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Using the singular value decomposition to extract 2D correlation functions from scattering patterns

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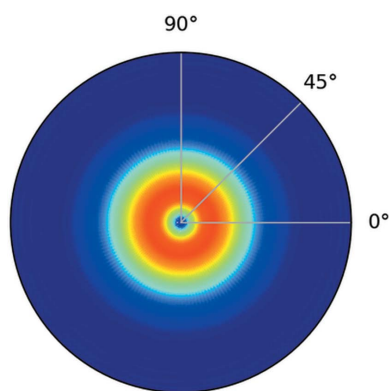
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The truncated singular value decomposition (TSVD) is applied to extract the underlying 2D correlation functions from small-angle scattering patterns. The approach is tested by transforming the simulated data of ellipsoidal particles and it is shown that also in the case of anisotropic patterns (*i.e.* aligned ellipsoids) the derived correlation functions correspond to the theoretically predicted profiles. Furthermore, the TSVD is used to analyze the small-angle X-ray scattering patterns of colloidal dispersions of hematite spindles and magnetotactic bacteria in the presence of magnetic fields, to verify that this approach can be applied to extract model-free the scattering profiles of anisotropic scatterers from noisy data.

1. Introduction

Small-angle scattering of X-rays (SAXS) or neutrons (SANS) is routinely used to investigate the structural properties of various materials, such as nanostructured bulk samples (Fritz-Popovski, 2013, 2015; Michels, 2014) or nanoparticle ensembles (Reufer *et al.*, 2010; Märkert *et al.*, 2011; Hoffelner *et al.*, 2015; Nack *et al.*, 2018). In many cases, the detected 2D scattering patterns $I(\mathbf{q})$ (here I is the scattering intensity and \mathbf{q} the scattering vector on the 2D detector plane) are isotropic and data analysis is performed on the 1D azimuthal average $I(q)$, by either fitting it in reciprocal space with model functions or by transforming $I(q)$ to real-space correlation functions $C(r)$ via Fourier transforms (FT) (Pedersen, 1997). For the latter, a direct FT can be used (Michels *et al.*, 2003) or, alternatively, an indirect FT (Glatter, 1977; Hansen, 2000; Bender *et al.*, 2017). Often the pair distance distribution function $P(r) = C(r)r^2$ is determined, which gives direct information about the average shape, size and structure of the scattering units (Glatter, 1979; Svergun & Koch, 2003). In the case of anisotropic nanostructures, the pattern $I(\mathbf{q})$ can be anisotropic, provided the nanostructures are preferentially aligned along a certain direction or texture axis (Heijden *et al.*, 2004; Reufer *et al.*, 2010; Märkert *et al.*, 2011; Fritz-Popovski, 2013; Hoffelner *et al.*, 2015; Nack *et al.*, 2018). Also, in this case, data analysis can be performed either by adjusting the whole scattering pattern in reciprocal space (Alves *et al.*, 2017) or by transforming the pattern *via* 2D FTs to the real-space 2D correlation functions (Fritz-Popovski, 2013, 2015; Mettus & Michels, 2015). For the indirect 2D FT proposed by Fritz-Popovski (2013), regularization functionals are appended to the system matrix, which is



necessary to obtain smooth profiles, but which can increase the computation times significantly. Here, we propose a similar but faster method, namely the truncated singular value decomposition (TSVD), to extract the underlying 2D correlation functions. We propose that this method could be used for live, model-free data analysis, *e.g.* in capillary flow devices (Nielsen *et al.*, 2012), time-resolved nanoparticle oscillation (Bender *et al.*, 2015) or rheo-SAXS/SANS experiments (Panine *et al.*, 2003; Calabrese *et al.*, 2016), and microfluidics (Stehle *et al.*, 2013; Poulos *et al.*, 2016; Adamo *et al.*, 2018), where the noise reduction of the singular value decomposition (SVD) helps to enhance the signal.

