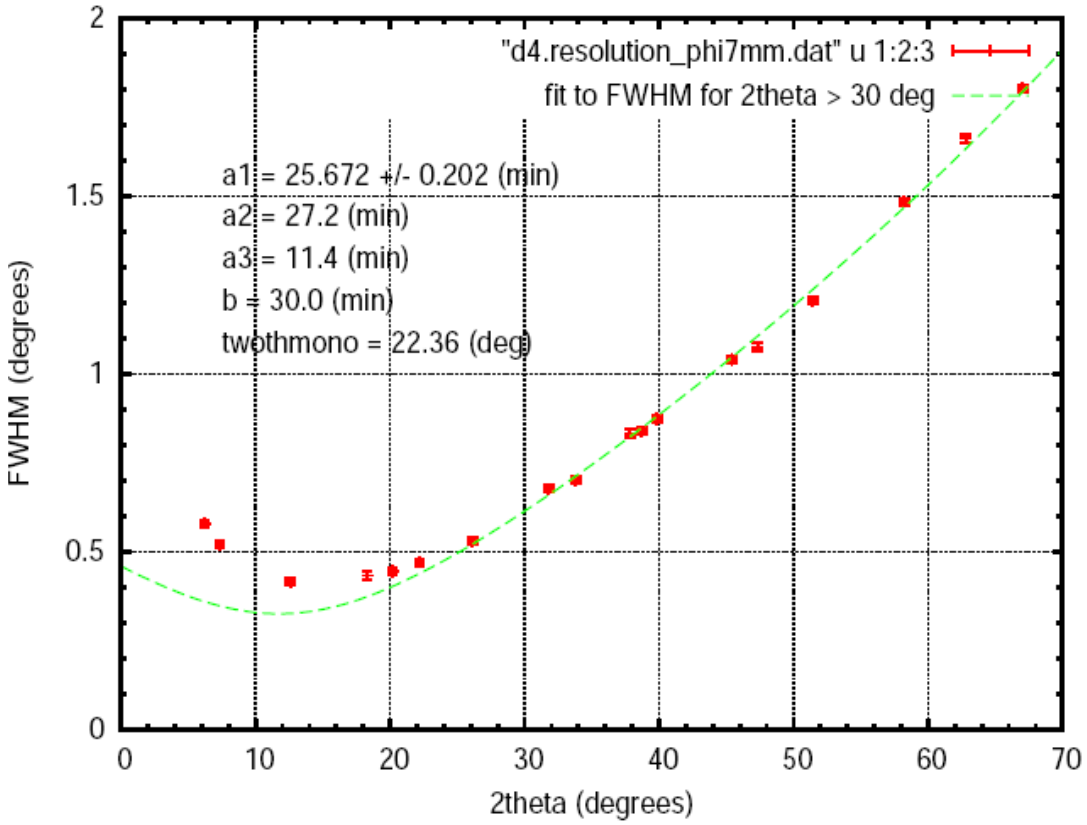
Case of a monochromated incident beam

For a reactor-source neutron diffractometer: The +/- scattering geometry leads to "Q-space focussing" that improves the FWHM of Bragg peaks and the resolution: $\Delta d/d = \Delta Q/Q = \Delta\theta \bullet \mathrm{ctg}(\theta)$ where 2θ is the diffraction angle. The 2θ-dependence of $\Delta\theta$ is described by coefficients U, V and W [1,2]; e.g: U,V,W = 9.3805,-1.9033, 0.2029 for one of the standard configurations (0.5 A, Cu220, ϕ5mm sample) of the ILL's D4c diffractometer for liquids and glasses.

[1] G. Caglioti, et al, *Nucl. Instrum.* **3** (1958) 223-228.
[2] A.W. Hewat, *Nucl. Instrum. Methods* **127** (1975) 361-370.

Example of D4's resolution: FWHM(2θ)



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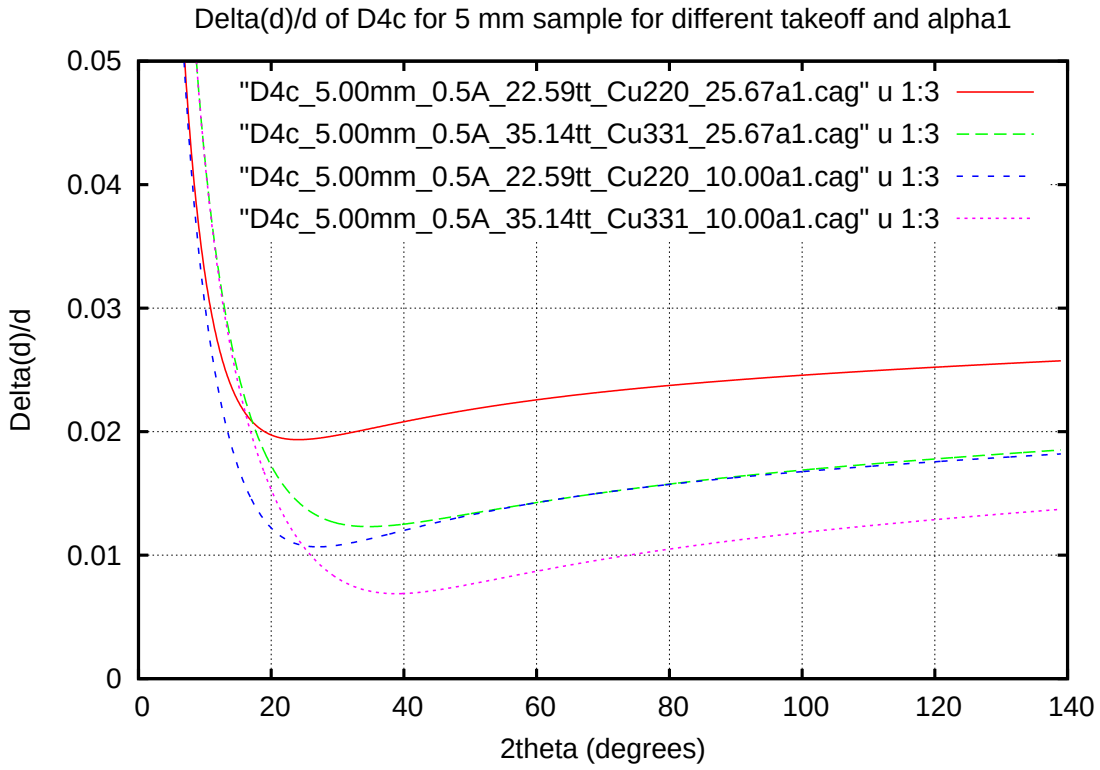
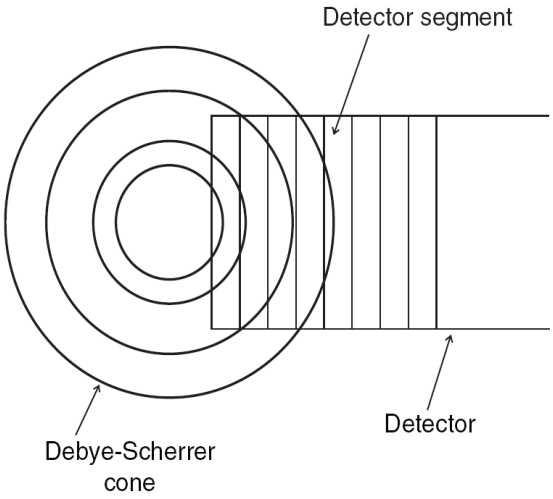
D4c's resolution plotted as $\Delta d/d = \Delta q/q$



Caglioti forgot his umbrella!

The "umbrella effect": At small diffraction angle 2θ, the diameter of Debye-Scherrer rings becomes comparable to, or smaller than, the detector-cell height of a 1-D position sensitive detector, leading to a modification of the Lorentz factor [3] and to an asymmetry+shift in the Bragg peak profile [4,5] that should be included in Rietveld refinement.

[3] M.J. Cooper and A.V. Glasspool, *J. Appl. Cryst.* **9** (1976) 63-67.
[4] B. van Laar and W.B. Yelon, *J. Appl. Cryst.* **17** (1984) 47-54.
[5] L.W. Finger, D.E. Cox and A.P. Jephcoat, *J. Appl. Cryst.* **27** (1994) 892-900.



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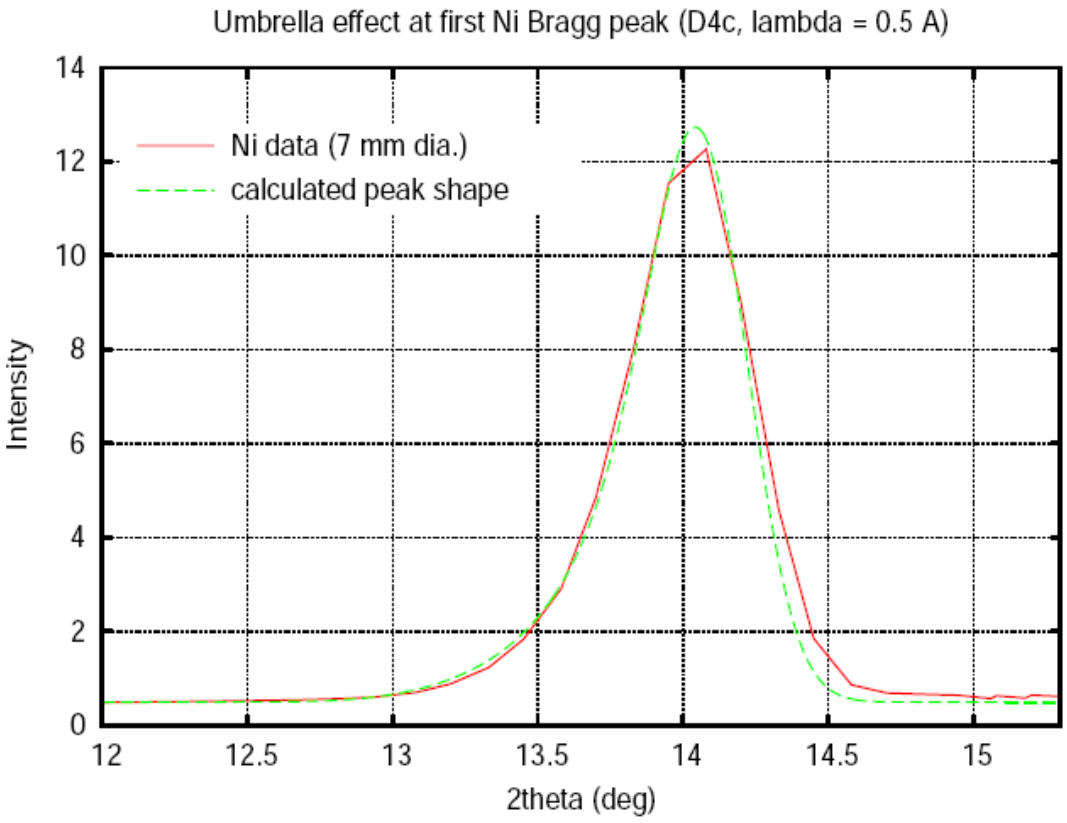
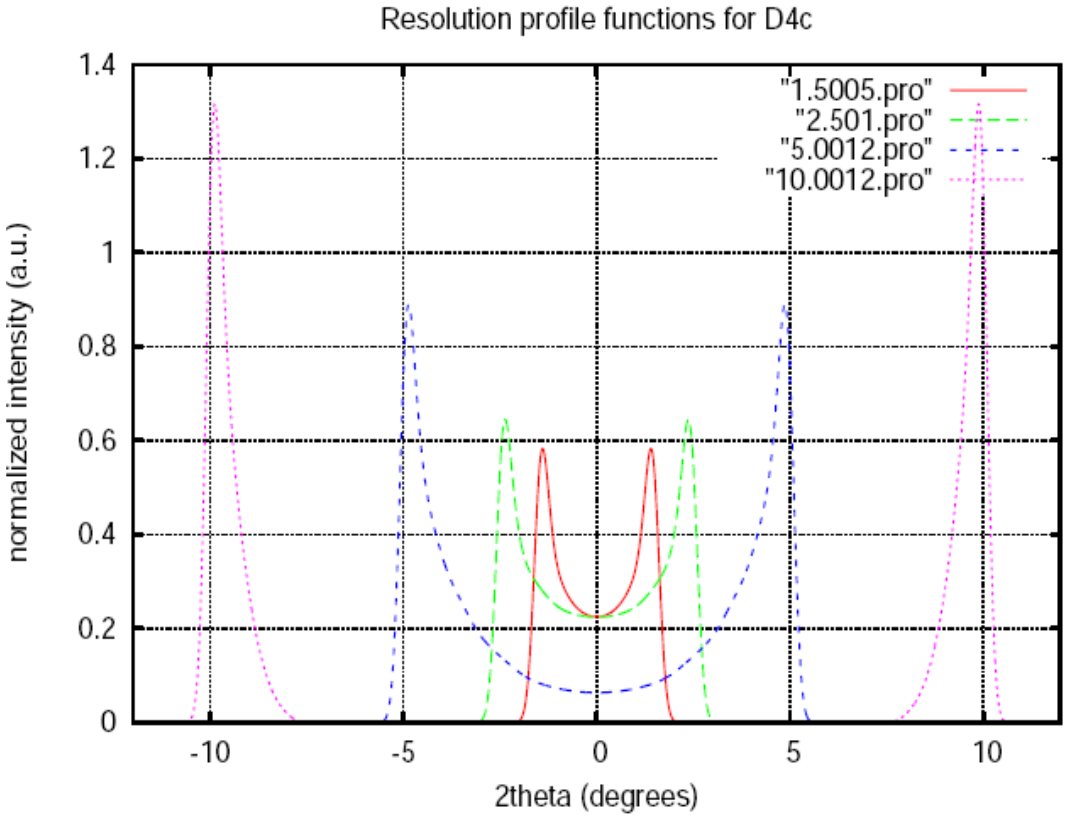
Low-angle "tail" of Umbrella Effect-ed peak profile



