X-Ray Total Scattering from Nano-crystalline and Amorphous Materials

Empa
Materials Science and Technology

The knowledge of a material atomic structure is at the basis of the theoretical understanding of its properties and of their following engineering. The diffraction pattern of a nano-crystalline powders usually displays broad peaks emerging from a high and modulated background. Extracting reliable information about the structure, chemical composition, domain size and shape requires taking into account also the broad diffuse contribution underneath the Bragg peaks and, possibly, also the small-angle scattering component.
The Debye Scattering Equation (DSE) [1] provides the spherical average of the differential cross-section of the sample intrinsic scattering, that is the total scattering intensity, without any assumption about order and periodicity of the structure.

$$I(Q) = \left\langle \frac{\partial \sigma}{\partial \Omega} \right\rangle_{\mathbb{S}} \propto \sum_{j=1}^{N} f_j(Q)^2 o_j^2 + \sum_{j \neq k}^{N} f_j(Q) f_k(Q) T_j(Q) T_k(Q) o_j o_k \frac{\sin(Q d_{jk})}{Q d_{jk}}$$

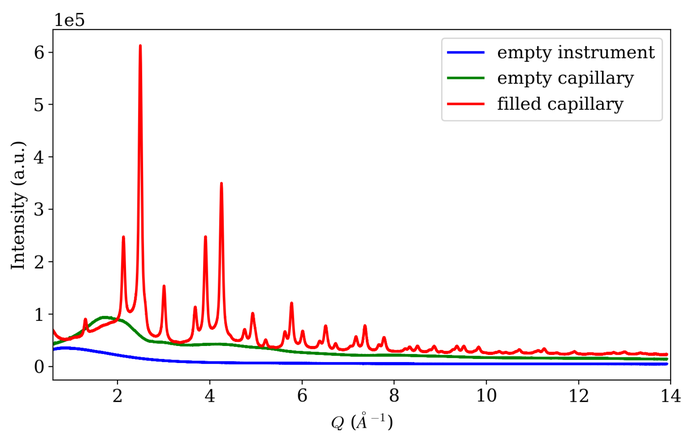
f atomic form factor
T thermal factor
o site-occupation factor
d atomic pair-distance
Q scattering vector modulus

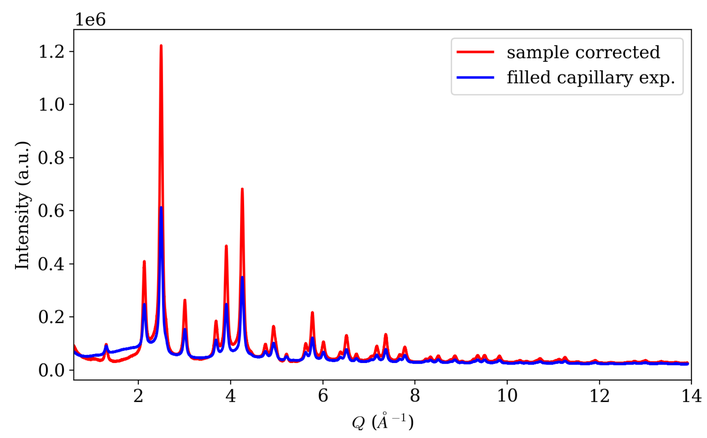
[1] P. Debye, *Phys. Z.* 1915 31, 797–798

Through the accurate calculation and optimisation of the DSE it is possible to retrieve a "bottom-up" structural model which takes into account also the size and shape effects. It is also possible to derive the atomic pair distribution function (PDF) and thus extract information about the very local structure.

Experiments

In a total scattering experiment, the sample pattern, the empty container, as well as the empty environment must be measured.
Dedicated algorithms allow to extract the sample scattering pattern from the experimental ones.