2. Methods

2.1. Singular value decomposition

In polar coordinates the 2D scattering intensity $I(q_y, q_z) = I(q, \Theta)$ (the beam is along the x direction, $\mathbf{k} \parallel \mathbf{e}_x$) is a function of the magnitude of the scattering vector $|\mathbf{q}|$ and the angle Θ . With $i = N$ unique data points (*i.e.* pixels of the detector for a monochromatic source) it can be written

$$I(q_i, \Theta_i) = \sum_{k=1}^K A_{ik} P(r_k, \varphi_k), \quad (1)$$

where the angle φ specifies the orientation of \mathbf{r} in real space in the yz plane. Here, the extracted 2D distribution function is $P(r, \varphi) = C(r, \varphi)r$ (Fritz-Popovski, 2013) and the matrix \mathbf{A} has the elements (Mettus & Michels, 2015)

$$A_{ik} = \cos[q_i r_k \cos(\Theta_i - \varphi_k)] \Delta r_k \Delta \varphi_k. \quad (2)$$

Here, we usually assume a linear spacing for the pre-determined r and φ vectors (*i.e.* Δr and $\Delta \varphi = \text{const.}$). By minimizing the deviation (*i.e.* performing a least-square fit)

$$\chi^2 = \sum_{i=1}^N \frac{[I(q_i, \Theta_i) - \sum_{k=1}^K A_{ik} P(r_k, \varphi_k)]^2}{\sigma_i^2} \quad (3)$$

the 2D correlation function $P(r, \varphi) = C(r, \varphi)r$ can be determined. In the case of significant measurement uncertainties σ_i , however, this distribution will exhibit strong, unphysical oscillations. While performing the indirect FT, regularization matrices are appended (*e.g.* a Tikhonov regularization can be applied) to force smooth distributions (Fritz-Popovski, 2013), and various approaches exist to estimate the optimal value for the regularization parameter (Glatter, 1977; Hansen, 2000).

With the SVD the decomposition of the system matrix $\mathbf{A} = \mathbf{U}\mathbf{S}\mathbf{V}^T$ is performed, where \mathbf{U} and \mathbf{V} are orthogonal $N \times N$ and $K \times K$ matrices, respectively, and \mathbf{S} is an $N \times K$