The Umbrella Effect at very low scattering angle 2θ



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General case for deconvolution of diffraction data

Although a detector of 2-D sensitivity permits following or "straightening" of the Debye-Scherrer rings, this only corrects (partially) for the umbrella effect, and not for other resolution effects coming from sample size, incident beam dispersion and detector resolution.

In addition, diffraction data for liquids and glasses cannot be Rietveld-refined since there is no spatial periodicity, and also since the diffraction peaks are of intrinsic width and hence not resolution-limited.

Finally, no FT deconvolution tricks (*e.g.* convolution theorem) are possible because the resolution depends on the diffraction angle 2θ.

In the general case then, the measured (1D) intensity $I(2\theta)$ for a neutron or x-ray diffractometer can be written as the convolution of the true intensity $S(2\theta)$ with the instrumental resolution function $\mathcal{R}$:

$$I(2\theta) = \int \mathcal{R}(\rho, 2\theta)\, S(2\theta - \rho)\, d\rho$$

where ρ is the (dummy) integration variable and the 2θ-dependence of $\mathcal{R}$ has been indicated explicitly.

The Moments Method for general deconvolution

Astuce: When the measured diffraction intensity is relatively slowly varying over the width of the resolution function (generally the case for liquids/glasses diffraction), one can try making a Taylor's expansion of $S(2\theta-\rho)$ in ρ around 2θ, and then to integrate separately each term of the series, which leads to calculation of the *moments of* $\mathcal{R}(\rho,2\theta)$:

$$\mathrm{M}_n(2\theta) = \frac{1}{n!}\int_{-180^\circ}^{180^\circ} (-\rho)^n\, \mathcal{R}(\rho,2\theta)\, d\rho$$

that can be normalised as (in principle $\mathrm{M}_0 = const$):

$$\mathrm{A}_n \stackrel{\mathrm{def}}{=} \mathrm{M}_n/\mathrm{M}_0 \qquad \text{and} \qquad J(2\theta) \stackrel{\mathrm{def}}{=} I(2\theta)/\mathrm{M}_0$$

where the notation emphasizes the 2θ dependence of the data $I(2\theta)$ which should be stronger than that of the moments M_n.

$\Rightarrow$ The moments of the resolution function are in fact sufficient for deconvolving the data within the range of convergence of the Taylor's expansion, leading to the "Moments Method" for general deconvolution: *W.S. Howells, Nucl. Instrum. Meth. Phys. Res.* **219** *(1984) 543–552*.

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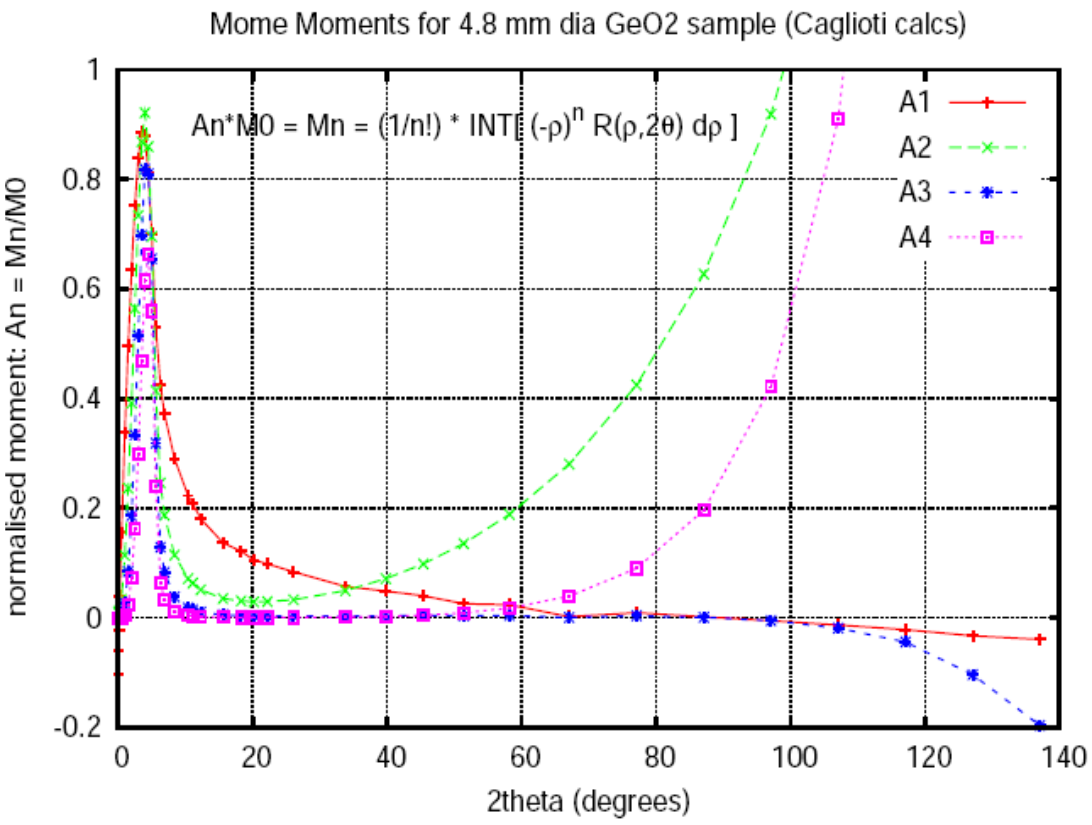
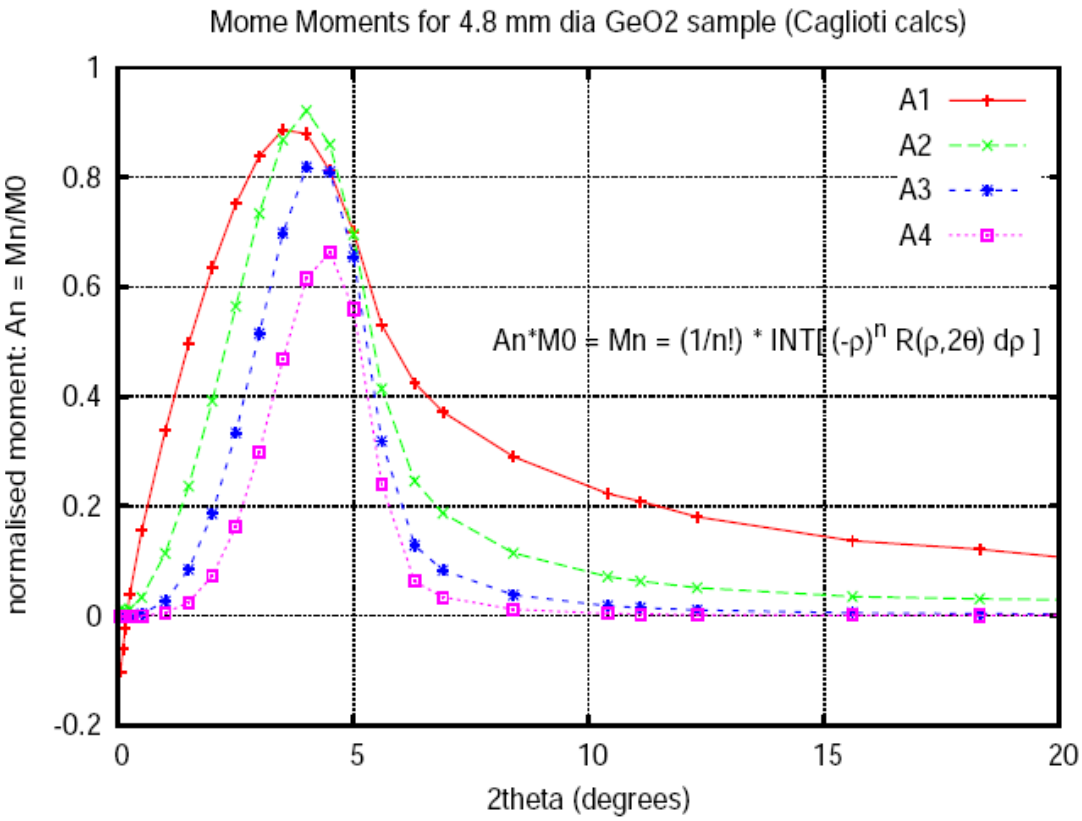
Moments as function of scattering angle 2θ



Moments at low 2θ



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Calculating and applying the correction coefficients

As compared to diffraction data, the normalised moments A_n are slowly varying functions of 2θ except at very low 2θ where the umbrella effect becomes severe. Ignoring thus the derivatives of $A_n(2\theta)$ w.r.t. 2θ and considering only the first 4 derivatives of $J(2\theta) = I(2\theta)/M_n$ w.r.t. 2θ, we can derive for the true (*i.e.* deconvolved) diffraction intensity:

$$S(2\theta) = J + c_1 J' + c_2 J'' + c_3 J''' + c_4 J''''$$

where the correction coefficients $c_n(2\theta)$ are given by:

