

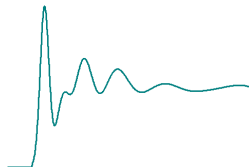


Data Treatment Neutron Total Scattering

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ADD2026, January 13th



Outline



- 1 Section 1: Experiments
- 2 Section 2: Background subtraction
- 3 Section 3: Cross section determination
- 4 Section 4: Static structure factor determination
- 5 Section 6: Real space correlations
- 6 Section 7: Final results



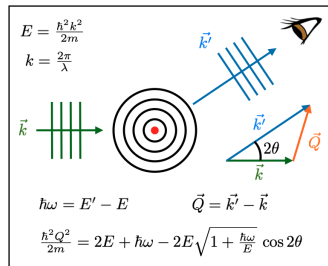
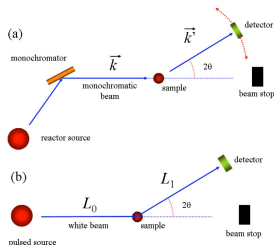


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Scattering experiment

Dynamic structure factor

$$I_{2\theta,\lambda}(\vec{Q}, \omega) = C \Phi_0(\lambda) N \frac{\lambda}{\lambda'} \frac{\sigma}{4\pi} S(\vec{Q}, \omega) \epsilon(\lambda')$$



Total scattering

$$I_{2\theta,\lambda}(\vec{Q}) = C \Phi_0(\lambda) N \frac{\sigma}{4\pi} \int_{-\infty}^{E_{\max}} \frac{\lambda}{\lambda'} S(\vec{Q}, \omega) \epsilon(\lambda') d\omega$$

Static structure factor: Ideal case

Approximations

- ① Monochromatic $\lambda' = \lambda$
- ② Elastic scattering
- ③ Single scattering (CW) $Q = \frac{4\pi}{\lambda} \sin \theta$
- ④ No attenuation
- ⑤ No background (TOF) $Q = \frac{2mL}{ht} \sin \theta$
- ⑥ Monoatomic

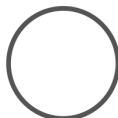


$$I_{2\theta,\lambda}(Q) = C \Phi_0(\lambda) \frac{N}{4\pi} \epsilon(\lambda) (\sigma_{\text{coh}} S(Q) + \sigma_{\text{inc}})$$

$$S(Q) = \frac{I_{2\theta,\lambda}(Q)/\sigma_{\text{coh}}}{C \Phi_0(\lambda) \epsilon(\lambda)} \frac{4\pi}{N} - \frac{\sigma_{\text{inc}}}{\sigma_{\text{coh}}}$$

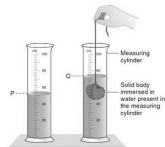
Scattering measurements

- ① **Sample:** sample in its container
- ② **Container:** empty container
- ③ **Instrument:** empty instrument
(or sample environment)
- ④ **Vanadium:** vanadium standard for normalisation
- ⑤ **Nickel:** nickel powder standard for calibration
(λ and $2\theta_0$)
- ⑥ **Absorber:** “black” sample for low-angle background

 I_{SCE}  I_{CE}  I_E  I_{VE}  I_{ACE}

Other required measurements

- **Sample:** mass and height in the container
- **Container:** inner and outer diameter
- **Beam:** beam dimensions on the sample
- **Beam:** wavelength (λ)
- Sample density (macroscopic density)
- For each element/isotope in the sample:
 - Atomic fraction
 - Neutron cross sections:
Coherent, incoherent and absorption
 - Scattering lengths: Coherent and incoherent
 - Mass number ($A = M_{\text{mol}}/M_{\text{neutron}}$)

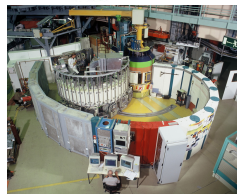
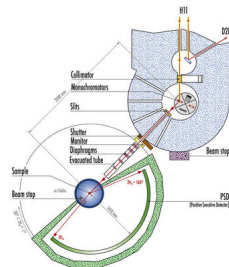