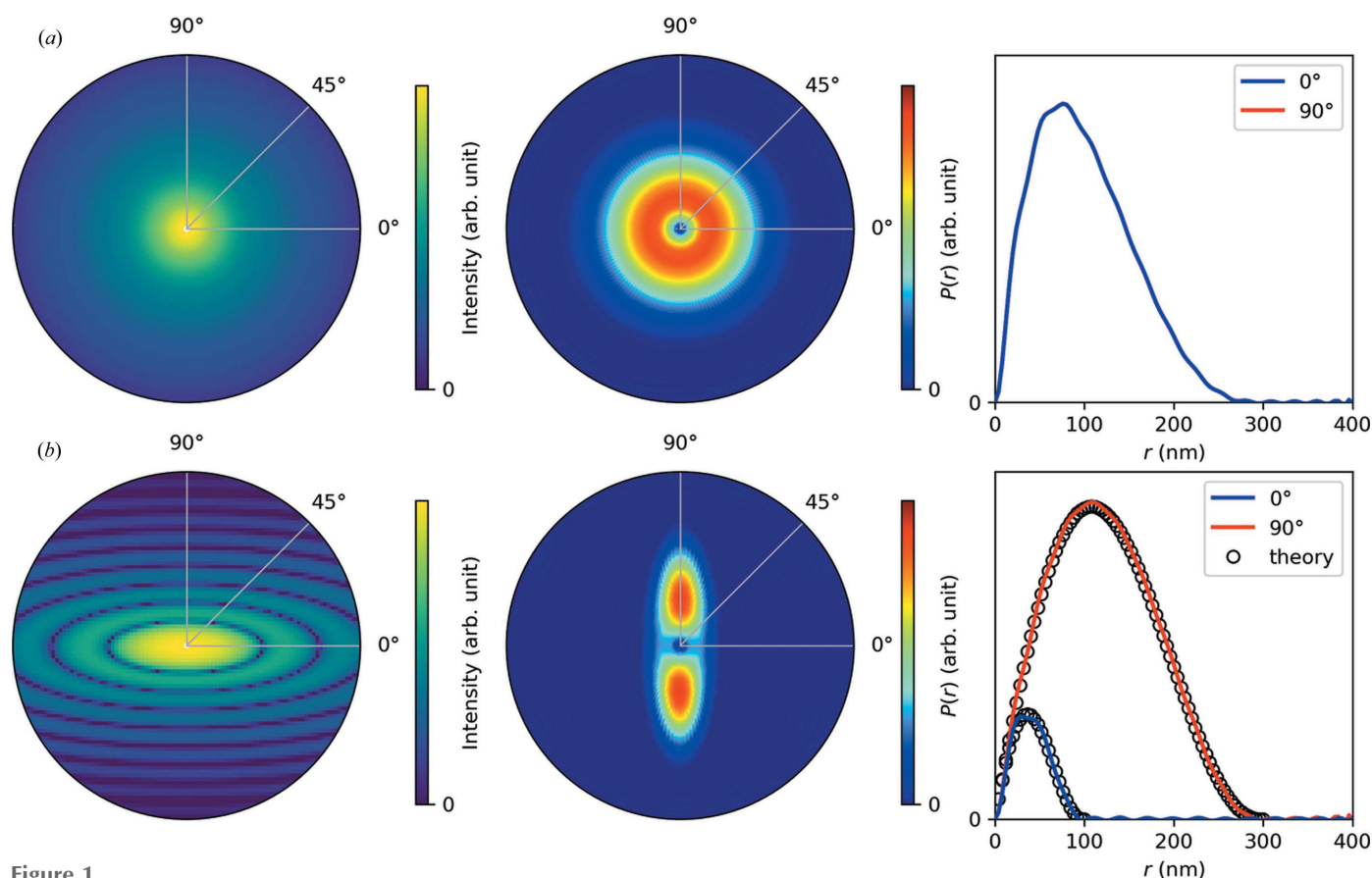


Figure 1

Determination of the 2D correlation functions by an SVD for a monodisperse ensemble of prolate rotational ellipsoids with an equatorial radius of 50 nm and a polar radius of 150 nm. (a) Ellipsoids are randomly oriented (isotropic ensemble). (b) Ellipsoids are aligned with their polar axis along $\Theta = 90^\circ$ (anisotropic ensemble). Left column: polar plot of the scattering pattern in logarithmic scale ($q_{\text{max}} = 0.2 \text{ nm}^{-1}$). Middle column: extracted 2D correlation function $P(r, \varphi)$ ($r_{\text{max}} = 400 \text{ nm}$). Right column: correlation function along $\varphi = 0^\circ$ and 90° , and in (b) additionally the calculated cross sections for spheres with diameters of 100 nm and 300 nm, respectively.

matrix whose main diagonal elements $s_i \equiv s_{ii}$ are the singular values (all other values are zeros). The solution $P(r, \varphi)$ of the functional $\mathbf{A}P(r, \varphi) = I(q, \Theta)$ is

$$P(r, \varphi) = \mathbf{V}\mathbf{S}^+\mathbf{U}^T I(q, \Theta), \quad (4)$$

where \mathbf{S}^+ has the reciprocal values $1/s_i$ in its diagonal, and otherwise zeros. Using the full-rank matrices for the reconstruction of $P(r, \varphi)$ according to equation (4) should result in the same distribution as minimizing equation (3). In particular, very small s_i values associated with noise result in strong oscillations of the reconstructed distribution. Thus, a smoothing of $P(r, \varphi)$ can be achieved by reducing the number of singular values s_i that are considered for \mathbf{S}^+ (Berkov *et al.*, 2000) (*i.e.* singular values which are smaller than a certain threshold are set to zero). Alternatively, a TSVD can be performed (Hansen, 1987; Viereck *et al.*, 2019), which further reduces the computation time compared with an SVD of the full-rank matrices.

