ESRF	**Experiment title:** **Crystallisation dynamics of hard-sphere colloids/polymer suspensions**	**Experiment number**: 26-02-90
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Report:

Our previous studies have shown that hard-sphere silica colloids are able to form large high-quality single crystals in the presence of nonadsorbing polymer. We have also obtained several indications that these crystals possess a randomly-stacked hexagonal close packed (rhcp) structure. The randomly stacked crystals possess a unique property, namely that interplanar periodicity is absent, while long-range positional correlation persists over the whole crystal. In a sense, the rhcp crystals are in between ordinary crystals with full three-dimensional periodicity, and liquid crystals lacking both true periodicity and positional order in at least one direction. Due to the absence of true interplanar periodicity, the reciprocal lattice of rhcp crystals possesses scattering rods, which are oriented normal to the hexagonal planes, as depicted in Fig. 1a. The scattering intensity along the rods is continuously varying and its profile is very sensitive to the probability α of finding an fcc sequence among three subsequent layers. However, since there are only three possible lateral positions of the hexagonal planes, some of the reciprocal lattice reflections are stacking-independent and remain sharp. Here the reciprocal lattice reflections of the fcc and hcp crystals coincide.

We have performed synchrotron small-angle X-ray diffraction experiments at the BM26 "DUBBLE" beam line with colloidal silica spheres of 224 nm diameter (as determined from the form factor), which are covered with 2 nm thin hydrocarbon layers to prevent their agglomeration in solvent cyclohexane. This system is known to behave as hard spheres. The crystals grow in the sediment within one to two weeks after sedimentation in flat glass capillaries with internal sizes of $0.2\times4\times100$ mm^3. A monochromatic beam (wavelength λ = 1.24 Å, spectral width $\Delta\lambda/\lambda = 2\ 10^{-4}$) has a size of about 0.1×0.1 mm^2 at the sample. Diffraction is registered at 8 metres distance by a 512×512 two-dimensional gas-filled detector.

In a small-angle X-ray diffraction experiment the diffraction vector is practically normal to the incident X-ray beam and the diffraction pattern brings information about the crystal structure in the directions normal to the beam. Thus, for a most direct way to study the interplanar order in the crystals using the diffraction

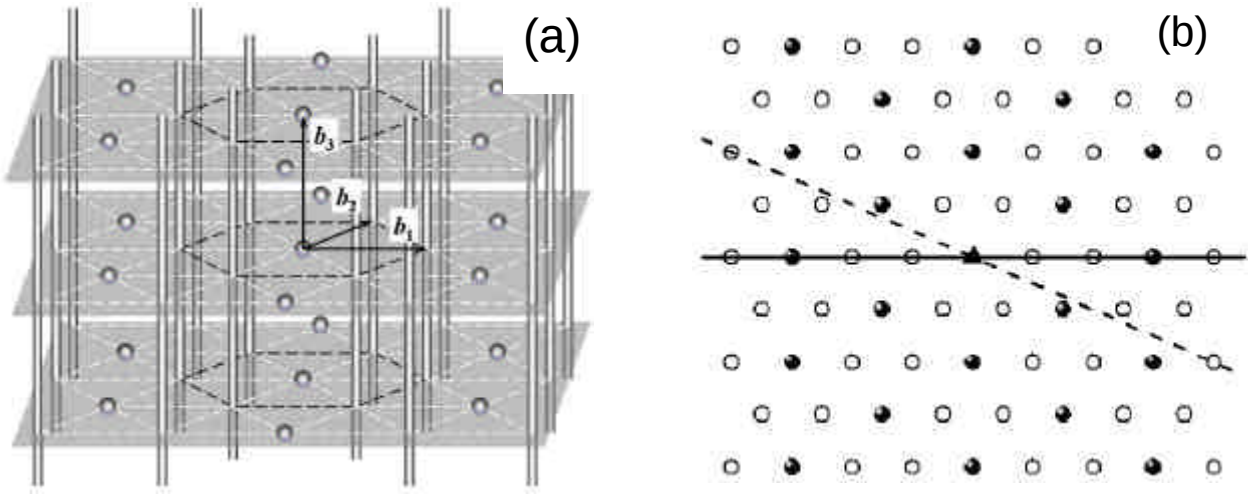

Figure 1. (a) Sketch of the reciprocal lattice of randomly stacked hexagonal close packed crystals. (b) Top view of the reciprocal lattice illustrating the orientation of the Ewald sphere in Fig. 2 (solid line) and Fig. 3 (dashed). The closed symbols correspond to lines of localised reflections (spots) while open symbols display the position of rods. The triangle marks the line of spots going through the origin of the reciprocal space.

