ND experimental procedure and data reduction

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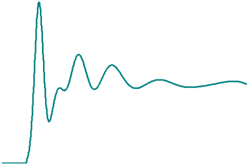
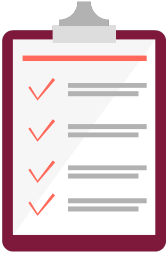


Outline

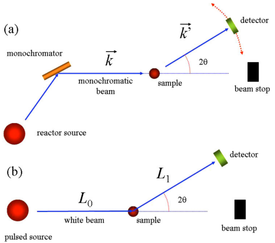
1. Section 1: Experiments
2. Section 2: Background subtraction
3. Section 3: Vanadium normalisation
4. Section 4: Inelasticity correction
5. Section 5: Structure factor determination
6. Section 6: Real space correlations
7. Section 7: Final results

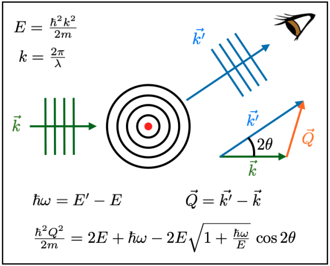


Scattering experiment

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

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

Static structure factor: Ideal case

Approximations

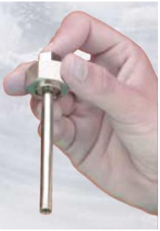
1. Monochromatic $\lambda' = \lambda$
2. Elastic scattering
3. Single scattering (CW) $Q = \frac{4\pi}{\lambda} \sin\theta$
4. No attenuation
5. No background (TOF) $Q = \frac{2mL}{ht} \sin\theta$
6. Monoatomic

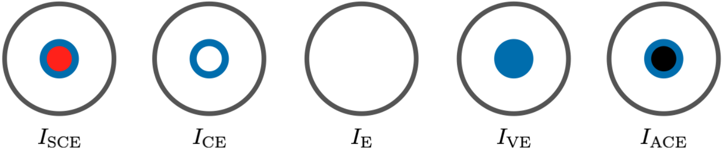
$$I_{2\theta,\lambda}(Q) = C\ \Phi_0(\lambda)\ \frac{N}{4\pi}\ \epsilon(\lambda)\ \left(\sigma_{\text{coh}}\ S(Q) + \sigma_{\text{inc}}\right)$$

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

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

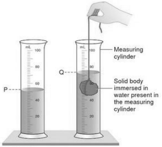




Other required measurements

- **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 ($A = M_{\text{mol}}/M_{\text{neutron}}$)

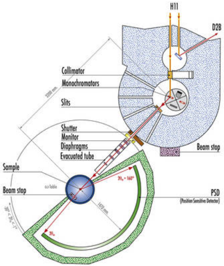


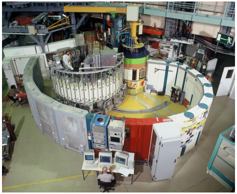
Same info for container and vanadium rod

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





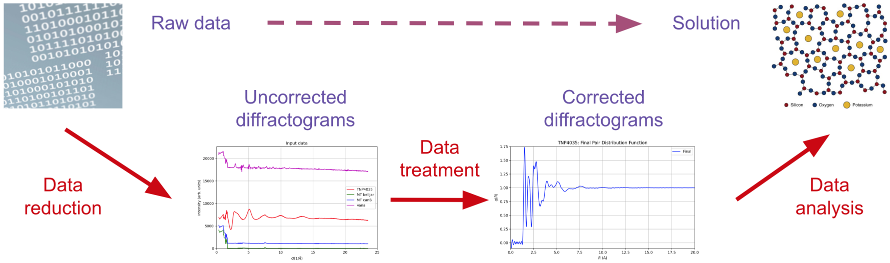
D20 at ILL.