Same information for container and vanadium rod

Data collection: From raw data to diffractograms

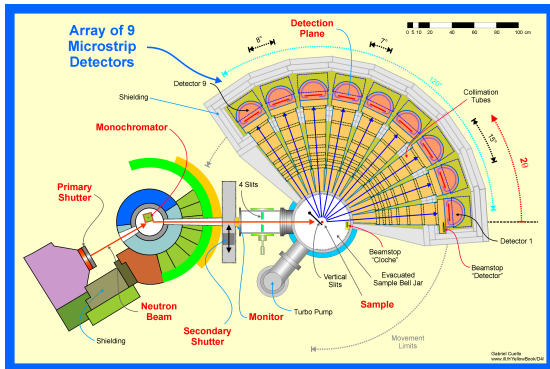
Basic instrument dependent programs

- Two-axis instruments, CW
- Software for data collection (NOMAD)
 - Raw data in ASCII or Nexus formats
- Basic software to produce diffractograms:
 - Dead-time correction
 - Relative efficiency (for multidetectors)
 - Instrumental geometric effects
 - Zero-angle correction
 - Measured angles or binning
- Output diffractograms (3-column files):
 - 2θ , I , σ
 - Q , I , σ



D20 at ILL.

D4: hot neutron 2-axis diffractometer

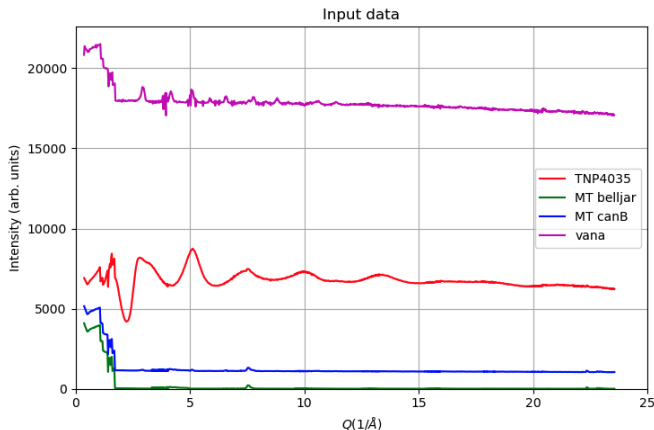


- Typical $\lambda = 0.5 \text{ \AA}$
- Q -range:
 $0.3 - 23.5 \text{ \AA}^{-1}$
- Very low and stable background
- Very high stability
- Bad resolution in Q -space

- Nine detection banks ($9 \times 64 = 576$ cells)
- Ten positions for a single diffractogram
- Disordered systems, PDF, mPDF, absorbing samples, NDIS

Raw diffractograms

Sample TNP4035: $(\text{TiO}_2)_{0.4}(\text{Nb}_2\text{O}_5)_{0.35}(\text{P}_2\text{O}_5)_{0.25}$



Atomic concentration: Ti = 0.0741, Nb = 0.1296, P = 0.0926, O = 0.7037

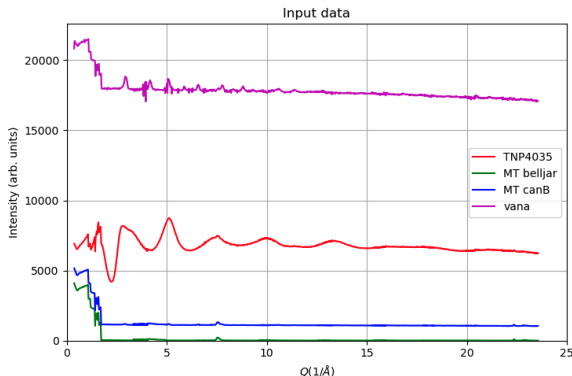


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The simplest method

0th-order: $I(Q) \approx I_{\text{SCE}}(Q)$

1st-order: $I(Q) \approx I_{\text{SCE}}(Q) - I_{\text{CE}}(Q)$



2nd-order: $I(Q) \approx I_{\text{SCE}}(Q) - [f_{\text{tr}} I_{\text{CE}}(Q) + (1 - f_{\text{tr}}) I_{\text{E}}(Q)]$