We will use the TSVD to analyze first the simulated scattering patterns of an ensemble of prolate ellipsoids and later the measured SAXS patterns of a colloidal dispersion of hematite spindles and of magnetotactic bacteria.

2.2. Samples

Details regarding the synthesis and characterization of the hematite spindles can be found in the work of Zákutná *et al.* (2019). Hematite nanospindles are weakly ferromagnetic and known to orient with their main axis perpendicular to an applied magnetic field (Reufer *et al.*, 2010; Märkert *et al.*, 2011; Roeder *et al.*, 2015; Hoffelner *et al.*, 2015; Nack *et al.*, 2018). According to electron microscopy, the sample studied here has a length of the short spindle axes of around 56 nm and of the long axis of around 375 nm. The SAXS measurements from the work of Zákutná *et al.* (2019), which we also analyze here, were performed at the ID02 instrument at the ESRF (Narayanan *et al.*, 2018) on a dilute, *i.e.* non-interacting, dispersion of the nanospindles. A static homogeneous magnetic field up to 520 mT was applied with an electromagnet in the horizontal direction perpendicular to the incoming beam.

A detailed study of the magnetotactic bacteria is presented by Orue *et al.* (2018). These bacteria contain on average about 15–20 iron oxide nanoparticles with diameters of around 40–50 nm, which are typically arranged in nearly linear chains. Here we analyze a SAXS measurement of the same colloidal dispersion of bacteria as presented in the work of Orue *et al.* (2018). This measurement was performed with a Xenocs Nano-InXider. The colloidal dispersion was filled into a quartz glass capillary and the bacteria aligned perpendicular to the incoming beam by positioning a small permanent magnet next to the capillary. With this setup only one full quadrant of the pattern is detected, but assuming symmetry the total 2π pattern can be easily reconstructed.

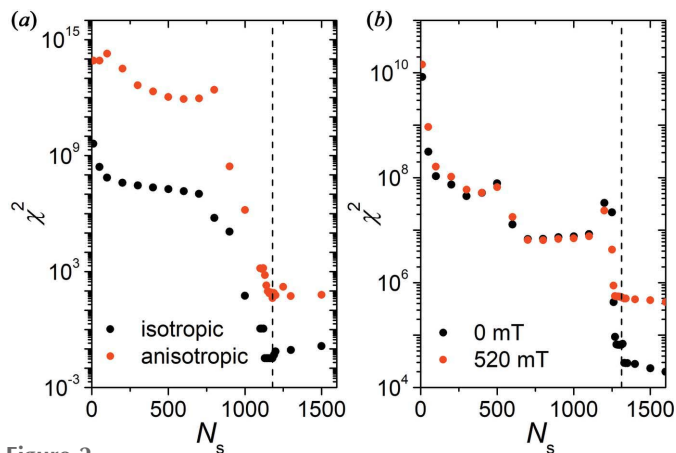


Figure 2
Error χ^2 [equation (3)] for the fit of (a) the simulated data (Fig. 1) and (b) the experimental data of the spindles (Fig. 3) at two different fields, with N_s being the number of singular values used for the reconstruction.