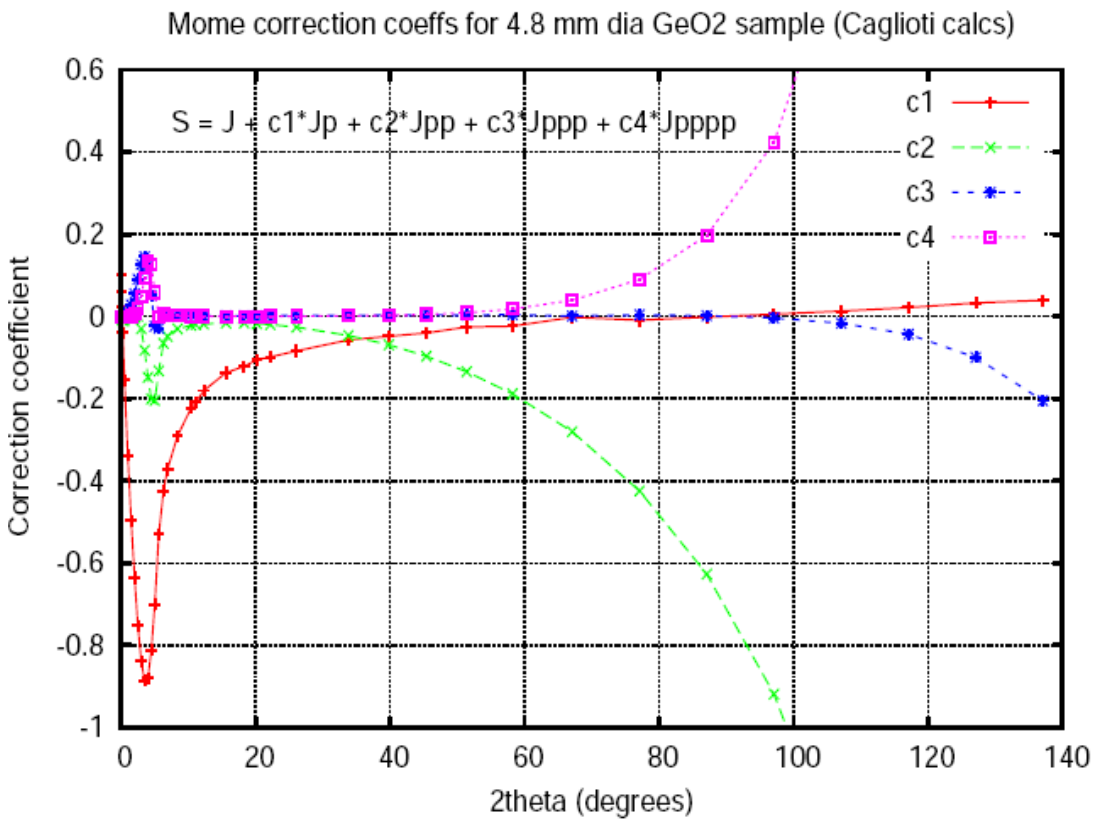
$$c_1 = -A_1 \qquad c_2 = -A_2 + A_1^2 \qquad c_3 = -A_3 + 2A_1A_2 - A_1^3$$

$$c_4 = -A_4 + 2A_1A_3 + A_2^2 - 3A_1^2A_2 + A_1^4$$

and for brevity the 2θ-dependences are not shown explicity.

⇒ Thanks to a fruitful collaboration with Spencer Howells (ISIS) and Phil Salmon (Univ. Bath), the **Decon** program has been developed and used to deconvolve diffraction data from the D4c instrument, *e.g.* for liquid Li (Salmon, *et al*, JPCM **16** (2004) 195) and for liquid and glassy $ZnCl_2$ (Zeidler, *et al*, PRB **82** (2010) 104208).

Correction coefficients as function of 2θ



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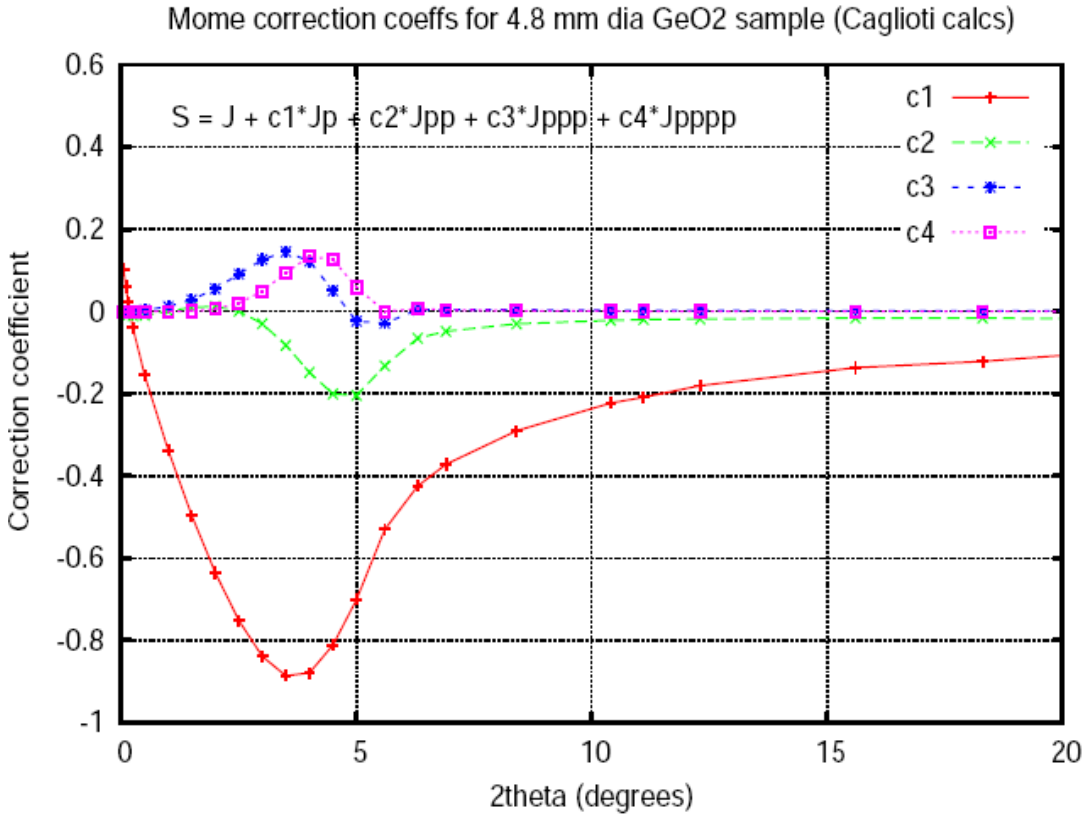
Correction coefficients at low 2θ



Testing Decon on Gaussian peak profiles

Gaussian tests: As a stringent test of our deconvolution algorithm, we convolved a Gaussian peak of FWHM = 0.4° by a typical D4c profile function at different 2θ angles and then used Decon to try to deconvolve the peaks back to the original Gaussian. At the lowest 2θ, the Taylor's expansion breaks down and the higher-order correction terms diverge (although the use of 2 correction terms remains quasi-stable). At the highest 2θ, more than 4 correction terms would be needed for complete convergence.

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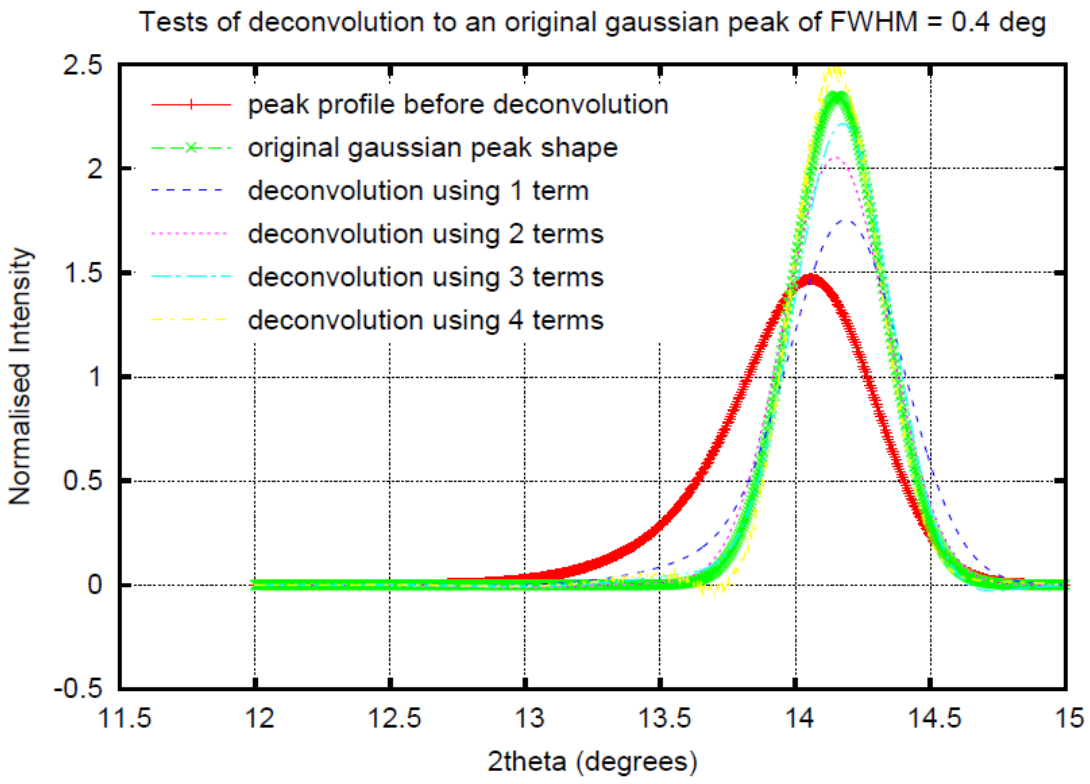
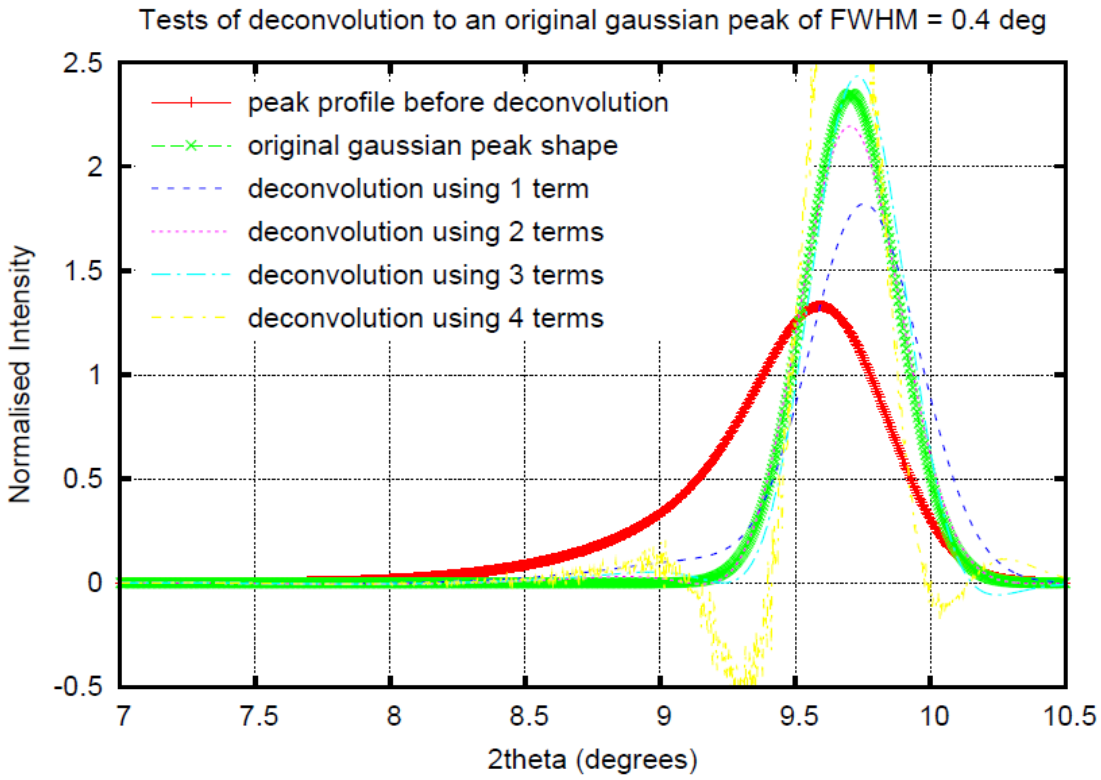
Gaussian test for mid 2θ values