A short parenthesis on terminology

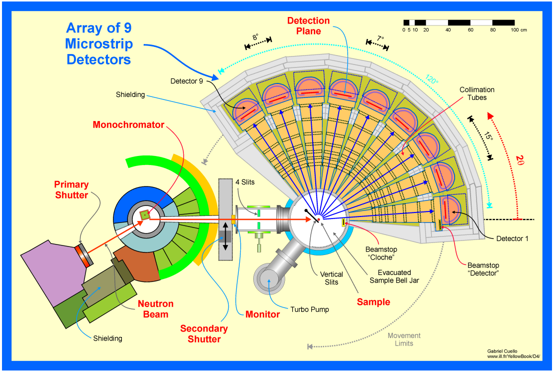
Data reduction: Getting uncorrected diffractograms from raw data

Data treatment: Getting structure factors or real space distributions from uncorrected diffractograms

Data analysis: Extracting physical magnitudes from the structure factors or real space correlations



D4: hot neutron 2-axis diffractometer

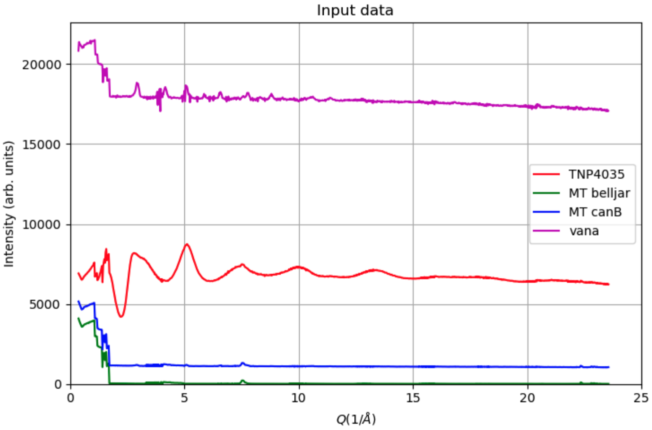


- Typical $\lambda = 0.5$ Å
- Q-range: $0.3 - 23.5$ Å^{-1}
- Very low and stable background
- Very high stability
- Bad resolution in Q-space

- 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: $(TiO_2)_{0.4}(Nb_2O_5)_{0.35}(P_2O_5)_{0.25}$

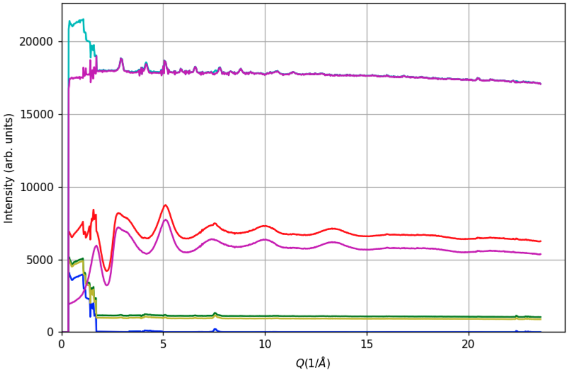


Atomic concentration: Ti = 0.0741, Nb = 0.1296, P = 0.0926, O = 0.7037

The simplest method

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

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



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

Classical method

Attenuation and multiple scattering

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

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

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

Attenuation factors: Paalman & Pings

Calculation

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

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

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

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

CW λ-dependent because of the inelasticity

TOF naturally λ-dependent

$$\mu(\lambda) = \rho\, \sigma(\lambda) = \rho\, (\sigma_\text{sca} + \sigma_\text{abs}(\lambda))$$

σ_sca: bound/free ($\Longrightarrow$ λ-dependent)

Multiple scattering: Blech & Averbach

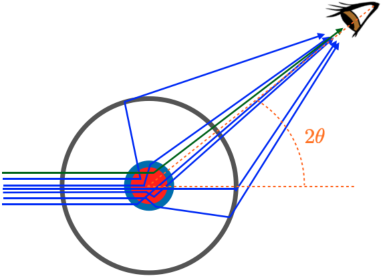
- Single: Only one scattering process in the sample

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

- Multiple: All other scattering processes

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

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



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

Monte Carlo method

- Weighted Monte Carlo simulating neutron trajectories
- Elastic scattering
- Angular distribution proportional to $I(2\theta)$

$$I^{\mathrm{MC}}(2\theta) = A(2\theta)\ I_0^{\mathrm{MC}}(2\theta)$$
$$I_{\mathrm{m}}^{\mathrm{MC}}(2\theta) = \delta(2\theta)\ I^{\mathrm{MC}}(2\theta)$$