3. Results

3.1. Simulated data

To test the TSVD, we first analyze the calculated scattering patterns of rotational ellipsoids with an equatorial radius of 50 nm and a polar radius of 150 nm [left column in Figs. 1(a) and 1(b)]. In Fig. 1(a) (upper row) we analyze the isotropic ensemble and in Fig. 1(b) (lower row) the anisotropic ensemble. The simulated scattering patterns had $N = 30480$ data points, and we calculated the system matrix \mathbf{A} (30480×10224 matrix) for 101 r values (0–400 nm, 4 nm steps) and 144 φ values ($2.5\text{--}360^\circ$, 2.5° steps). We then varied the number of singular values N_s considered for the reconstruction. Usually, N_s is much smaller than the dimensions of the system matrix, and thus the TSVD significantly reduces the computational complexity compared for example with the classical indirect FT (IFT) approaches. As shown in Fig. 2(a), the total error χ^2 is significantly reduced by increasing N_s and exhibits a minimum at around $N_s = 1180$, which is marked by the dashed line [here we used $\sigma_i^2 = I(q_i, \Theta_i)$ for the calculation of χ^2 , equation (3)]. Further increasing N_s does not further minimize the deviations, but will generate strong oscillations due to the restricted q range (Qiu *et al.*, 2004). In Fig. 1 we plot the reconstructed distributions for $N_s = 1180$, and in the case of the anisotropic ensemble compare them with the theoretically expected profiles $C(r)r$ (Fritz-Popovski, 2015), which we calculated for spheres with diameters of 100 nm and 300 nm, respectively. The good agreement shows that the TSVD can be readily used for a fast determination of the underlying 2D correlation functions from 2D scattering patterns, at least in the case of smooth data.

3.2. Experimental data

3.2.1. Hematite spindles. In Fig. 3 we show the analysis results of the field-dependent scattering patterns of the colloidal dispersion of hematite spindles. In the upper row [Fig. 3(a)] we display the results for 0 mT and in the lower row [Fig. 3(b)] the results for $\mu_0 H = 520$ mT. For both, the isotropic and the anisotropic pattern, the SVD was performed