Gaussian test for low 2θ values



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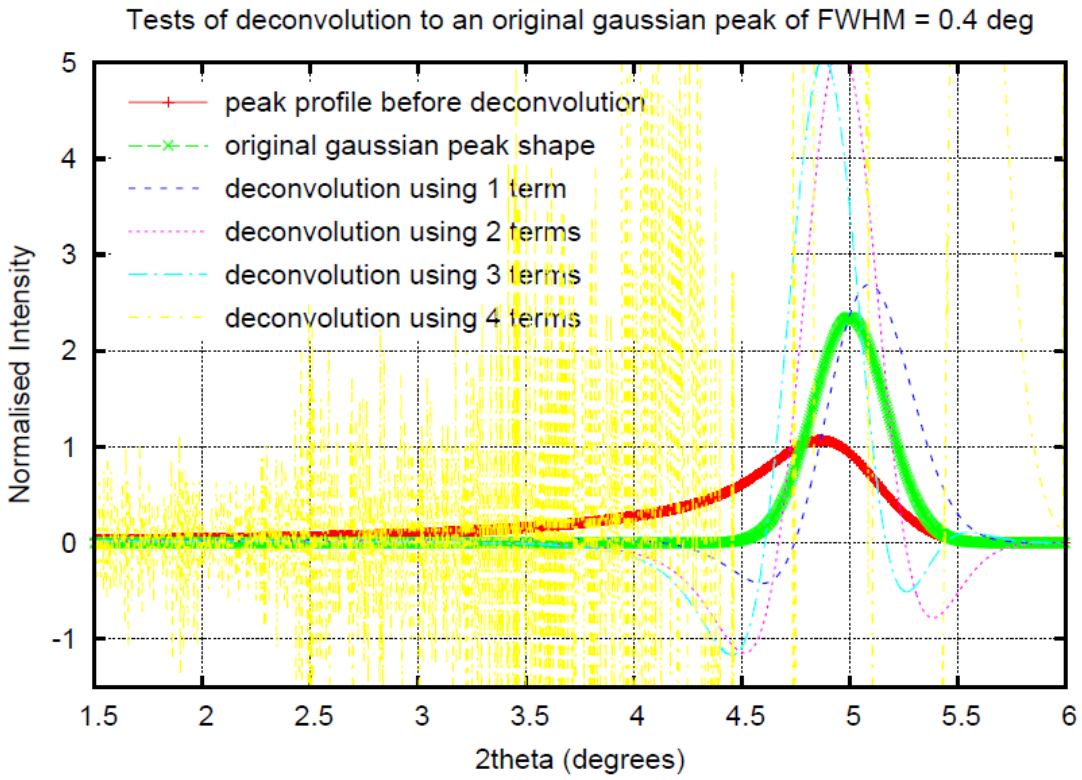
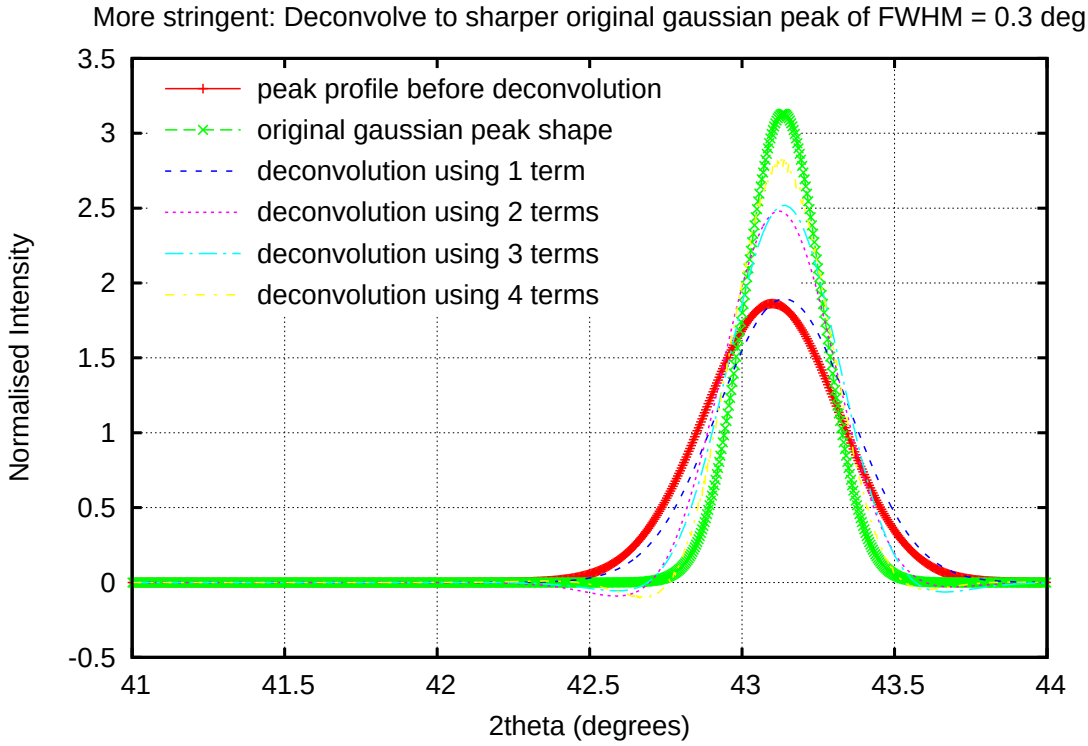
Gaussian test for very low 2θ values



More stringent: sharper peak at higher 2θ values



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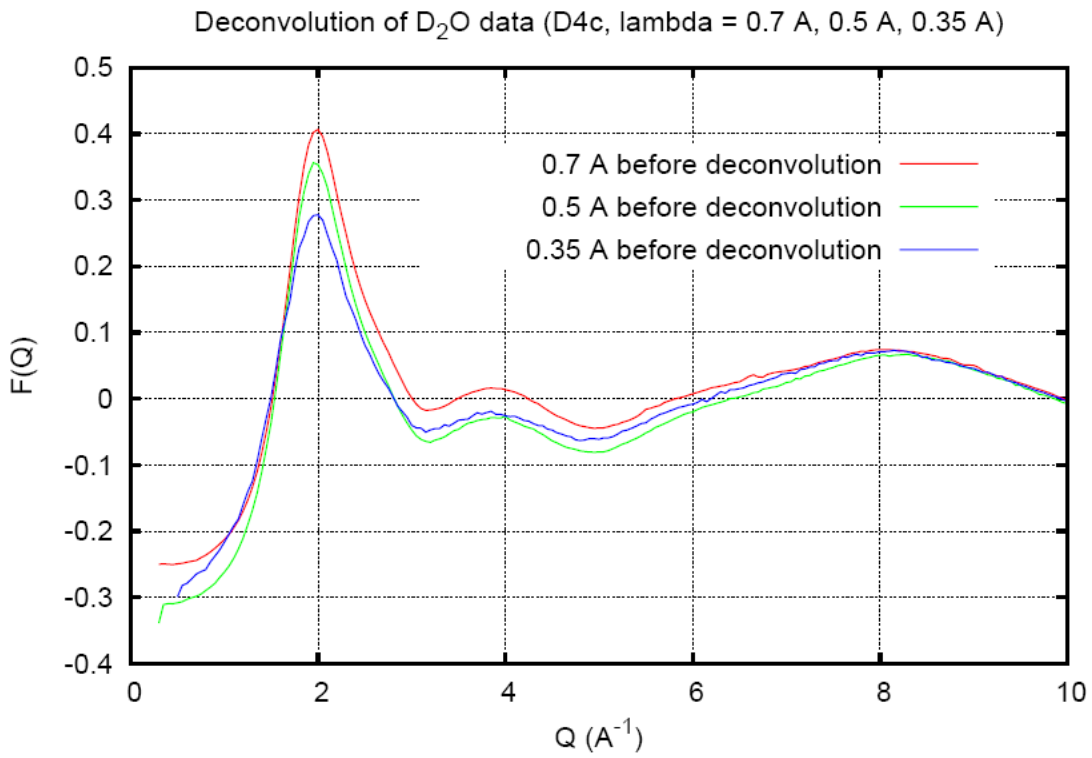
Decon applied to liquid/glass $S(q)$

Applied to the structure factor of liquids/glasses: The main effect of the deconvolution procedure is to shift and sharpen the First Sharp Diffraction Peak (FSDP) where the resolution function is worst, especially at short wavelengths for a reactor-source diffractometer. The Decon results converge after 2 or 3 correction terms and not only agree for different wavelengths (D2O data), but also approach the high Q-space resolution that would be obtained from a synchrotron x-ray diffractometer (l-ZnCl2 data).

D4c data on D_2O before Decon



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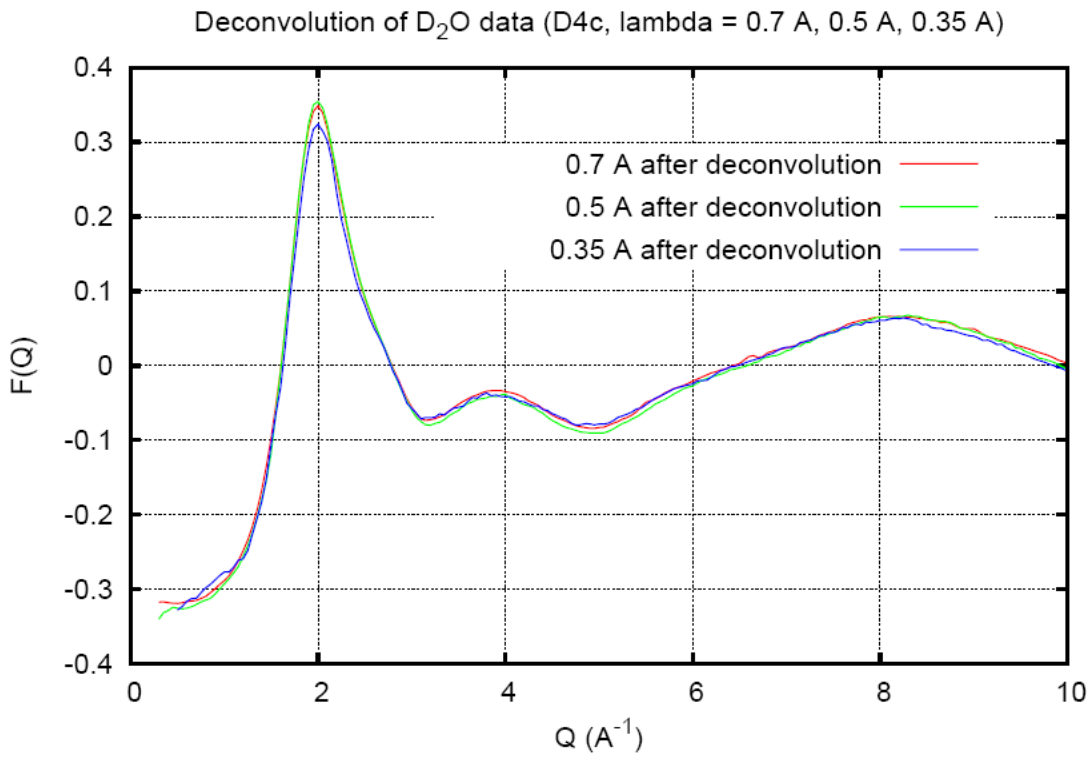
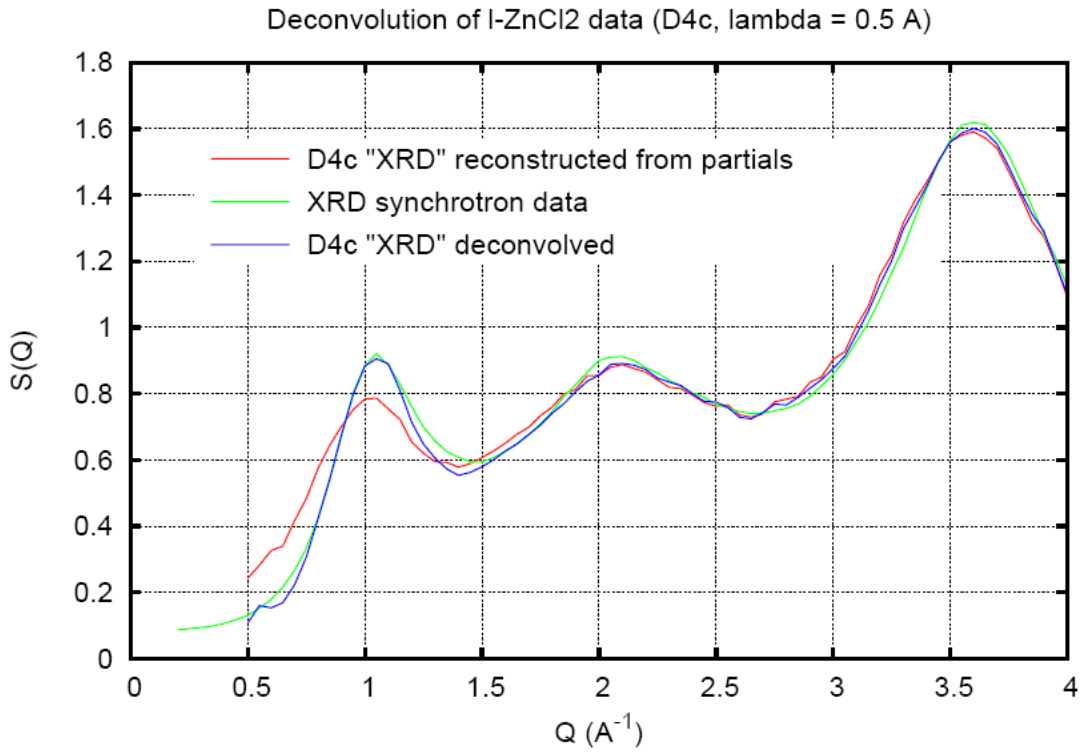
D4c data on D_2O after Decon



