



	<b>Experiment title:</b> <b>Crystallisation in colloid/polymer suspensions</b>	<b>Experiment number:</b> <b>26-02-77</b>
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## Report:

Following our previous studies (experiment 26-02-36), we have performed a small-angle x-ray diffraction study of crystals grown in sediments of sterically stabilised (covered by a 2 nm thick hydrocarbon layer) hard-sphere silica colloids. The growth is assisted by a non-absorbing polymer (PDMS, 14 nm radius of gyration), which is observed to accelerate crystallisation and give large high-quality crystals. The diameter of the silica core is determined from SAXS pattern of a dilute suspension (the form factor) to be 224 nm. A detailed crystallographic analysis is performed by measuring SAXS diffraction patterns at various orientations of the sample. The key issue addressed in this study is the characterisation of various order parameters of the crystals.

In figure 1(a,b) examples of observed diffraction patterns are given. The predominantly hexagonal features of the pattern are a consequence of (Fourier transformed) hexagonally packed planes of spheres within the crystal normal to the beam. Panel (b) illustrates the extreme sensitivity of the diffraction pattern to the sample orientation (rotations by less than  $0.1^\circ$  can be easily detected). We observed that the pattern does not change noticeably upon translating the sample vertically and horizontally indicating a very high degree of orientational order within this single crystal area of the size  $0.5 \times 0.2 \times 2 \text{ mm}^3$ , surrounded by crystals with other orientations. Thus, a high degree (within  $0.1^\circ$ ) of orientational correlation on sub-millimetre distances is observed, suggesting extreme flatness (within a couple of sphere diameters across the crystal) and rigidity of hexagonal planes.

The spatial scale over which the positional order is kept by the crystal translates into the (reversed) width of the reflections. However, its determination is a challenging problem for SAXS as it requires extremely high resolution in the reciprocal space in comparison to the wavevector of the x-ray beam. However, it can be done in the single-crystal diffraction mode from the pattern shown in panel (b). The scattering vector  $\mathbf{q} = \mathbf{k}_s - \mathbf{k}_0$  must lie on the so-called Ewald sphere [1] since the wavevectors,  $\mathbf{k}_0$  and  $\mathbf{k}_s$ , of the incident and scattered waves have the same length of  $2\pi/\lambda$  as schematically illustrated in Figure 1(c). Diffraction is only observed whenever the Ewald sphere crosses the reciprocal lattice. In our studies the scattering angles  $2\theta$  between  $\mathbf{k}_s$  and  $\mathbf{k}_0$  are smaller than 10 mrad and the corresponding part of the Ewald sphere is nearly planar. However, its curvature clearly reveals itself in the diffraction pattern shown in Figure 2(b), leading to a strongly asymmetric pattern with much brighter diffraction peaks in the bottom part of the detector. For the tilted sample the Ewald sphere intersects the reciprocal lattice plane along a circle, which is marked in panel (b) by the dotted line. The centre of this circle is at  $2\theta = \xi$ , where the Ewald sphere deviates from the plane by as little as  $\Delta = (1 - \cos\xi) k_0 = 6 \cdot 10^{-6} k_0$ . However, the intensity of the diffraction spots here is very much reduced due to the mismatch suggesting that the reciprocal lattice spots are much smaller than  $\Delta$ .

To quantify the size  $\delta q$  of the reciprocal lattice spots we show in Figure 2(d) the profile of the structure factor (obtained after dividing out the form factor) along a line of diffraction peaks. Two very strong reflections (denoted 3 and -3) are closest to the Ewald sphere for this sample orientation as can be seen from a simple geometrical construction. For the neighbouring reflections  $\pm 2$  and  $\pm 4$  the mismatch from the Ewald sphere amounts to  $2 \cdot 10^{-6} k_0$  and  $3 \cdot 10^{-6} k_0$ , respectively. They are seen to be weaker than the brightest  $\pm 3$  reflections by at least one order of magnitude indicating that the width of the reciprocal lattice spots  $\delta q$  is smaller than  $10^{-6} k_0$ . A similar estimate of  $\delta q$  is obtained by measuring the rocking curve, i.e. the dependence of the intensity of particular reflections on the sample orientation. The inverse of this width  $1/(2\delta q)$  translates into a positional correlation between more than 500 crystal layers along the beam. We thus find high positional order, possibly ranging from wall to wall (the capillary width of 0.2 mm would allow to accommodate 1000 layers parallel to the walls). This remarkably accurate determination of the spot width is only possible due to the high longitudinal coherence of the beam (at such small angles over 1 mm!). Unfortunately, a much smaller transverse coherence and the detector resolution preclude a similar determination of the in-plane correlations by looking directly at

the spot size of the diffraction patterns. Combining the results of high orientational and interplanar positional order, however, suggests a high in-plane positional order as well.