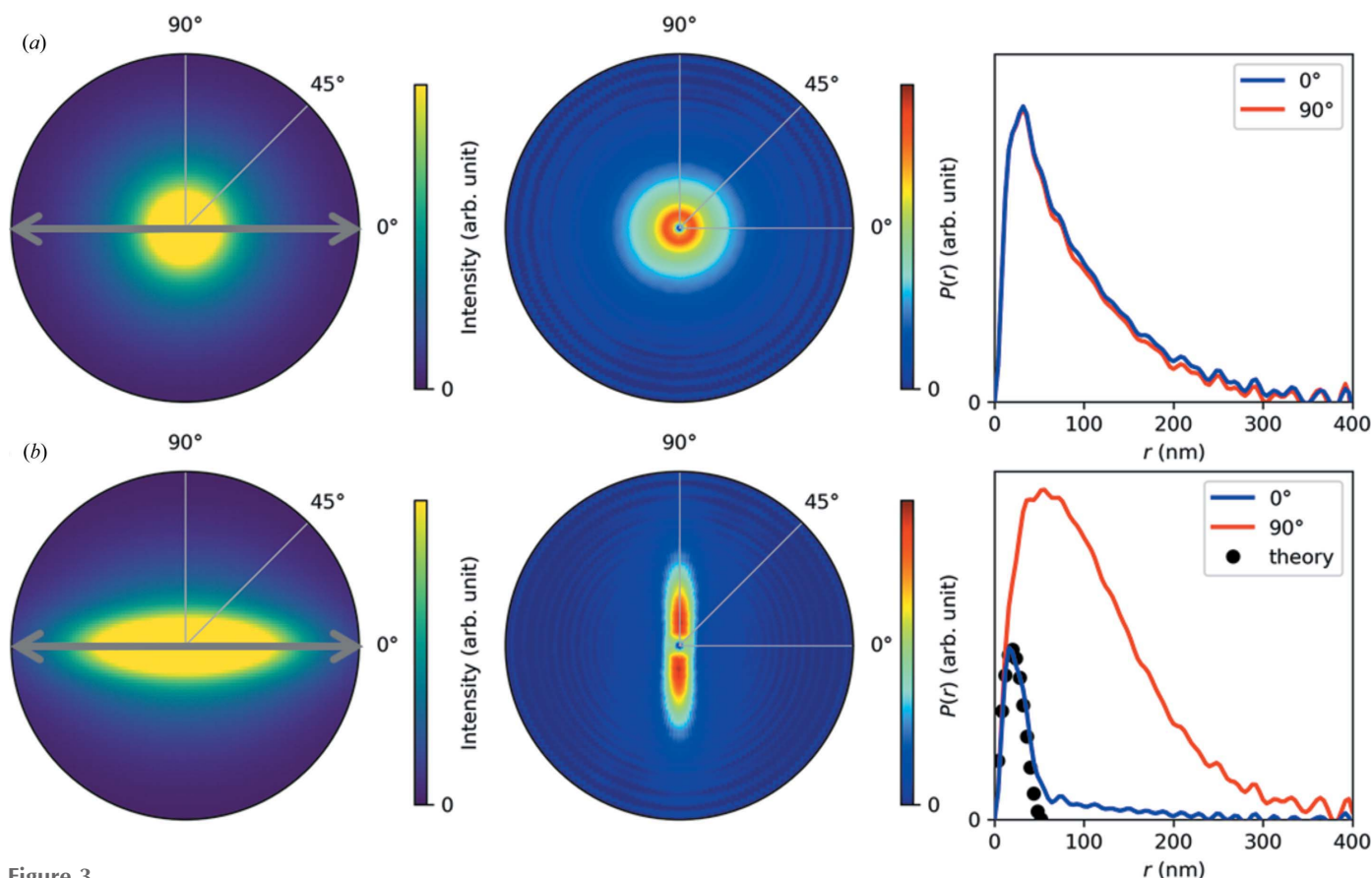


Figure 3

Analysis of the 2D SAXS patterns of the colloidal dispersion of hematite spindles; the magnetic field was applied in the horizontal direction ($\Theta = 0^\circ$) with a field strength of (a) 0 mT and (b) 520 mT. Left column: polar plot of the scattering pattern in logarithmic scale ($q_{\max} = 0.1 \text{ nm}^{-1}$). Middle column: extracted 2D correlation function $P(r, \varphi)$ ($r_{\max} = 400 \text{ nm}$). Right column: correlation function along $\varphi = 0^\circ$ and 90° , and the theoretically expected cross sections for a sphere with a diameter of 56 nm (black dots).

for 101 r values (0–400 nm) and 144 φ values ($2.5\text{--}360^\circ$, 2.5° steps). The correlation functions plotted in Fig. 3 were determined for $N_s = 1270$, for which the total error was already close to the minimum [Fig. 2(b)]. For both cases the extracted correlation functions exhibit some oscillations, which increases significantly with increasing N_s (i.e. smaller singular values are associated with signal noise).

At 0 mT, the anisotropic particles are randomly oriented within the viscous matrix (water), and thus the scattering pattern and the derived correlation function are both isotropic. The extracted profile has a pronounced peak at around 50 nm and a long tail, and hence corresponds well to the expected profile of randomly oriented, shape-anisotropic nanoparticles (Svergun & Koch, 2003).

At 520 mT, on the other hand, the particle moments are mostly oriented in the field direction. The dominance of the magnetocrystalline anisotropy leads to a net magnetic moment in the basal plane of the hematite spindles, i.e. perpendicular to the long particle axis (Reufer *et al.*, 2010; Hoffelner *et al.*, 2015; Nack *et al.*, 2018). Therefore, the long spindle axes are oriented within the plane perpendicular to the field direction, which explains the anisotropy of both the scattering pattern and the extracted correlation function. Along $\varphi = 90^\circ$ [right column of Fig. 3(b)] the profile indicates a

maximum length of the spindles of around 400 nm, whereas the profile along $\varphi = 0^\circ$ agrees well with the expected correlation function for spindles with an equatorial diameter of 56 nm. Thus, the extracted 2D correlation function is in good agreement with our previous results (Zákušná *et al.*, 2019).