Classical method

Attenuation and multiple scattering



$$I(2\theta) = \frac{1}{R_1(2\theta)} \cdot (I_{\text{SCE}}(2\theta) - M_{\text{SCE}}(2\theta)) - \frac{R_2(2\theta)}{R_1(2\theta)} \cdot (I_{\text{CE}}(2\theta) - M_{\text{CE}}(2\theta)) - \frac{R_3(2\theta)}{R_1(2\theta)} \cdot (I_{\text{E}}(2\theta) - M_{\text{E}}(2\theta))$$

$$R_1(2\theta) = NA_{\text{S,SCE}}(2\theta) \qquad R_2(2\theta) = \frac{A_{\text{C,SCE}}(2\theta)}{A_{\text{C,CE}}(2\theta)}$$

$$R_3(2\theta) = \frac{1}{A_{\text{E,E}}(2\theta)} \left(A_{\text{E,SCE}}(2\theta) - \frac{A_{\text{C,SCE}}(2\theta) A_{\text{E,CE}}(2\theta)}{A_{\text{C,CE}}(2\theta)} \right)$$

Attenuation factors: Paalman & Pings

Calculation

$$I_{\mathbb{N}}(Q) = A_{\mathbb{N},\mathbb{M}}(2\theta) I_{\mathbb{N}}^{\text{theo}}(Q)$$

$$\mathbb{N} = [\text{S}, \text{C}, \text{E}, \dots] \quad \mathbb{M} = [\text{SCE}, \text{SC}, \text{E}, \dots]$$

$$A_{\mathbb{N},\mathbb{M}}(2\theta) = \frac{1}{V_{\text{b}}} \int_{V_{\text{b}}} dV \exp \left(- \sum_{k \in \mathbb{M}} \mu_k \ell_k(\vec{r}, 2\theta) \right)$$

$$\begin{bmatrix} A_{\text{S},\text{SCE}}(2\theta) & A_{\text{C},\text{SCE}}(2\theta) & A_{\text{E},\text{SCE}}(2\theta) \\ & A_{\text{C},\text{CE}}(2\theta) & A_{\text{E},\text{CE}}(2\theta) \\ A_{\text{V},\text{VE}}(2\theta) & & A_{\text{E},\text{VE}}(2\theta) \\ & & A_{\text{E},\text{E}}(2\theta) \end{bmatrix}$$

CW λ -dependent because
of the inelasticity

TOF naturally λ -dependent

$$\mu(\lambda) = \rho \sigma(\lambda) = \rho (\sigma_{\text{sca}} + \sigma_{\text{abs}}(\lambda)) \quad \sigma_{\text{sca}}: \text{bound/free} (\implies \lambda\text{-dependent})$$



Multiple scattering: Blech & Averbach

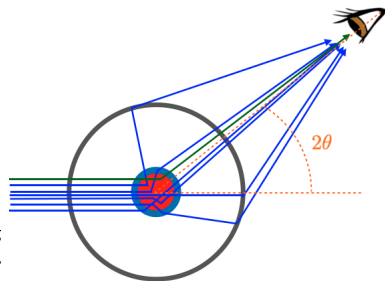
- Single: Only one scattering process in the sample

$$I_1(2\theta) = I(2\theta) - M(2\theta)$$

- Multiple: All other scattering processes

$$M(2\theta) = I(2\theta) \frac{\frac{\sigma_{\text{sca}}}{\sigma_{\text{tot}}} \delta(R/h, \mu R)}{1 - \frac{\sigma_{\text{sca}}}{\sigma_{\text{tot}}} \delta(R/h, \mu R)}$$

$$\begin{bmatrix} M_{\text{SCE}}(2\theta) & M_{\text{CE}}(2\theta) \\ M_{\text{VE}}(2\theta) & M_{\text{E}}(2\theta) \end{bmatrix}$$



Software: CORRECT (Studsvik, ILL), GO (LLB), GUDRUN → DISSOLVE (ISIS), ...