Then

$$I_{\mathrm{cor}}(2\theta) = I_0(2\theta) - I_{\mathrm{m}}(2\theta) = \frac{I(2\theta)}{A(2\theta)} - \delta(2\theta)\ I(2\theta)$$

$$I_{\mathrm{cor}}(2\theta) = \left(\frac{1 - A(2\theta)\ \delta(2\theta)}{A(2\theta)}\right) I(2\theta)$$

Vanadium Q-dependence

Incoherent cross section

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

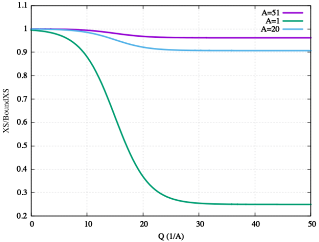
Logistic model

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

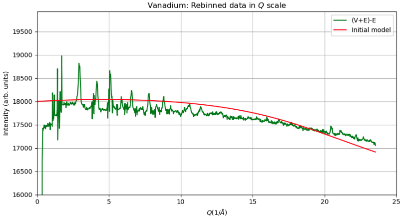
Instrument dependent behaviour:
mainly resolution

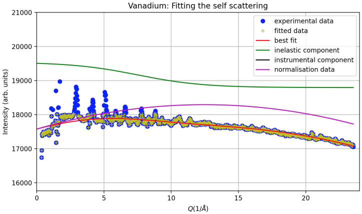
$$p_\text{V}(Q; (a_i, i=0,P)) = \sum_{i=0}^{P} a_i\, Q^i$$

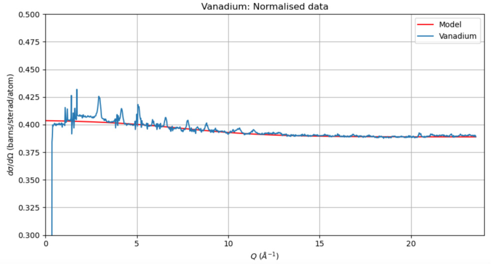
$$v(Q) = p_\text{V}(Q; (a_i, i=0,P)) \times s(Q; I_\text{b}, \delta Q, Q_0)$$



Vanadium model fitting



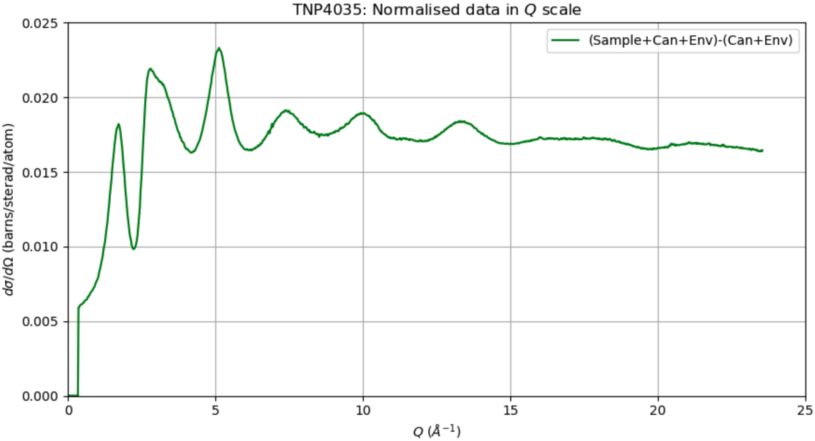




$$I_{\mathrm{V,norm}}(Q) = \frac{\sigma^{\mathrm{bound}}_{\mathrm{V,incoh}}}{4\pi} \frac{I_{\mathrm{V}}(Q)}{p_{\mathrm{V}}(Q)}$$

Vanadium normalisation

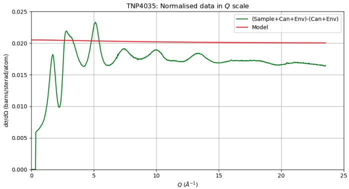
$$I_{\mathrm{S,norm}}(Q) = \sigma^{\mathrm{bound}}_{\mathrm{V,incoh}} \frac{N_{\mathrm{V}}}{N_{\mathrm{S}}} \frac{\rho_{\mathrm{V}}}{\rho_{\mathrm{S,eff}}} \frac{V_{\mathrm{V}}}{V_{\mathrm{S,eff}}} \frac{I_{\mathrm{S}}(Q)}{p_{\mathrm{V}}(Q)}$$