l-$ZnCl_2$: X data versus Decon-ed N data



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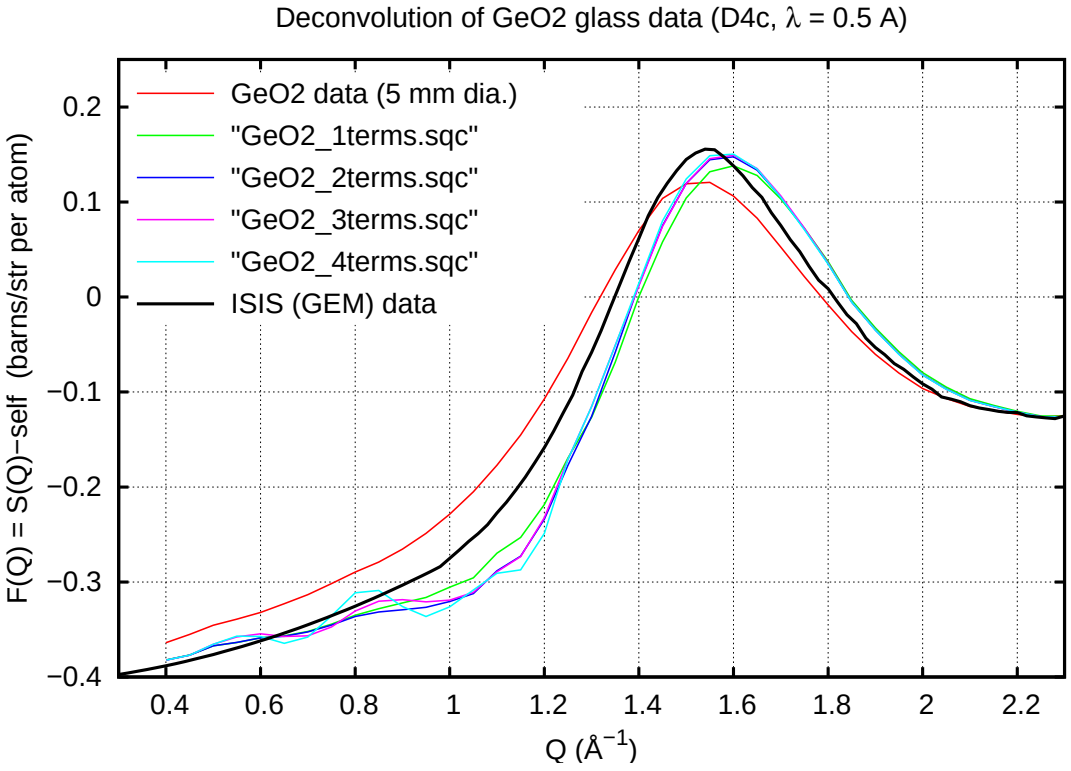
GeO_2 glass: GEM@ISIS versus D4c@ILL

NB: results are before correcting the Decon-induced *q*-shift.



Decon applied to PDF analysis: *q*-space effects

Applied to PDF analysis of powder diffraction data: Here the Bragg peaks are resolution-limited, thus offering an even harsher test of the deconvolution method. For this Ni powder data, we see that the Bragg peaks continue to be sharpened on applying all 4 Decon correction terms, although some noise becomes evident, and the final resolution is still less than that of spallation-source data, and certainly less than the theoretical limit of a δ-function.

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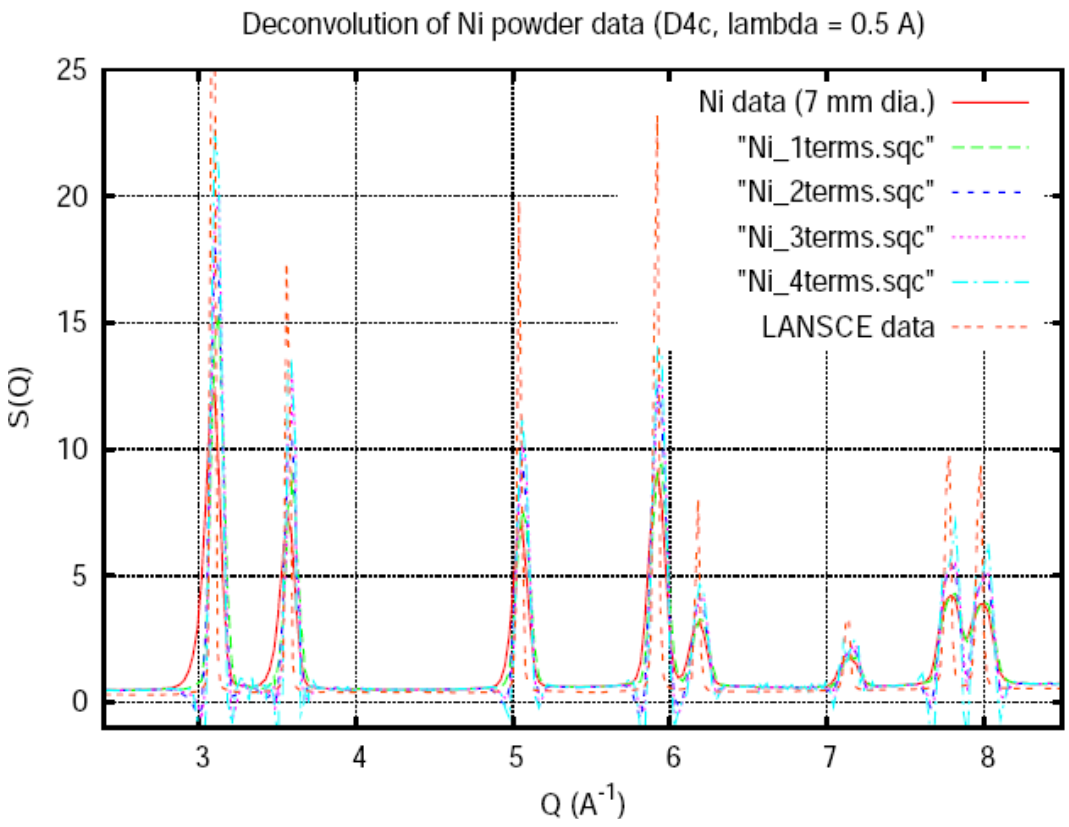
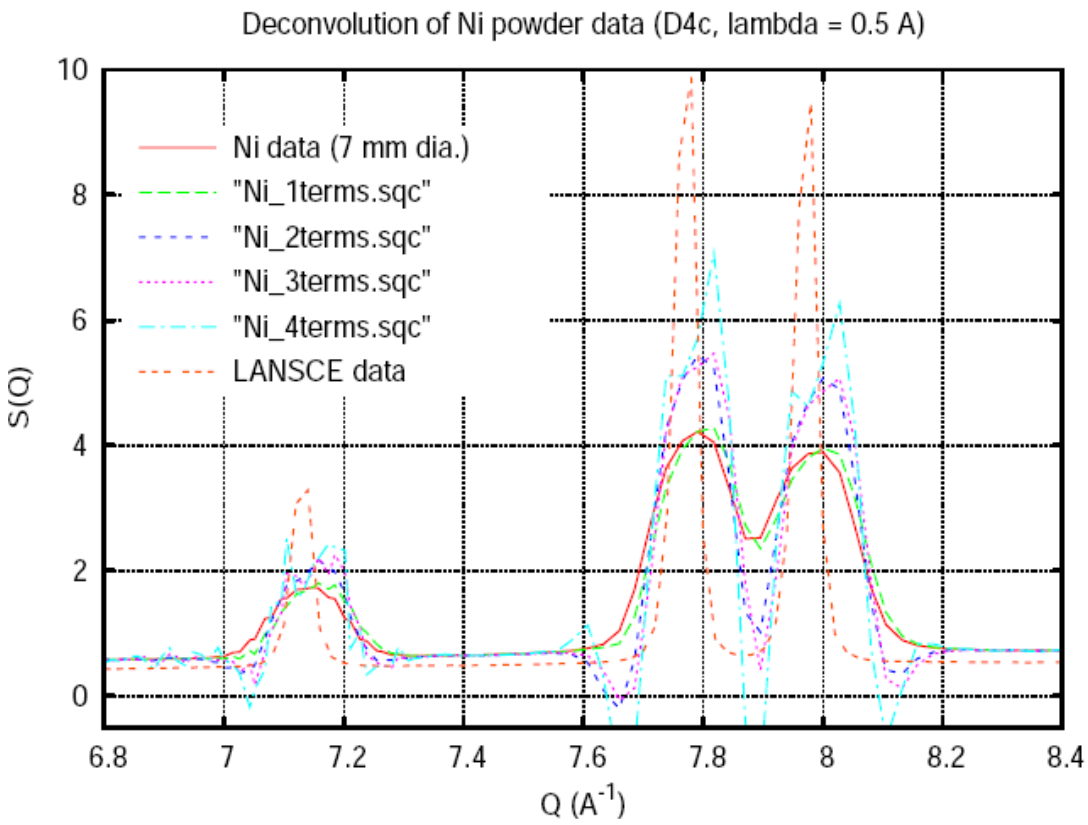
Decon-ed Ni data at low to mid *q* values



