SAXS-Data Classification
01 - Basics

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SAXSquant 2D: Create 1D Profiles

Box Average

Pie Average
SAXSquant 1D: Subtract the Background

Intensity [a.u.]

- Red: Clay in Glycerol
- Green: Glycerol
- Blue: Clay

$q$ [1/nm]
(1) Does the profile contain peaks?

**Yes:** The sample is crystalline.
- The peak position $q_{\text{peak}}$ gives the distance $d$ between the crystal planes:
  \[ d = \frac{2\pi}{q_{\text{peak}}} \]
- The peak width tells about the crystal size and the degree of ordering. The smaller the size, the broader the peak.

**No:** The sample is amorphous.
- The curvature (≈ slope) at small angles gives the particle size: The steeper, the bigger.
(2) Does it contain oscillations with deep minima?

**Yes:** The sample is monodisperse (and close to spherical)
- All particles are identical and have the same size.

**No:** The sample is either polymorphous or polydisperse.
- All particles have different shapes.
- All particles have different sizes.
(3) Does the intensity drop down at small angles?

**Yes:** The sample is too concentrated or interacting (e.g., charged particles)

- The peak position $q_{\text{peak}}$ indicates the approximate inter-particle distance $d$.

$$d = \frac{2\pi}{q_{\text{peak}}}$$

**No:** The sample is dilute.
(4) What is the power law of the curve? (Works only with background subtracted data.)

**In point collimation:**
1. $q^0$: The particles are globular.
2. $q^{-1}$: The particles are cylindrical.
3. $q^{-2}$: The particles are lamellar (or vesicles).
4. $q^{-4}$: Particles with all sizes and shapes and too big to be resolved.

**In line collimation:**
1. $q^0$: The particles are globular.
2. $\ln(q)$: The particles are cylindrical.
3. $q^{-1}$: The particles are lamellar (or vesicles).
4. $q^{-3}$: Particles with all sizes and shapes and too big to be resolved.
Power Laws (Point Collimation)

Globular

\[ q^0 \]

Cylindrical

\[ q^{-1} \]

Lamellar

\[ q^{-2} \]
Power Laws (Line Collimation)

Globular

\[ q^0 \]

Cylindrical

\[ -\ln(q) \]

Lamellar

\[ \sim q^{-1} \]
Information Domains / Power Laws

- **Size**
  - Guinier
    - Radius of Gyration
  - Fourier
    - Cross-section Structure

- **Shape**
  - Porod
    - Surface per Volume
  - Guinier
    - Fourier
  - $q^{-0}$
  - $q^{-1}$
  - $q^{-2}$
  - $q^{-4}$ / $q^{-3}$

- **Surface**
  - Guinier
  - Fourier
  - Porod
Particle Size (Guinier Analysis)

Straight-line fitting via

\[ \ln(I) = \ln(I_0) - \left( \frac{R_G^2}{3} \right) q^2 \]

delivers the radius of gyration, \( R_G \). \( R_G \) is model independent.

**Sphere (R):** \[ R_G^2 = \frac{3}{5} R^2 \]

**Disk (R, L):** \[ R_G^2 = \frac{1}{2} \left( R^2 + \frac{L^2}{6} \right) \]

The same equations also apply approximately to line-collimation curves. (Error in \( R_G \) ~ +4%)
Porod Analysis (1)

Determination of:
(1) Constant background $B$
(2) Surface-to-Volume ratio (from $K$)

\[ q^3 I(q) \]

\[ q^3 \text{ [1/nm}^3]\]
Porod Analysis (2)

The final slope $K_S$:

$$I_S(q \to \infty) = B + \frac{K_S}{q^3}$$

The invariant $Q_S$:

$$Q_S = \int_{q=0}^{\infty} qI_S(q) dq$$

Surface per Volume:

$$\frac{S}{V} = 4000 \cdot \frac{K_S}{Q_S} \cdot \phi \cdot (1 - \phi)$$

Background: B

Main Application: Background Determination!

* Modified equations are used for point-collimation data:

$$\frac{S}{V} = \pi \cdot 1000 \cdot \frac{K}{Q} \cdot \phi \cdot (1 - \phi)$$

$$I(q \to \infty) = B + \frac{K}{q^4}$$

$$Q = \int_{q=0}^{\infty} q^2 I(q) dq$$
Pathways of Interpretation

Dense system

Experimental Intensity $I(q)$
Particle Form Factor $P(q)$
Interparticle Structure Factor $S(q)$

$P(q) \cdot S(q)$

$I(q) / S(q)$

Dilute system

Experimental Intensity $I(q)$
Particle Form Factor $P(q)$
Interparticle Structure Factor $S(q)$

$P(q) \cdot S(q)$

$I(q) / S(q)$

Modelling

Interpretation

FT

FT$^{-1}$

$\pm \sqrt{(...)}$

$E(q)$

$p(r)$

$\rho(r)$

PDDF
How Desmearing works

Measured (smeared) scattering curve  "Desmeared" scattering curve  \( p(r) \) not smeared!