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Vanadium Q -dependence



Incoherent cross section

$$\sigma_{\text{inc,free}} = \sigma_{\text{inc,bound}} \left(\frac{A}{A+1} \right)^2$$

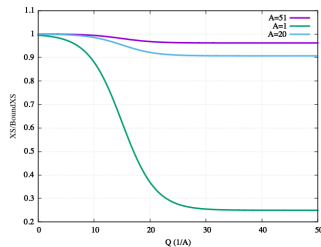
Logistic model

$$s(Q; I_b, \delta Q, Q_0) = I_b \frac{1 + \frac{A^2}{(1+A)^2} \exp\left(\frac{Q-Q_0}{\delta Q}\right)}{1 + \exp\left(\frac{Q-Q_0}{\delta Q}\right)}$$

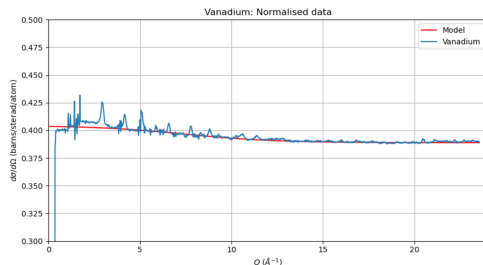
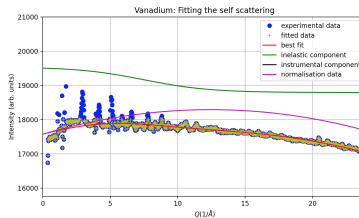
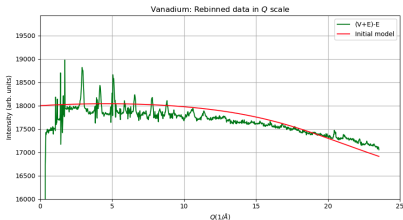
Instrument dependent behaviour:
mainly resolution

$$p_V(Q; (a_i, i = 0, P)) = \sum_{i=0}^P a_i Q^i$$

$$v(Q) = p_V(Q; (a_i, i = 0, P)) \times s(Q; I_b, \delta Q, Q_0)$$



Vanadium model fitting

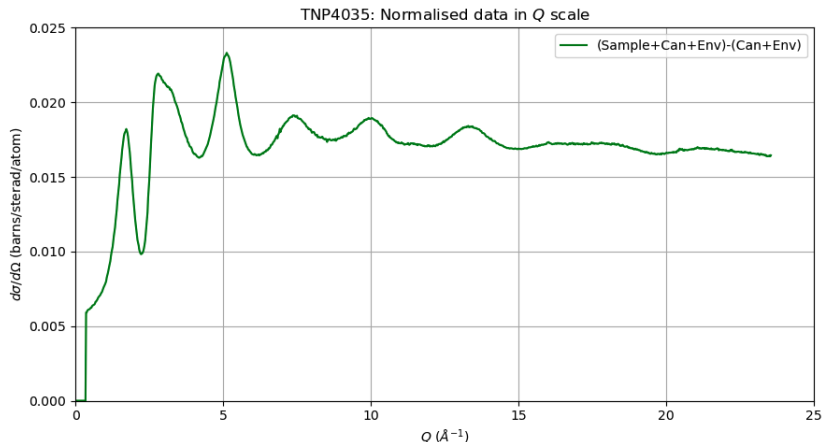


$$I_{V,\text{norm}}(Q) = \frac{\sigma_{V,\text{incoh}}^{\text{bound}}}{4\pi} \frac{I_V(Q)}{p_V(Q)}$$

Vanadium normalisation



$$I_{S,\text{norm}}(Q) = \sigma_{V,\text{incoh}}^{\text{bound}} \frac{N_V}{N_S} \frac{\rho_V}{\rho_{S,\text{eff}}} \frac{V_V}{V_{S,\text{eff}}} \frac{I_S(Q)}{p_V(Q)}$$



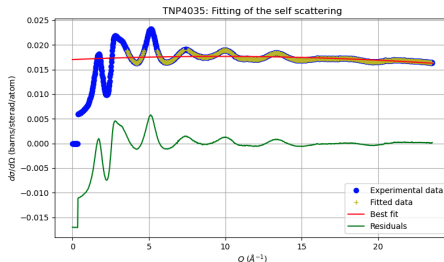
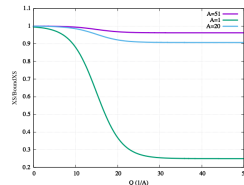
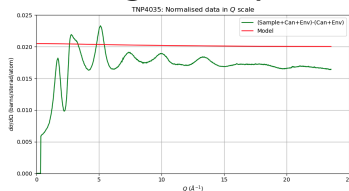


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Sample self Q -dependence

Mass dependent model:

- **Low- A :** Pseudo-Voigt or sigmoidal functions
- **High- A :** Polynomial (or Placzek) function



Removing the self contribution



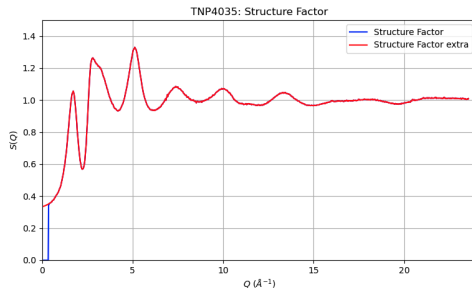
$$\frac{d\sigma}{d\Omega}(Q) = \left(\frac{d\sigma}{d\Omega}\right)_{\text{dist}}(Q) + \left(\frac{d\sigma}{d\Omega}\right)_{\text{self}}(Q)$$

$$\frac{\frac{d\sigma}{d\Omega}(Q)}{\left(\frac{d\sigma}{d\Omega}\right)_{\text{self}}(Q)} = \frac{\left(\frac{d\sigma}{d\Omega}\right)_{\text{dist}}(Q)}{\left(\frac{d\sigma}{d\Omega}\right)_{\text{self}}(Q)} + 1$$

$$S(Q) = \frac{\frac{d\sigma}{d\Omega}(Q)}{\left(\frac{d\sigma}{d\Omega}\right)_{\text{self}}(Q)}$$

$$F(Q) = \frac{\left(\frac{d\sigma}{d\Omega}\right)_{\text{dist}}(Q)}{\left(\frac{d\sigma}{d\Omega}\right)_{\text{self}}(Q)}$$

$$F(Q) = S(Q) - 1$$





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Definition of the correlation functions

Pair Correlation Function

$$G(r) = \frac{2}{\pi} \int_0^{\infty} Q (S(Q) - 1) \sin(Qr) dQ$$

Pair Distribution Function

$$g(r) = 1 + \frac{G(r)}{4\pi\rho r}$$

Radial Distribution Function

$$\text{RDF}(r) = 4\pi r^2 \rho g(r) = r G(r) + 4\pi r^2 \rho$$

Linearised Radial Distribution Function

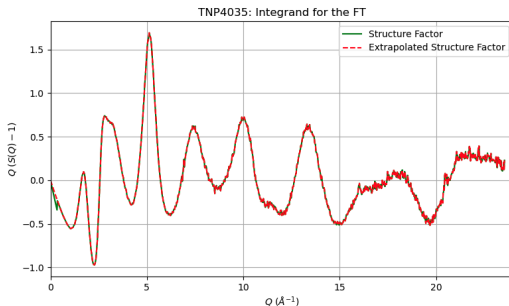
$$T(r) = \text{RDF}(r)/r = G(r) + 4\pi r \rho$$

Running Coordination Number

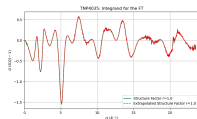
$$C(r) = \int_0^r \text{RDF}(r') dr'$$



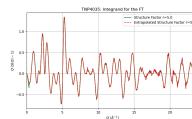
The integrand in the Fourier transform



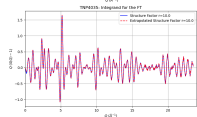
$$\int_0^{\infty} Q (S(Q) - 1) \sin(Qr) dQ$$



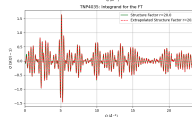
$$r = 1 \text{ \AA}$$



$$r = 5 \text{ \AA}$$



$$r = 10 \text{ \AA}$$



$$r = 20 \text{ \AA}$$

The window function: Lorch

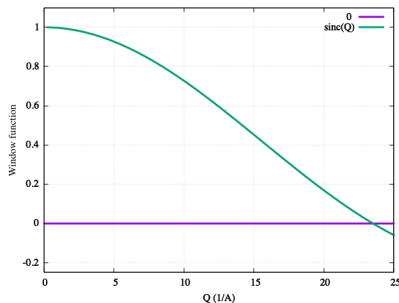


$$L(Q) = A \frac{\sin\left(\frac{Q\pi}{Q_{\max}}\right)}{\frac{Q\pi}{Q_{\max}}} = A \operatorname{sinc}\left(\frac{Q\pi}{Q_{\max}}\right)$$