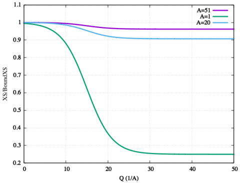


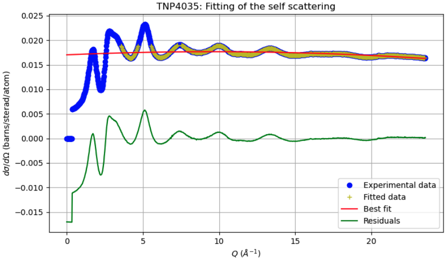
Sample self Q-dependence

Mass dependent model:

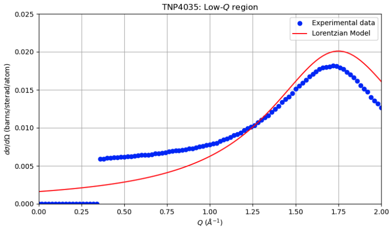
- **Low-A:** Pseudo-Voigt or sigmoidal functions
- **High-A:** Polynomial (or Placzek) function

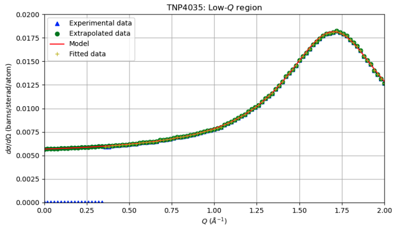


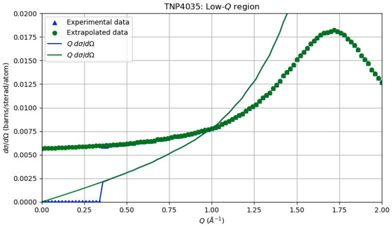




Extrapolation to low-Q







Removing the self contribution

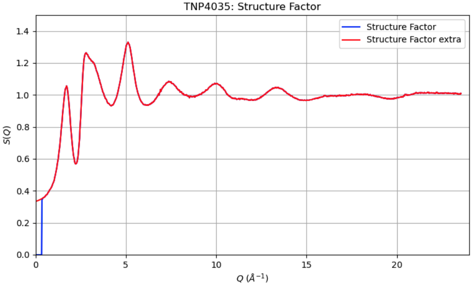
$$\frac{d\sigma}{d\Omega}(Q) = \left(\frac{d\sigma}{d\Omega}\right)_{\text{dist}}(Q) + \left(\frac{d\sigma}{d\Omega}\right)_{\text{self}}(Q)$$

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

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

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

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



Definition of the correlation functions

Pair Correlation Function

$$G(r) = \frac{2}{\pi}\int_0^\infty Q\ \left(S(Q)-1\right)\ \sin(Qr)\,\mathrm{d}Q$$

Pair Distribution Function

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

Radial Distribution Function

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

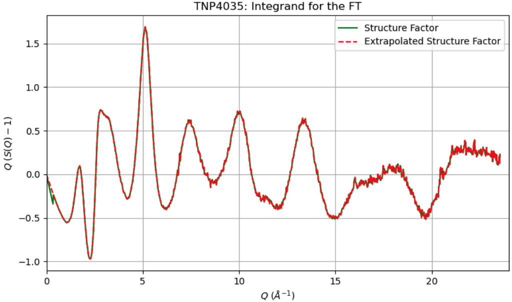
Linearised Radial Distribution Function

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

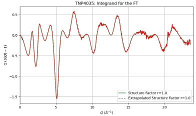
Running Coordination Number

$$C(r) = \int_0^r \mathrm{RDF}(r')\,\mathrm{d}r'$$

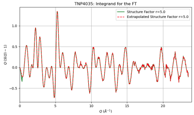
The integrand in the Fourier transform



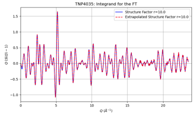
$$\int_0^\infty Q\ (S(Q)-1)\ \sin(Qr)\,\mathrm{d}Q$$