Decon-ed Ni data at mid *q* values



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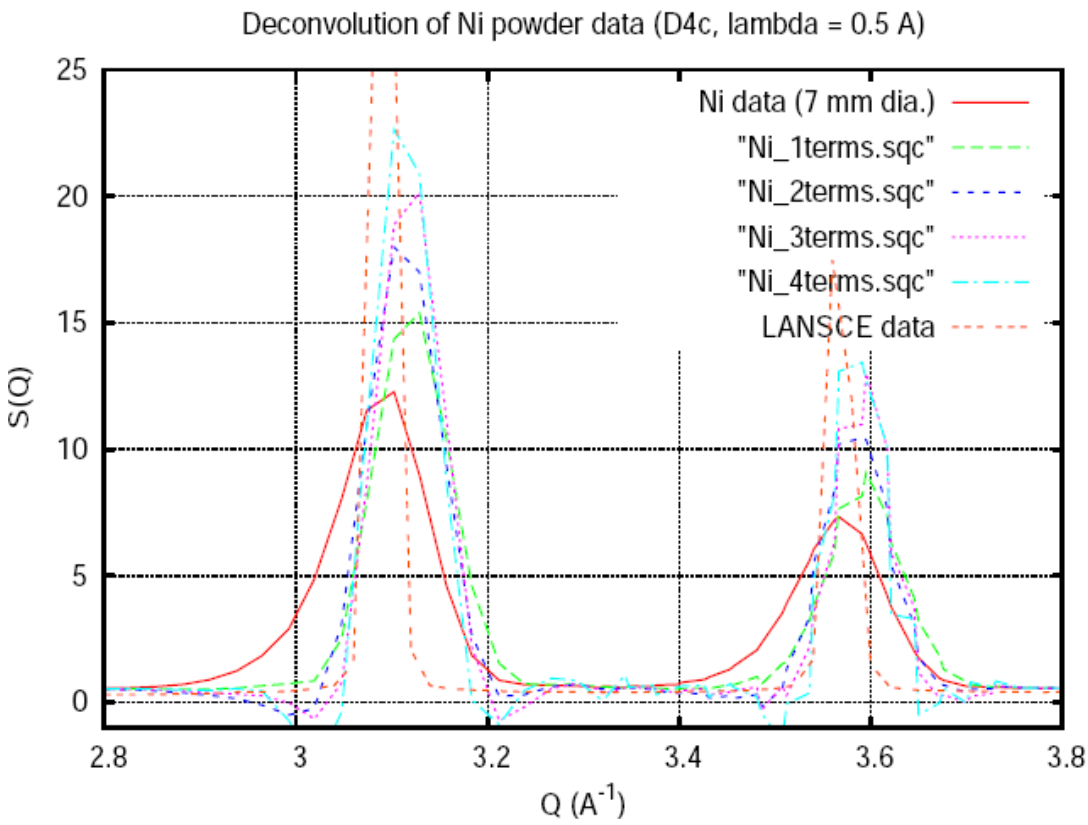
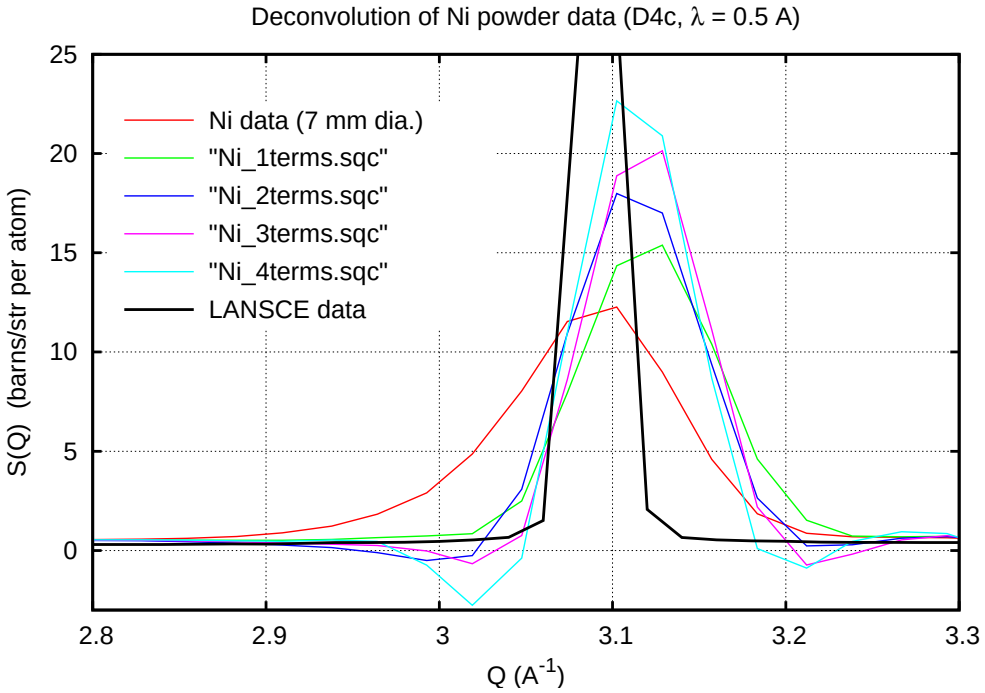


Zoom in on peak at $q = 3.1$ Å^{-1} ($2\theta = 14.1°$)



⇒ Although limited by the coarse data-point spacing, the deconvolution of the D4c data continues to converge towards the "δ-function" as approximated by spallation-source data.

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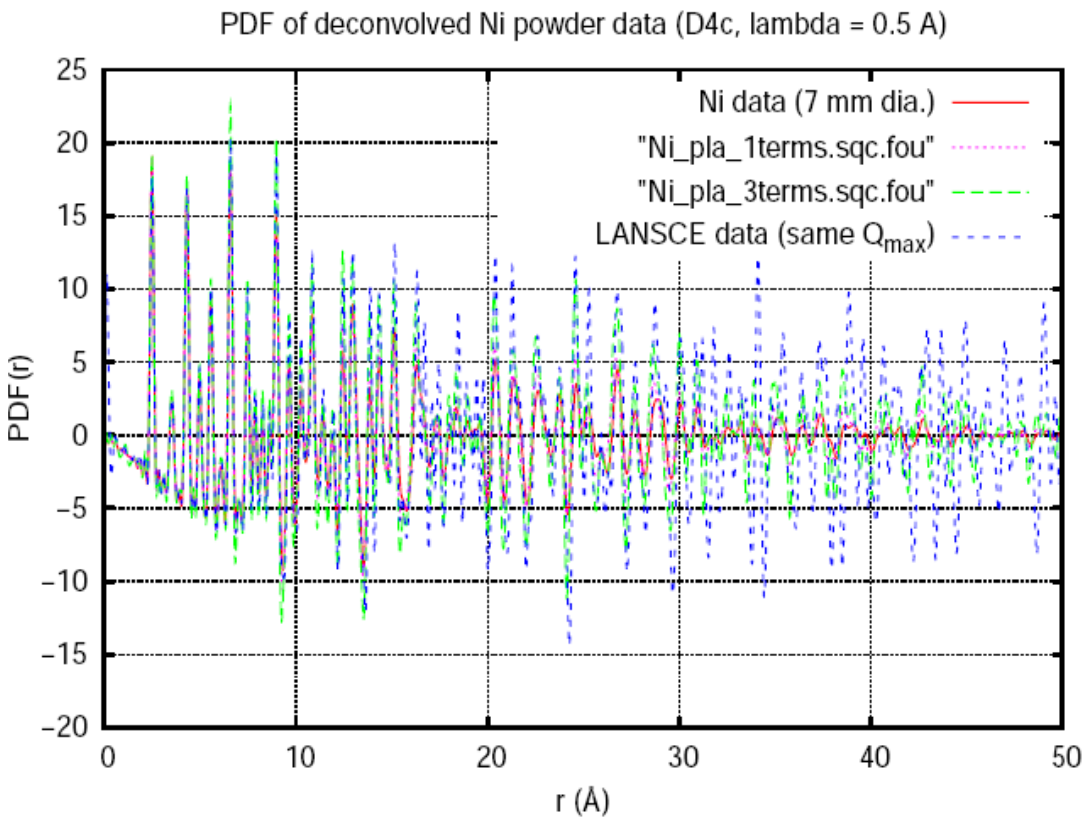
Decon applied to PDF analysis: *r*-space effects

Perhaps more interesting are the effects in r-space after Fourier transform of the powder diffraction pattern (i.e. PDF analysis). In the special case of a Gaussian resolution function [9] with the same FWHM of ΔQ at all Q = (4π/λ) • sin(θ), the PDF in r-space is modulated (i.e. multiplied) by a Gaussian centred at r = 0 and with a FWHM of about Δr = 5.55 / ΔQ corresponding to the neutron coherence volume size [10]. For D4c at λ= 0.5 Å, FWHM_Δr = 60 Å and thus at r = HWHM = 30 Å the intensity of the PDF already falls by a factor of 2. Application of 3 correction terms has the effect of "extending" the coherence volume: the D4c PDF then has an amplitude resembling the spallation-source PDF out to r ~ 30 Å.

[9] P.S. Salmon, *J. Phys. Condens. Matter* **18** (2006) 11443–11469.
[10] P. Chirawatkul, et al, *Phys. Rev. B* **83** (2011) 014203.