3.2.2. Magnetotactic bacteria. In Fig. 4 we show the highly anisotropic SAXS pattern of the aligned magnetotactic bacteria along the horizontal field direction. The extracted correlation function was determined, as before, for 101 r values (0–200 nm) and 144 φ values ($2.5\text{--}360^\circ$, 2.5° steps). The function plotted in Fig. 4 was determined for $N_s = 1000$, which shows that the particles are preferentially spheres (radially symmetric spots), and that the bacteria and thus the magnetosome chains are well aligned along the applied field showing no spreading of the spots in the azimuthal direction. From the profile along $\varphi = 0^\circ$ (right column of Fig. 4) we can estimate the average center-to-center distance between the particles in the chain from the peak-to-peak distance to be around 50 nm and the particle size from the peak width to be around 40 nm, which agrees well with previous results (Orue *et al.*, 2018). Along $\varphi = 90^\circ$ we only see the cross section of a single particle. However, for $r > 40 \text{ nm}$ the profile oscillates around zero. This indicates a variation of the scattering length density profile, which we attribute to a lower scattering length

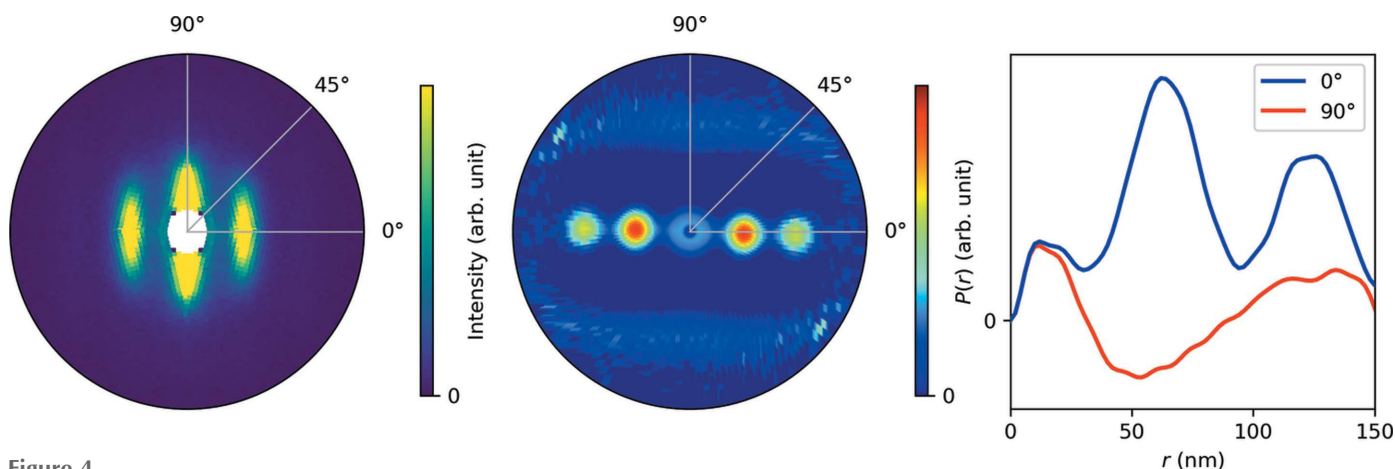


Figure 4 Analysis of the 2D SAXS pattern of the colloidal dispersion of magnetotactic bacteria; the magnetic field was applied in the horizontal direction ($\Theta = 0^\circ$). Left column: polar plot of the scattering pattern in logarithmic scale ($q_{\max} = 0.5 \text{ nm}^{-1}$). Middle column: extracted 2D correlation function $P(r, \varphi)$ ($r_{\max} = 150 \text{ nm}$). Right column: correlation function along $\varphi = 0^\circ$ and 90° .

density in the vicinity of the particle (*i.e.* the bacteria) compared with the surrounding matrix (*i.e.* the water).

4. Conclusions

Here, we introduce the truncated singular value decomposition (TSVD) to extract the denoised 2D correlation functions from small-angle scattering patterns. First, we analyze simulated data of ellipsoidal particles and show that the derived correlation functions correspond well to the theoretically predicted profiles. Furthermore, we use this method to successfully extract the underlying 2D correlation functions from experimental SAXS patterns of colloidal dispersions of hematite spindles and magnetotactic bacteria. We emphasize that this method is a fast and easy way to obtain model-free information about the structural properties of anisotropic scatterers, which we propose for example for the analysis of live data.

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