Fitted to the measured data

"Smeared" Fourier-transformed splines  Fourier-transformed splines  Basic functions (splines)
SAXS-Data Classification
02 - Transforms

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Pathways of Interpretation

⇒ Reconstruct the electron-density profile $\rho(r)$ from the experimental form factor $P(q)$
The PDDF: (1) General 3D

(1) The PDDF \([p(r)]\) is a **histogram of all distances** that appear inside a particle.

(2) It is weighted by the product of the 2 electron-density values that are connected by the distance \(r\).

\[
\gamma(\vec{r}) = \iiint_V \rho(\vec{s}) \rho(\vec{s} - \vec{r}) d\vec{s}
\]

\[
p(r) = 4\pi \cdot r^2 \cdot \langle \gamma(\vec{r}) \rangle_{\theta,\phi}
\]
The PDDF: (2) Homogeneous

Characteristic Features (Homogeneous Particles):

Globular:

Cylindrical:

Lamellar:

Aggregates:
The PDDF: (3) Inhomogeneous

Characteristic Features (Core-Shell Particles):

\[ \Delta \rho_2 = 1.0 \]
\[ \Delta \rho_2 = 0.5 \]
\[ \Delta \rho_2 = 0.0 \]
\[ \Delta \rho_2 = -0.5 \]
The PDDF: (4) Cross-Section Structure

$q \cdot I(q)$

\[ q \cdot I(q) = \int \rho(\mathbf{s}) \rho(\mathbf{s} - \mathbf{r}) d\mathbf{s} \]

\[ p_C(r) = 2\pi \cdot r \cdot \langle \gamma(\mathbf{r}) \rangle \phi \]

$q^2 \cdot I(q)$

\[ q^2 \cdot I(q) = \int \rho(s) \rho(s - r) ds \]

\[ p_T(r) = \gamma(r) \]
The Ingredients of Program GIFT

\[ p(r) = \sum_{i=1}^{20} c_i \cdot \varphi_i(r) \]

\[ I_D(q) = \sum_{i=1}^{20} c_i \cdot \chi_i(q) \]

\[ I(q) = \sum_{i=1}^{20} c_i \cdot \Phi_i(q) \]
The beam profiles are required by program GIFT.

**Beam-Length Profile**

Use the box-average method.

**Beam-Width Profile**
The Active Beam-Length Profile

(A) Footprint of the Beam
Sample
Active Beam Profile

(B) Footprint of the Beam
Sample
Beam Profile

Calculate the profile from the Beam or from the Sample Scattering!
The stability parameter (Lagrange Multiplier) mixes two desired conditions:

1. good fit
2. smooth PDDF
GIFT: Stable Fitting

Plateau

PDDF just right

Good fit
GIFT: Over-fitting

Log $N_z'$

Mean deviation

Curve height

Noisy PDDF

Fitting of noise
GIFT: The Largest Distance too Small

When the largest distance was chosen too small.
When the largest distance was chosen too big. Select the first negative minimum in the PDDF as the next $D_{\text{max}}$. 
The smallest resolvable distance is determined by the number of splines (basis functions).

**Spline number too small = bad resolution!**

Mean deviation still high

Cannot fit at large q
Too many splines never hurt!
The effect is compensated by a larger stability parameter.
GIFT: Excluded Volume Interaction

\[ \rho = \overline{\rho} \]

As seen from far away:
**Bulk Density**

As seen from close by:
**Local Density**

Next neighbour cannot come closer: **Excluded Volume**

- Is it a CORE-SHELL particle?
- Is it a homogeneous particle with a solvent layer?
Is the depletion layer (excluded volume) part of the particle (e.g., as a hydration shell) or not? 

**The operator has to decide!**
Use Perkus-Yevick Hard-Sphere model to remove structure factor.

Additionally fit:
- Interparticle Distance: 11.9 nm
- FWHM-Spread of Distances: 20.5%
- Effective Volume Fraction: 23.5%

Structure factor compensates peak

Better fit
Deconvolution Program

Scattering Profile

Pair-Distance Distribution

GIFT

$\log T(q)$

$q_{\text{min}} \rightarrow q \rightarrow q_{\text{max}}$

$\rho(r)$

$r$

Modelling

Reconstruction

Given Symmetry, arbitrary density profile!

DECON: Interpretation

Anton Paar
DECON: Stable Fitting

Mean deviation is small

Reasonable similarity to experiment

Reasonable fit to PDDF
DECON: Under-fitting

Homogeneous Sphere?

No similarity to experiment

Bad fit
DECON: Check for Symmetry

When the symmetry is not correct, e.g., cylinders instead of spheres.

No similarity to experiment

Reasonable fit to PDDF