Decon-ed Ni data at low to high *r* values



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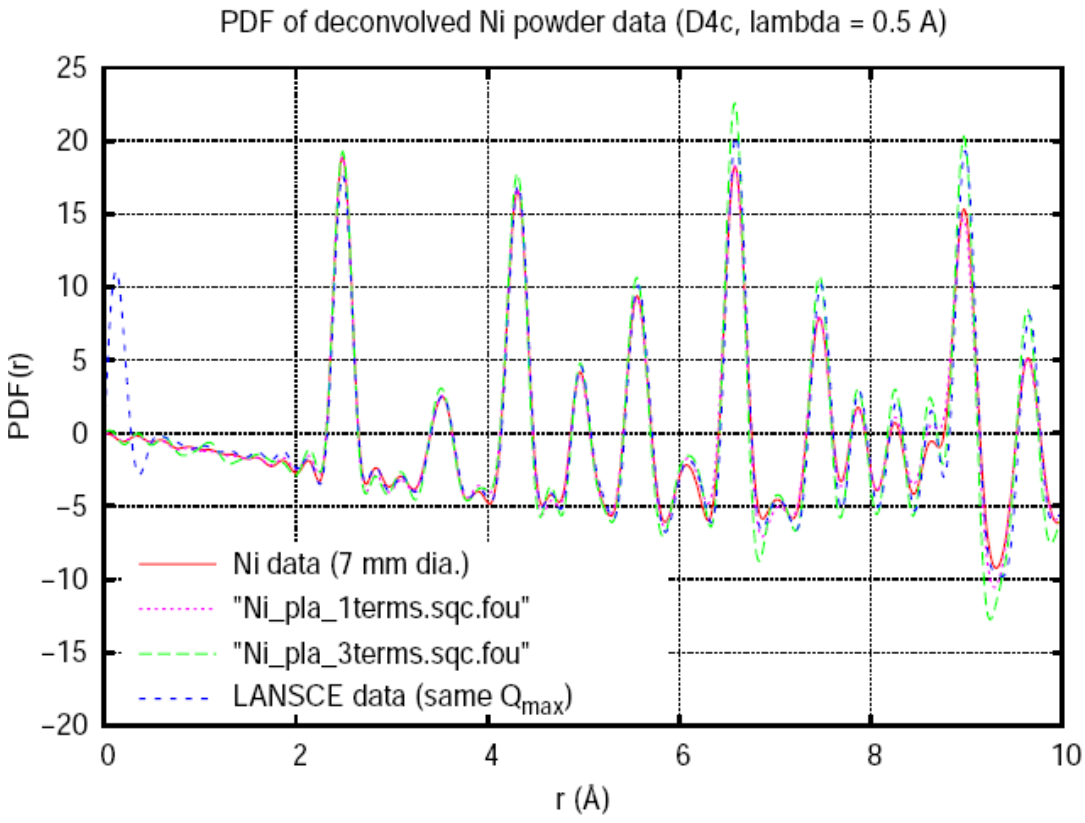
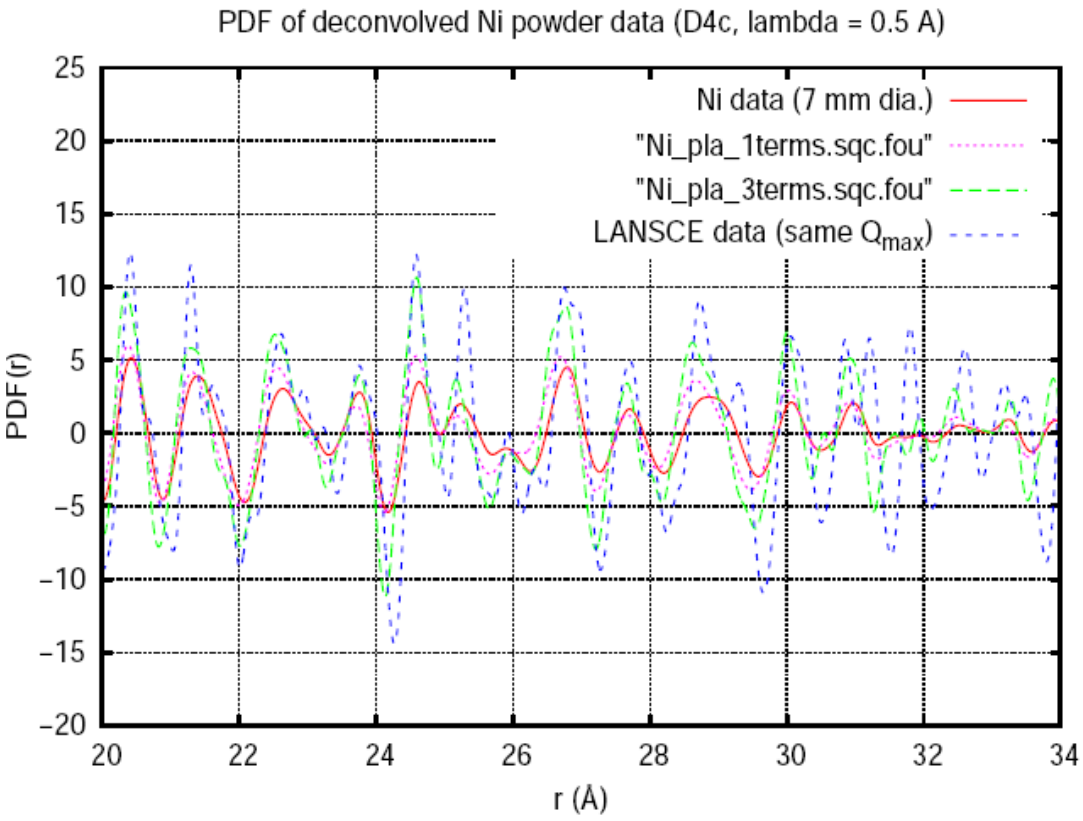
Decon-ed Ni data at low *r* values



Decon-ed Ni data at high *r* values



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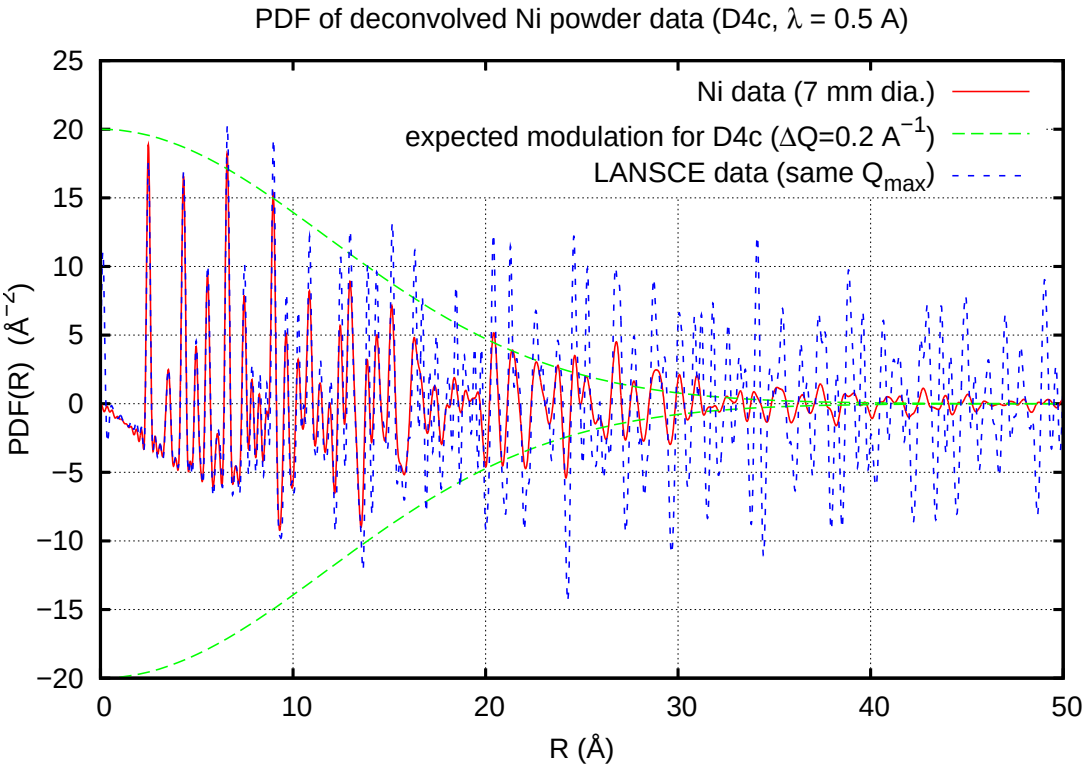
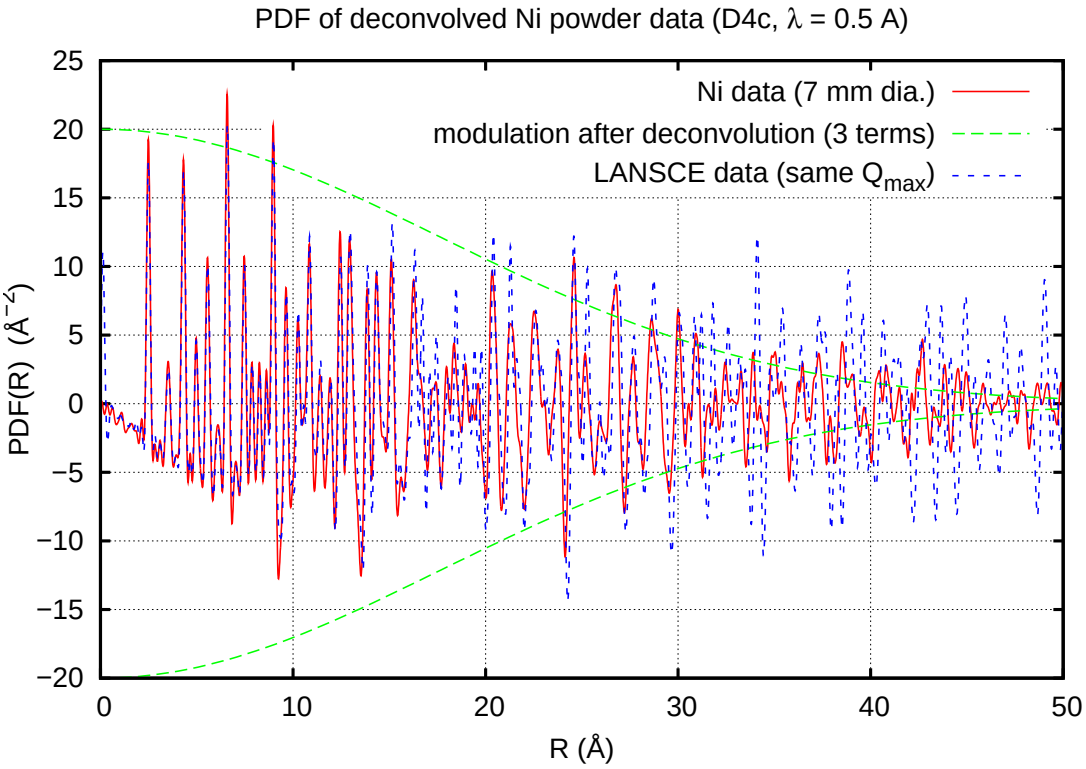
Extension of D4c's coherence volume

$\Rightarrow$ Effect on *r*-range: $r_{\max} = (5.55/2)/\Delta q$



Extension of D4c's coherence volume

⇒ Effect on r-range: $r_{\max} = (5.55/2)/\Delta q$



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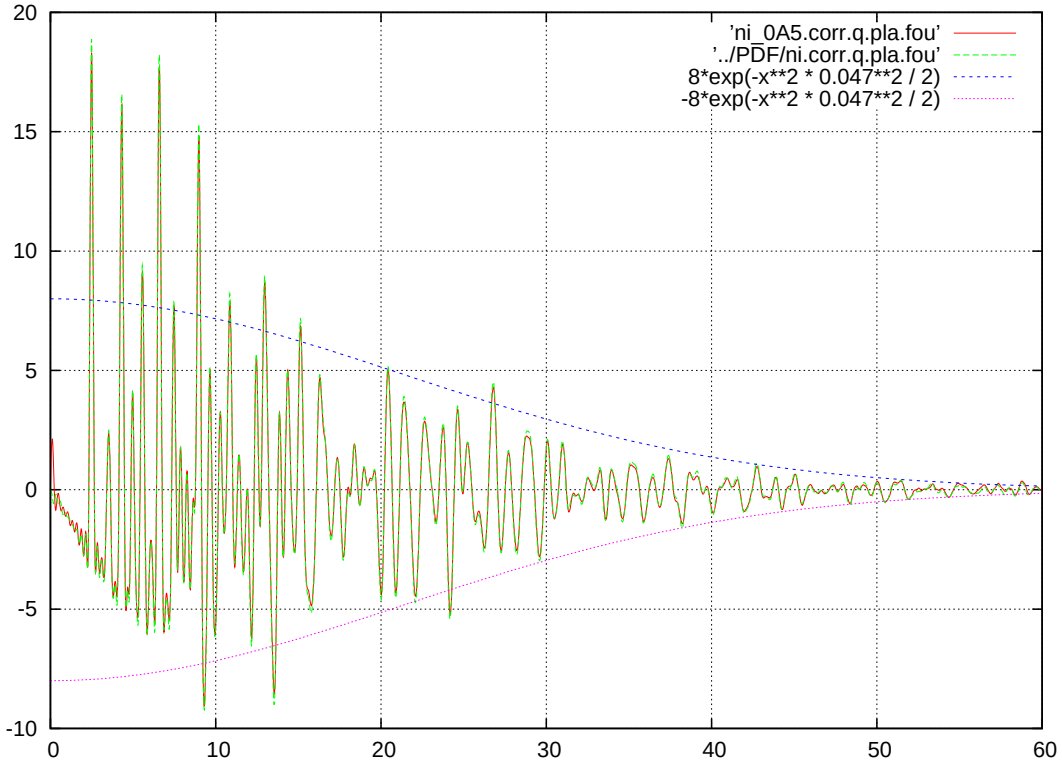
Effect of correlated atomic vibrations at low-r

NB: D4c coherence volume FWHM is actually ∼ 60 Å



The myth of "scattering power"

Myth of "scattering power": In all generality, diffraction measures $I = d\sigma/d\Omega = |\Sigma\, b_i \exp(i\,\mathbf{Q}\bullet\mathbf{r}_i)|^2$, a function of **Q** *only*. Changing the wavelength λ simply redistributes this intensity over Ω, so that for a *constant intrinsic* peak width of dQ, the intensity falling on a 1-D sensitive detector is integrated over $d\theta = (dQ/4\pi)\bullet\lambda/\cos(\theta)$, giving an *integrated* intensity increase ~ $\lambda/\cos(\theta)$ that *appears* as a peak-height increase for resolution-limited Bragg peaks. In fact, the (scattering_power)•(Lorentz_factor) is nothing more than this:

$\lambda^3 / [\sin(\theta)\sin(2\theta)/2] = \lambda^3 / [\sin^2(\theta)\cos(\theta)] = (4\pi/Q)^2 \bullet \lambda/\cos(\theta)$

leading to the same λ and θ dependence as derived above.