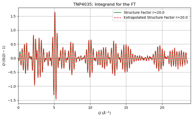
$r = 1$ Å



$r = 5$ Å

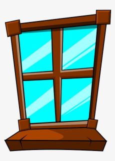


$r = 10$ Å



$r = 20$ Å

The window function: Lorch



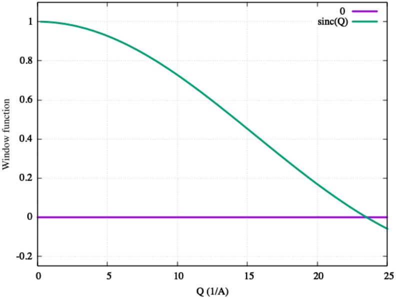
$$L(Q) = A \frac{\sin\left(\frac{Q\pi}{Q_{\max}}\right)}{\frac{Q\pi}{Q_{\max}}} = A \,\mathrm{sinc}\left(\frac{Q\pi}{Q_{\max}}\right)$$

Normalisation

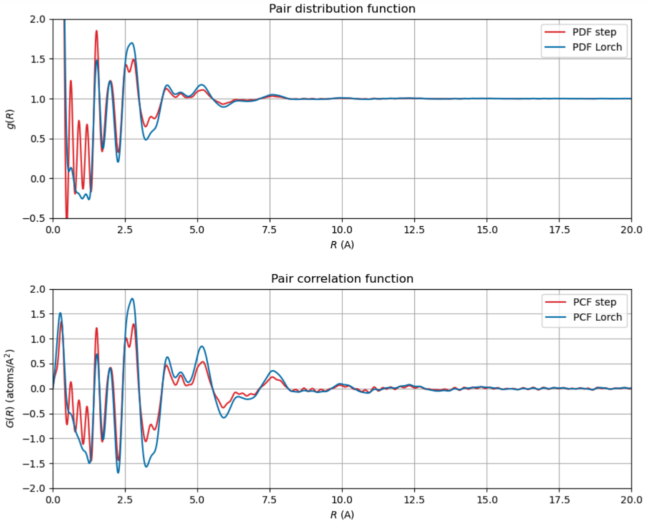
$$1 = A \frac{Q_{\max}}{\pi} \int_0^{\pi} \frac{\sin(x)}{x}\, \mathrm{d}x$$

$$= A \frac{Q_{\max}}{\pi} \mathrm{Si}(\pi) = A \frac{Q_{\max}}{\pi} 1.851937$$

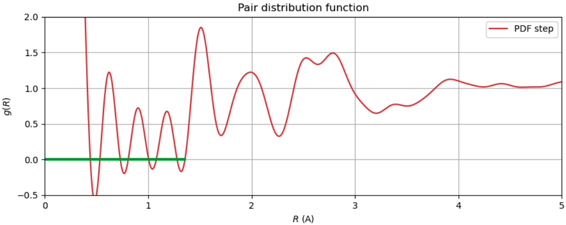
$$L(Q) = 0.54 \ \frac{\pi}{Q_{\max}} \ \mathrm{sinc}\left(\frac{Q\pi}{Q_{\max}}\right)$$