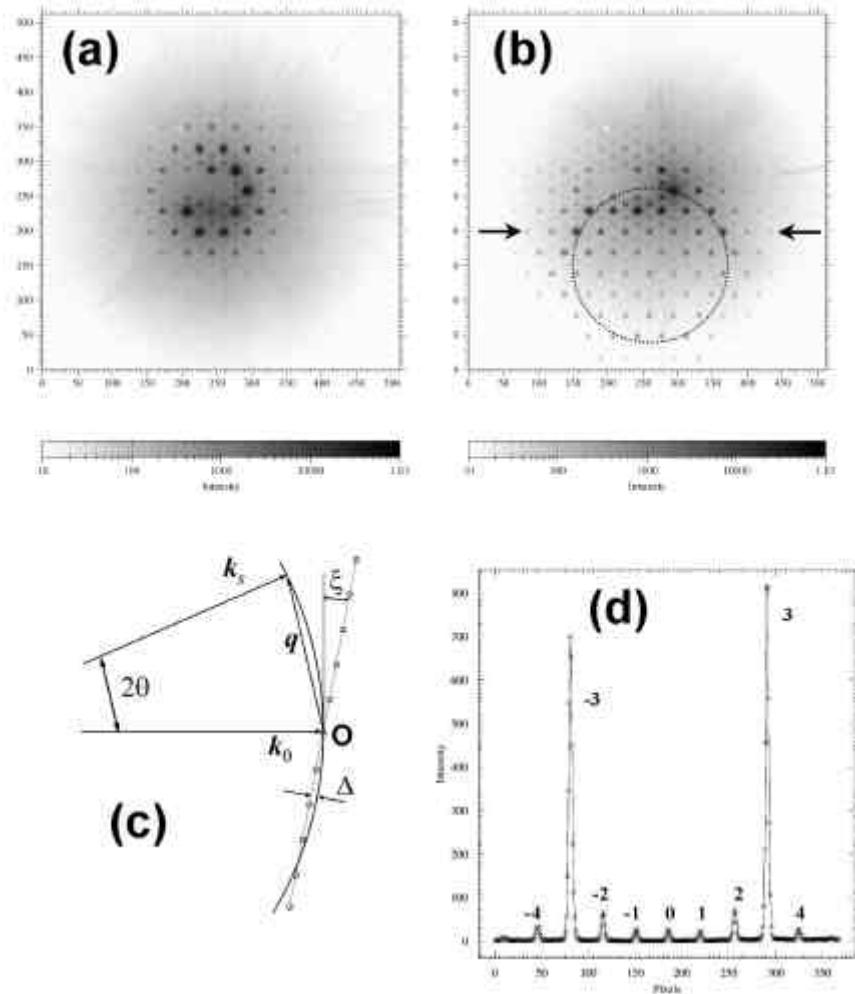


Figure 1. (a) Diffraction pattern of a sample mounted on a goniometer head, which allows for careful orientation around three orthogonal axes. The sample is illuminated by a 10 keV X-ray beam (wavelength  $\lambda = 1.24 \text{ \AA}$ , band pass  $\Delta\lambda/\lambda = 2 \cdot 10^{-4}$ , size  $0.1 \times 0.1 \text{ mm}^2$  at the sample). Scattering is registered at 8 metres distance by a two-dimensional ( $512 \times 512$  pixels) gas-filled detector. (b) Diffraction pattern measured after rotating the sample around the horizontal axis by  $\xi = 0.2^\circ$ . (c) Intersection of the Ewald sphere through a set of reflections in reciprocal space for a tilted sample. O denotes the origin of the reciprocal space. The curvature of the Ewald sphere is greatly enhanced for clarity. (d) Structure factor profile along the stripe indicated by arrows in panel (b).

In addition to the orientational and positional order we have characterised the stacking of consecutive hexagonal planes. In agreement with our previous study (experiment 26-02-36), for one year older crystals the stacking is found to be random with the probability  $\alpha = 0.55 \pm 0.05$  of finding an fcc (ABC) stacking sequence.

To summarise, the accurate characterisation of various order parameters in hard-sphere colloidal crystals achieved here with high-resolution single-crystal SAXS demonstrates the great potential of this technique. The measurements clearly reveal that the inherent size polydispersity of colloids does not prevent the formation of high-quality large single crystals possessing long-range orientational and positional order. Theory predicts [2] that for monodisperse hard spheres the face-centred cubic structure is the most stable. However, our results show that the stacking stays disordered over more than a year and may be caused by the polydispersity. It is interesting to note that the structure displayed by our hard-sphere crystals distinctly differs from the structure of charge-stabilised colloidal crystals [3], which display a mosaic structure with high degree of stacking order but low positional correlation.

## References

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