Few powder diffractionists understand this.

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Is the glass/liquid structure "locally cubic"?

*A variety of experimental results suggest a similarity in structure and dynamics between the glass/liquid and high-symmetry (*i.e. *cubic) phases of a number of systems:*

1) The amorphous and orientational glass (bcc) phases of ethanol show quantitatively similar structural and dynamical features.

2) Rapid crystallisation of some metallic glasses (*e.g.* $Nd_2Fe_{23}B_3$, $NiZr_2$, $CoZr_2$, $FeZr_2$) leads first to forming large cubic unit-cell metastable phases before forming lower-symmetry stable crystal phases.

3) A reversible transition between confined (in meso-porous silica) super-cooled water and cubic (bcc) ice has been observed at −40°C.

4) Thermal conductivity and inelastic neutron scattering measurements give evidence for "diffuse" Umklapp scattering in glasses.

5) The dispersion relations of some glasses show phonon softening just beyond the pseudo-Brillouin zone, similar to that due to bond-angle bending for L[111] phonons (bcc crystals) or for L[110] phonons (fcc).

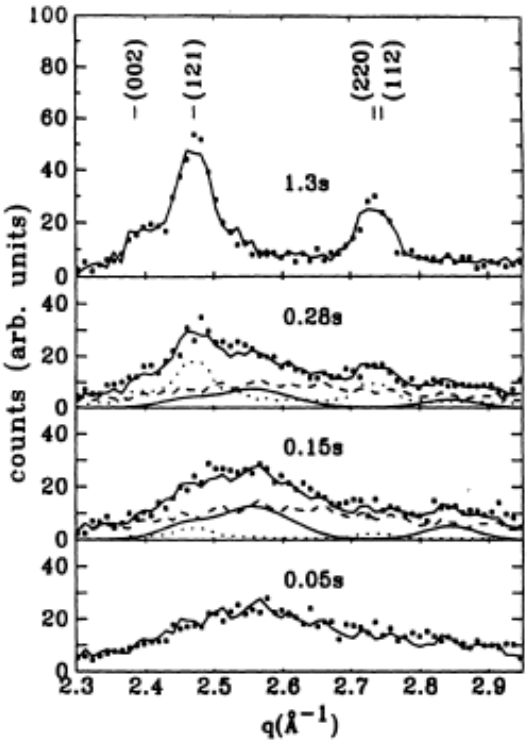
6) Other systems showing these structural similarities include silica *vs* β-cristobalite/β-tridymite (*e.g.* modern "crystallite theory" for glass structure) and liquid *vs* crystalline Ag_2Se.

Rapid crystallisation of amorphous $NiZr_2$

High-speed, low-resolution x-ray diffraction data on a single melt-spun ribbon held at 757 K:

The metastable precursor phase (fcc, $a = 12.6$ Å) appears at 0.15 s (smooth solid line) before the stable phase (bct, $a = 6.48$ Å, $c = 5.24$ Å) appears at 0.28 s (dotted line). The dashed-line is the initial amorphous phase. All phases have the same $NiZr_2$ stoichiometry.

⇒ Example of *kinetically-limited* nucleation/crystallisation, governed by activation energies of (collective) atomic displacement/diffusion, as opposed to free-energy (ΔG) limited nucleation/crystallisation in undercooled liquids.



S. Brauer, et al, *Phys. Rev. B* **45** *(1992) 7704–15.*

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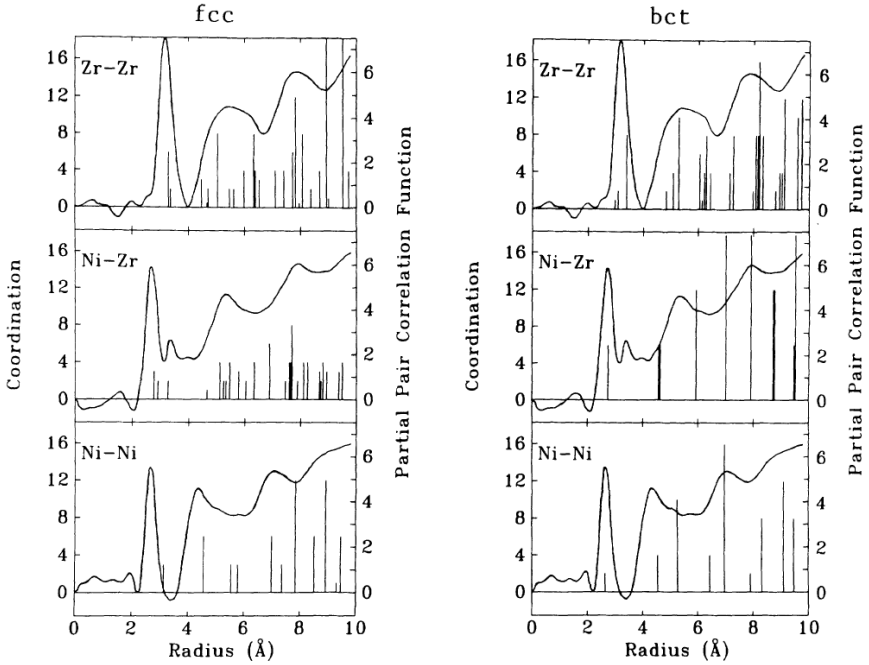
Comparison of partial PDF's for $NiZr_2$ phases

Cubic large-cell metastable: **Tetragonal small-cell stable:**

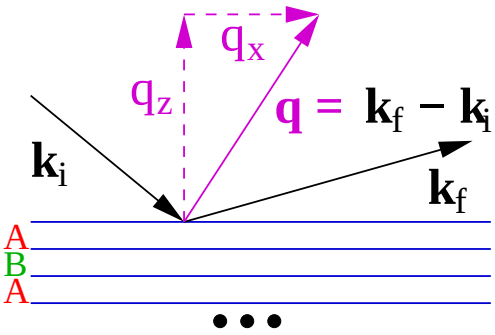


⇒ *The cubic phase approximates better the initial amorphous structure.*
Such is *not* the case in undercooled (metallic) liquids, where the local structure resembles that of icosahedrons or small fcc/hcp/bcc unit-cells, and where nucleation/crystallisation normally proceeds directly to stable phases, presumably thanks to the greater atomic diffusion in a liquid.

Appendix

(if time permits)

Off-specular X-ray diffraction from multilayers

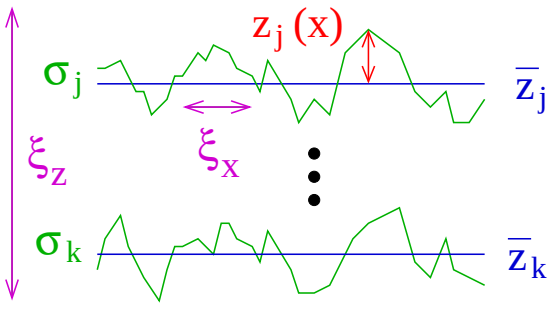


Off-specular scattering comes from interfacial roughness, whose lateral structure can be probed since $q_x \neq 0$.

Theory: the Distorted-Wave Born Approximation (DWBA) introduced by Sinha *et al* (1988) and developed later by *e.g.* Daillant & Bélorgey (1992).

$\Rightarrow$ Define a height-height correlation function for 2 interfaces j and k:

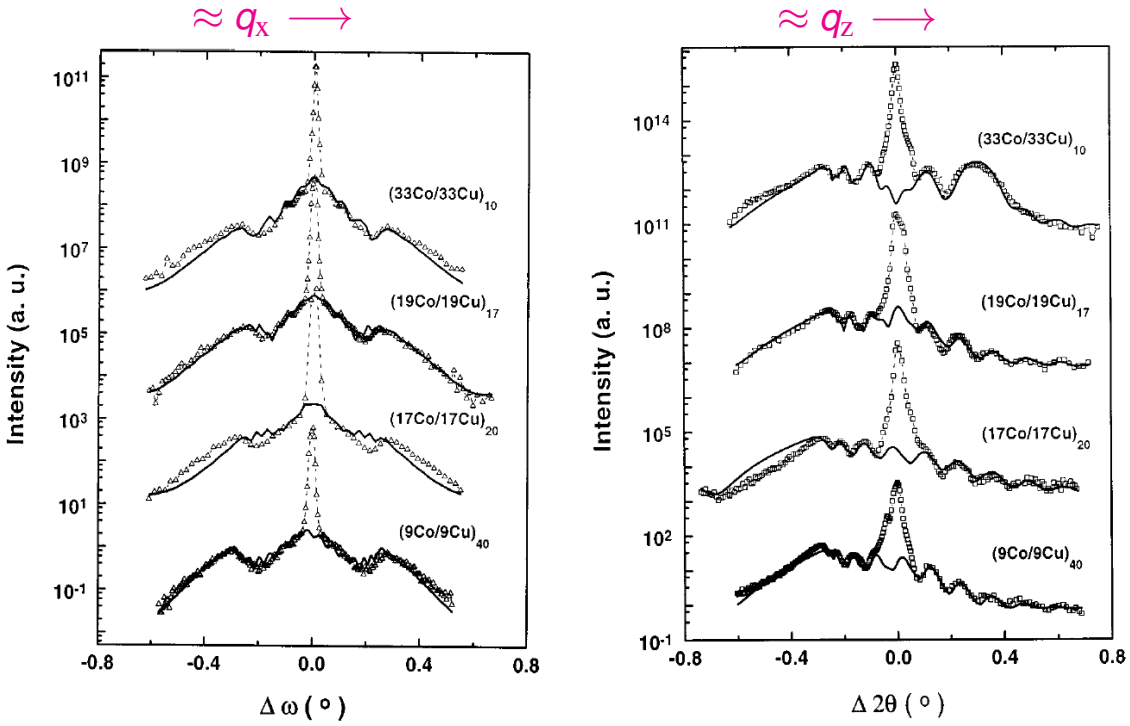
$$\langle z_j(x) z_k(0) \rangle = \sigma_j \sigma_k \, e^{-(x/\xi_x)^{2h}} \, e^{-(\Delta z_{jk}/\xi_z)^2}$$ (Fischer *et al* 1995)



$z_j(x)$ = deviation from average $\overline{z_j}$
σ_j = roughness amplitude
ξ_x = lateral correlation length
$\Delta z_{jk} = |\overline{z_j} - \overline{z_k}|$
ξ_z = transverse correlation length
$3 - h$ = Hausdorf (fractal) dimension

Off-specular X-ray diffraction/multilayers (cont'd)

Example refinements of off-specular intensity (Co/Cu multilayers):



⇒ Relate giant magnetoresistance (GMR) in Fe/Cr superlattices to lateral correlation length ξ_x (Schad, *et al*, PRB 1999, **48** cit.).

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