The correlation functions: First step

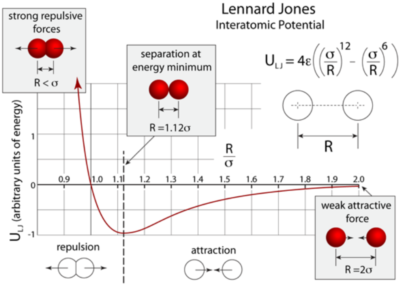


Repulsion region



Removing oscillations at low-R

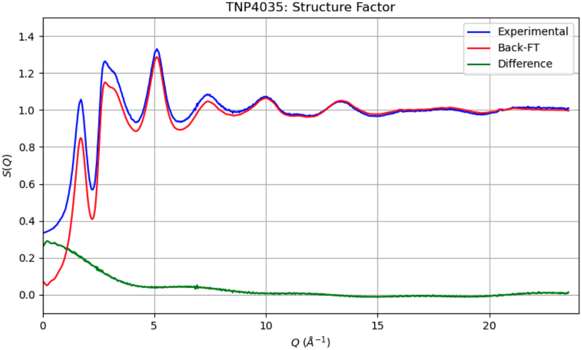
Social distancing



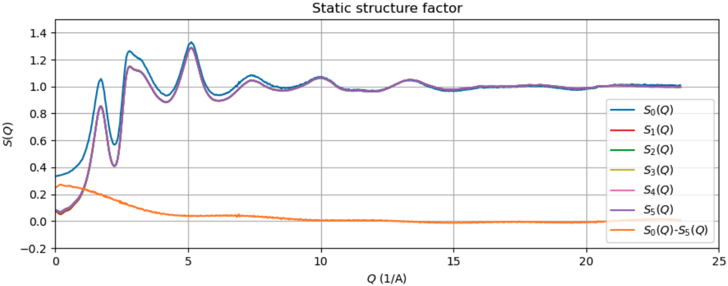
Back Fourier transform

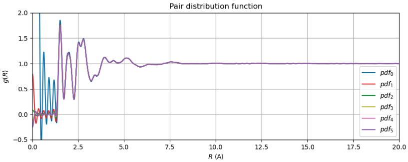
$$g(r)-1 = \frac{1}{4\pi\rho r} \quad \frac{2}{\pi} \int_0^\infty Q \; (S(Q)-1) \; \sin(Qr) \, \mathrm{d}Q$$

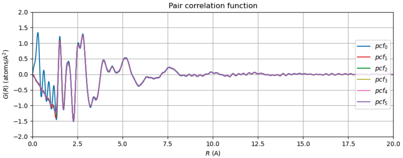
$$S(Q)-1 = \frac{2\pi^2\rho}{Q} \quad \frac{2}{\pi} \int_0^\infty r \; (g(r)-1) \; \sin(Qr) \, \mathrm{d}r$$



Iterative process







Correlation functions in real space: A reminder

Pair Correlation Function

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Pair Distribution Function

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Radial Distribution Function

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Running Coordination Number

$$C(r) = \int_0^r \mathrm{RDF}(r')\, \mathrm{d}r'$$

Pair Correlation Function

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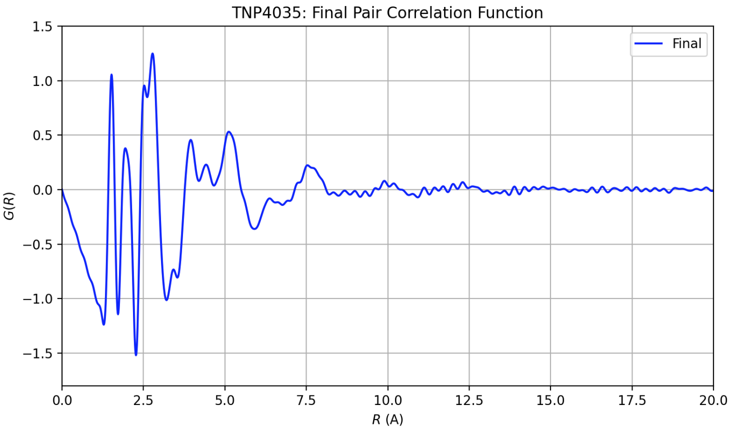
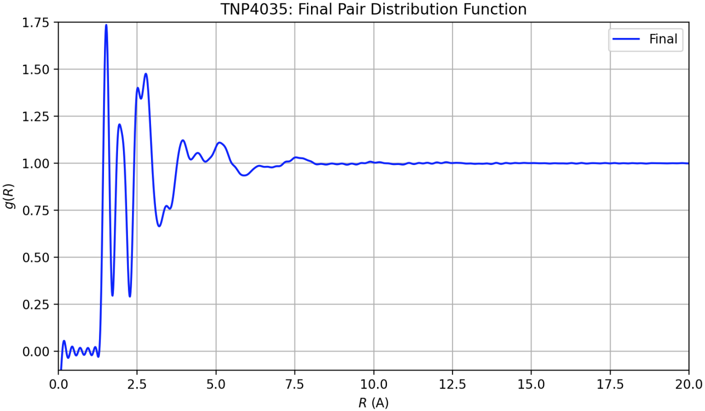