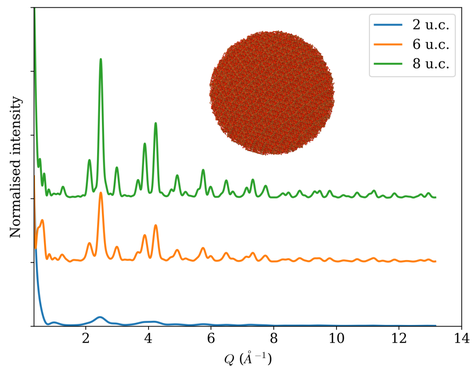




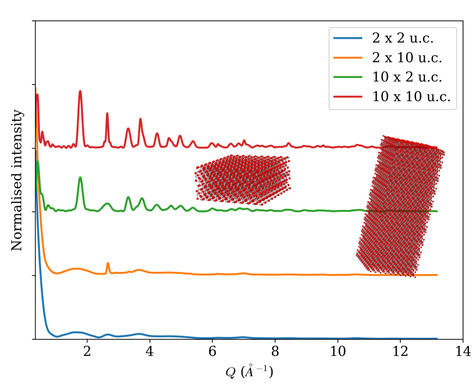
Building Structural Models

generation of a mono- or bi-variate population of nano-crystals with increasing size and desired shape: spherical, cylindrical, parallelepiped with rectangular or hexagonal base

Magnetite- Fe_3O_4 NC



Anatase - TiO_2 NCs



Model Optimisation

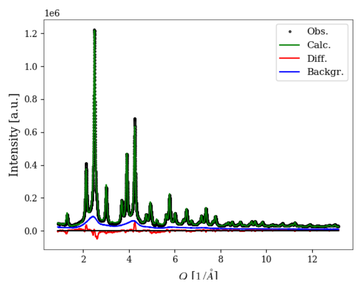
a. <u>calculation</u> using a algorithm the NCs diffraction patterns with accuracy within 1 ppm
b. <u>optimisation</u> of the model parameters *vs* the experimental data

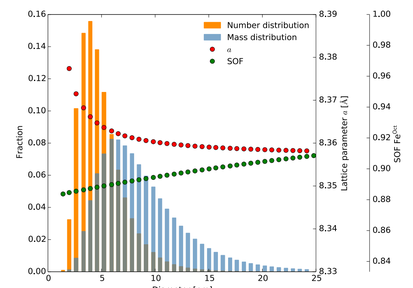
The experimental diffraction pattern is interpreted as a weighted sum of polydispersed NCs patterns.

Evaluation of the structural parameters on a statistically robust approach, delivering quantitative information on:

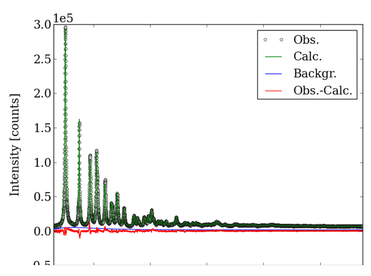
- mono- and bi-variate NCs number- and mass-based size distributions (i.e. diameter or base&height)
- the size-dependent structural parameters:
  - ✶ lattice parameter (different models available)
  - ✶ site occupancy factors
  - ✶ thermal factors

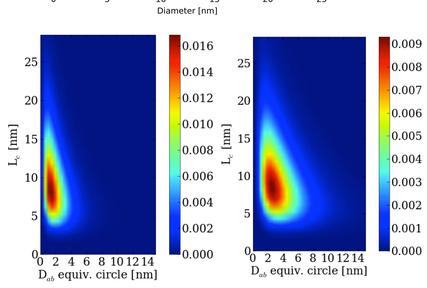
Fits and Statistical Distributions



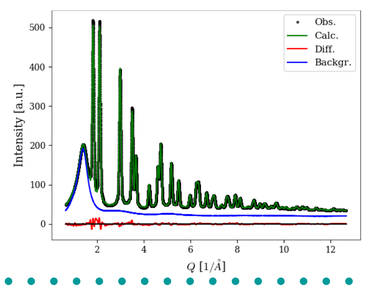


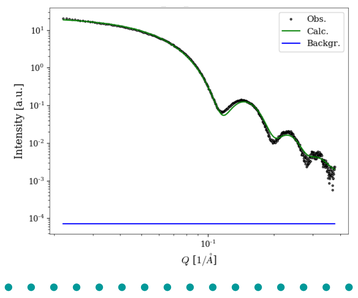
Best fit, size distributions, lattice parameter and occupation factor in magnetite NCs.
Chem. Mat, 2013, 25, 4820





Best fit, number- and mass-weighted size distributions in TiO_2 NCs
Angew. Chem. Int. Ed., 2011, 50, 10828





Best fit of wide and small angle datasets
Nature Materials, 2016, 15, 987

http://debussy.sourceforge.net

DEBUSSY - Debye User System
(*J. Appl. Cryst.*, 2015, 48, 2026-2032) a suite of programs for the analysis of powder diffraction data from nanocrystalline, defective and/or non-periodic materials.

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