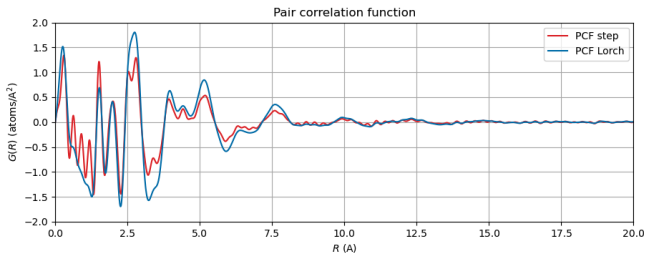
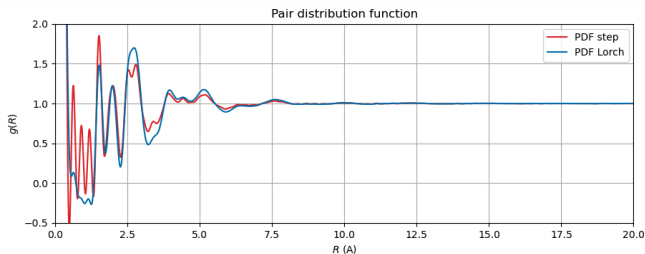
Normalisation

$$\begin{aligned} 1 &= A \frac{Q_{\max}}{\pi} \int_0^{\pi} \frac{\sin(x)}{x} dx \\ &= A \frac{Q_{\max}}{\pi} \operatorname{Si}(\pi) = A \frac{Q_{\max}}{\pi} 1.851937 \end{aligned}$$

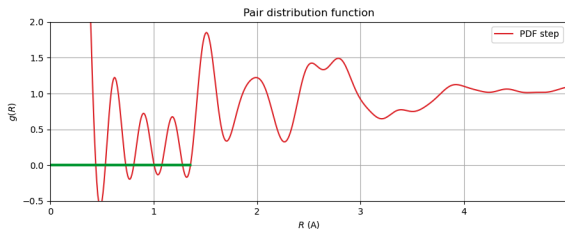
$$L(Q) = 0.54 \frac{\pi}{Q_{\max}} \operatorname{sinc}\left(\frac{Q\pi}{Q_{\max}}\right)$$



The correlation functions: First step

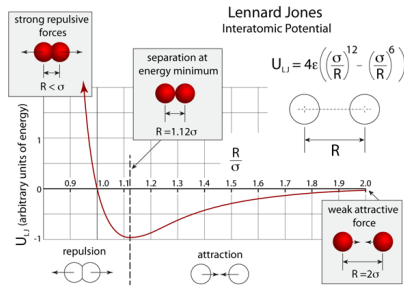
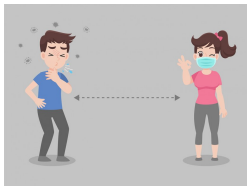