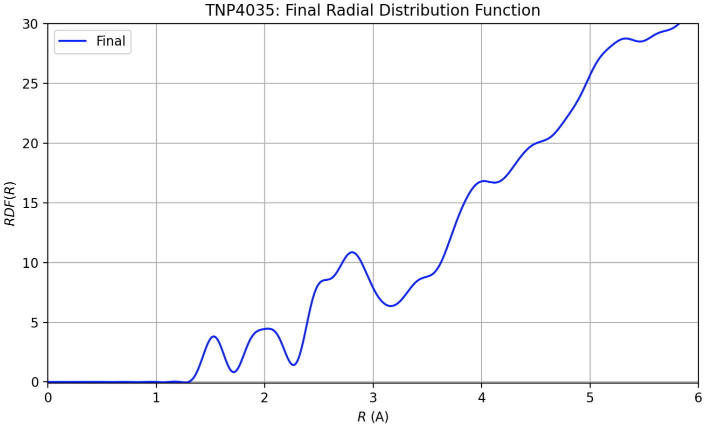
Pair Distribution Function

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



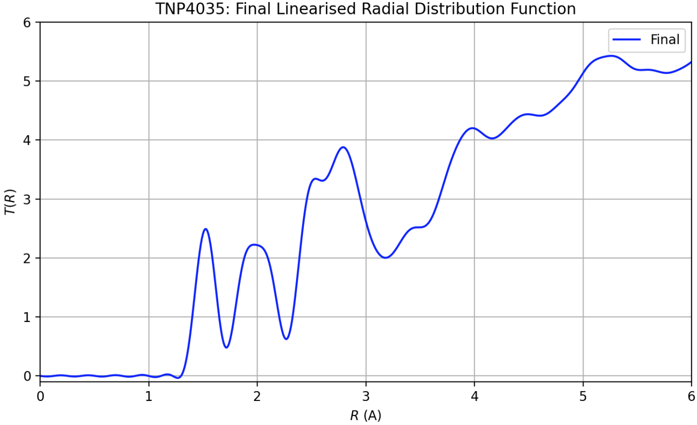
Radial Distribution Function

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

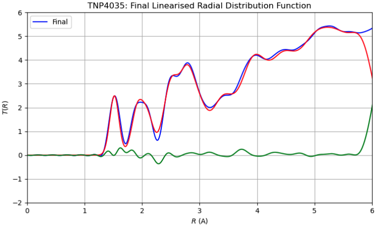


Linearised Radial Distribution Function

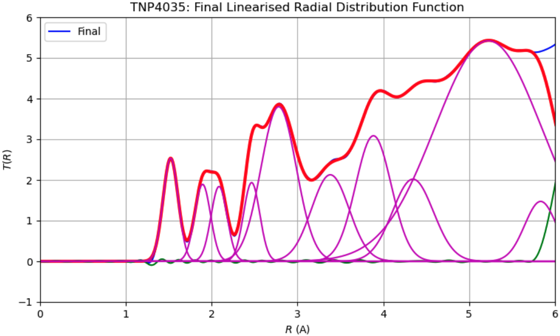
$$T(r) = \mathrm{RDF}(r)/r = G(r) + 4\pi r\rho$$



Correlation distances



Multi Gaussian fit



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

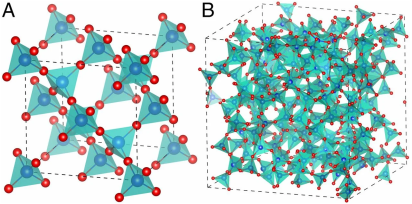
$$\mathrm{FWHM} = 2\sqrt{2\ \ln 2}\ \sigma$$

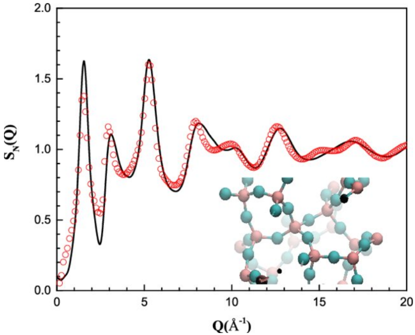
Distance (Å)	CN	FWHM (Å)
1.524	0.854	0.208
1.897	0.831	0.217
2.088	0.898	0.220
2.468	1.128	0.222
2.782	5.456	0.485
3.383	3.942	0.515
3.886	6.237	0.488
4.346	5.231	0.560
5.222	44.116	1.463
5.833	3.997	0.437

Beyond the experiments

Numerical simulations

- RMC: Reverse Monte Carlo
- EPSR: Empirical Potential Structure Refinement
- MD: Molecular Dynamics





Further reading

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Thanks for your attention!