Repulsion region



Removing
oscillations at
low- R

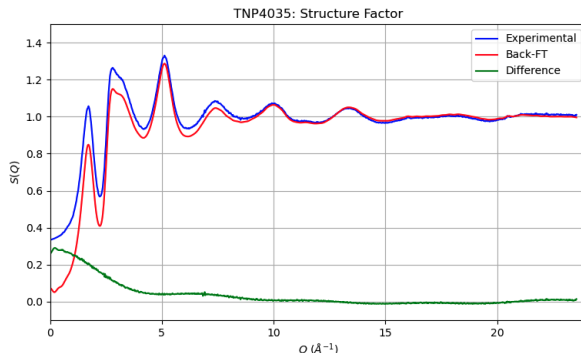
Social distancing



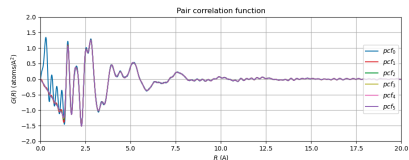
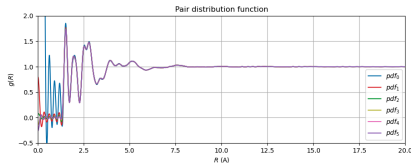
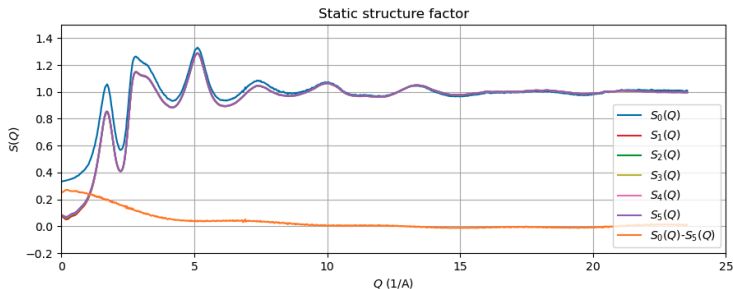
Back Fourier transform

$$g(r) - 1 = \frac{1}{4\pi\rho r} \frac{2}{\pi} \int_0^\infty Q (S(Q) - 1) \sin(Qr) dQ$$

$$S(Q) - 1 = \frac{2\pi^2\rho}{Q} \frac{2}{\pi} \int_0^\infty r (g(r) - 1) \sin(Qr) dr$$



Iterative process

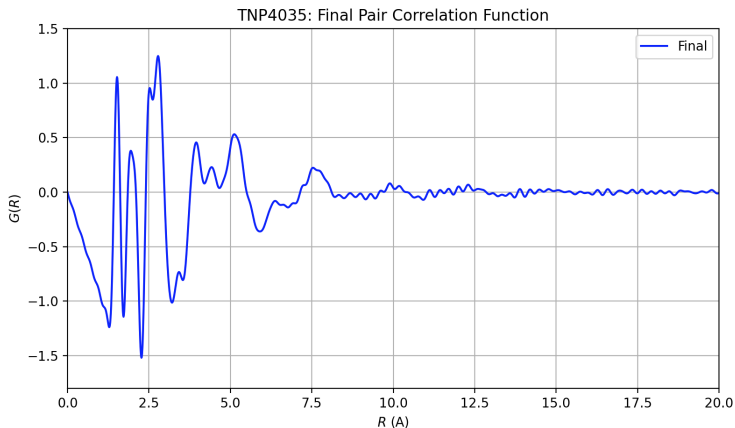




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Pair Correlation Function

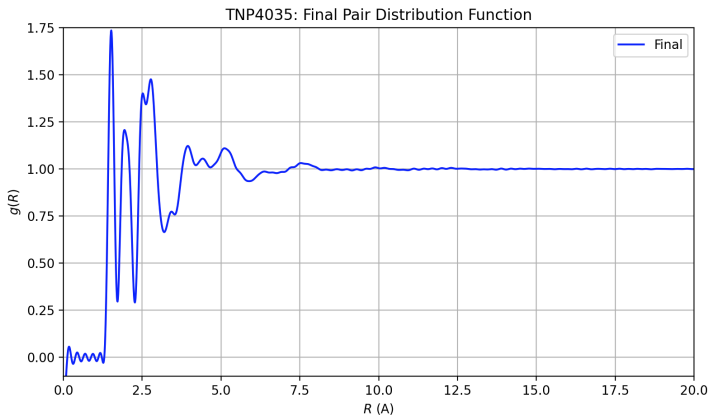
$$G(r) = \frac{2}{\pi} \int_0^{\infty} Q (S(Q) - 1) \sin(Qr) dQ$$



Pair Distribution Function



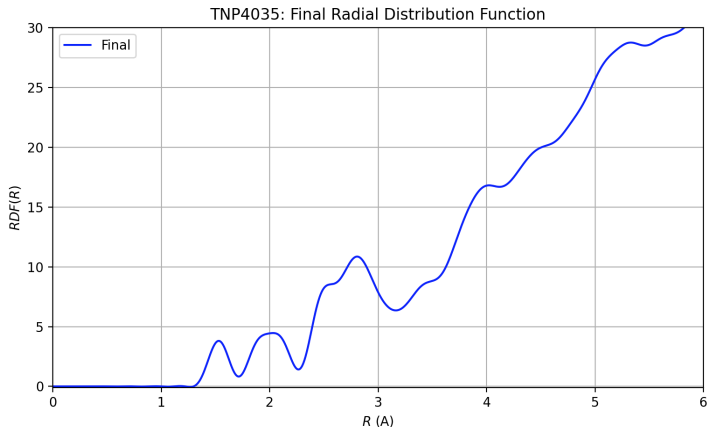
$$g(r) = 1 + \frac{G(r)}{4\pi\rho r}$$



Radial Distribution Function



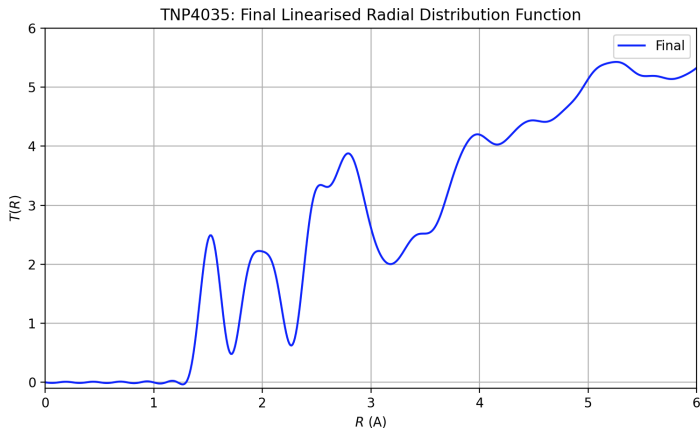
$$\text{RDF}(r) = 4\pi r^2 \rho g(r) = r G(r) + 4\pi r^2 \rho$$



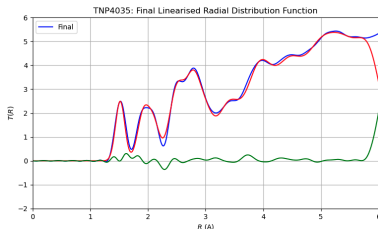
Linearised Radial Distribution Function



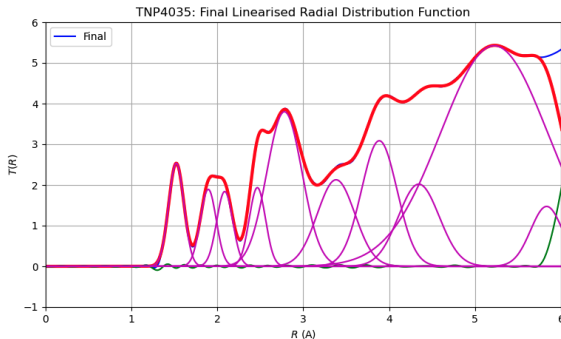
$$T(r) = \text{RDF}(r)/r = G(r) + 4\pi r\rho$$



Correlation distances



Multi Gaussian fit



$$CN = \text{Area} \cdot \text{Center}$$

$$FWHM = 2 \sqrt{2 \ln 2} \sigma$$

Distance (Å)	CN	FWHM (Å)
1.524	0.854	0.208
1.897	0.831	0.217
2.088	0.898	0.220
2.468	1.128	0.222
2.782	5.456	0.485
3.383	3.942	0.515
3.886	6.237	0.488
4.346	5.231	0.560
5.222	44.116	1.463
5.833	3.997	0.437

Beyond the experiments

Numerical simulations

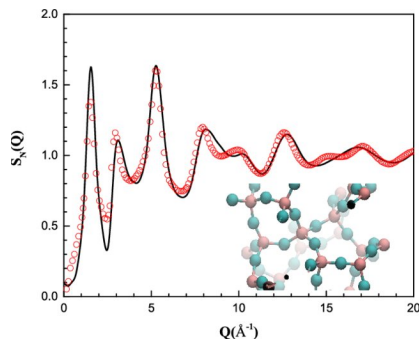
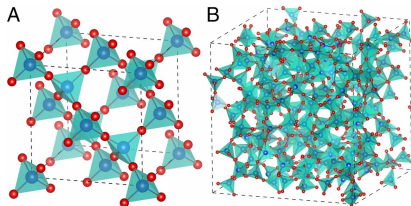
RMC, TOPAS: Reverse Monte Carlo

EPSR: Empirical Potential Structure Refinement

MD: Molecular Dynamics

Structure refinement

PDFgui, Diffpy



Thanks and questions



Thank you for your attention!