technique, one has to fulfil two conditions. First of all, the incident X-ray beam must be parallel to the hexagonal planes in the crystal. In our flat capillaries one can find crystals with different orientations of hexagonal planes. This variety of orientations suggests that the crystals were not nucleated at the glass wall but rather at the top interface of the concentrated sediment. We have chosen a crystal with hexagonal planes making an angle of about 60 degrees with respect to the capillary wall. This enables us to send the incoming X-ray beam parallel to the crystal planes without having a too strong absorption. Secondly, the in-plane direction of propagation of the incident X-ray beam should also be tuned to one of the low-index in-plane directions.

Careful orientation of the sample leads to a diffraction pattern as the one shown in figure 2. The X-ray scattering is observed on the detector within a wide q-range along many lines, which originate from the scattering rods of the reciprocal lattice and (each third line) from the localised spots of Fig. 1a. However, the distinction between them is not very pronounced. Some scattering is also observed between the spots. We

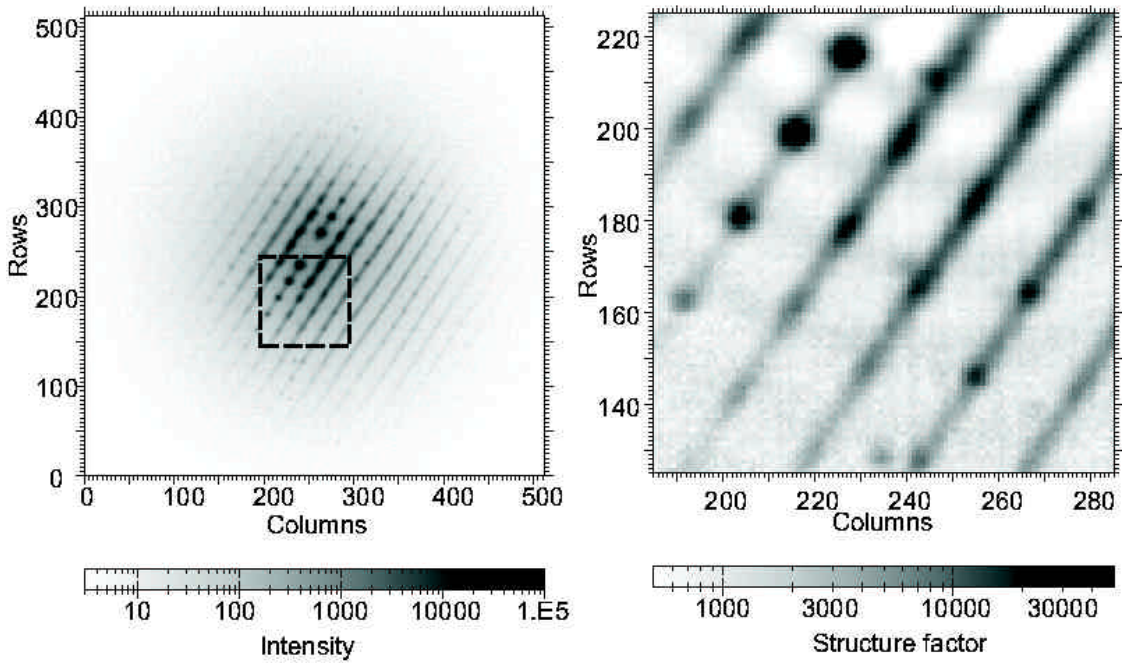

Figure 2. (left) Raw diffraction pattern $I(\boldsymbol{q})$ measured for the crystal orientation illustrated by the solid line in Fig.1b. The straight beam is absorbed by a small beam stop in the middle of the detector. (right) Magnified view of the structure factor $S(\boldsymbol{q})$ profile within the area marked on the left panel.

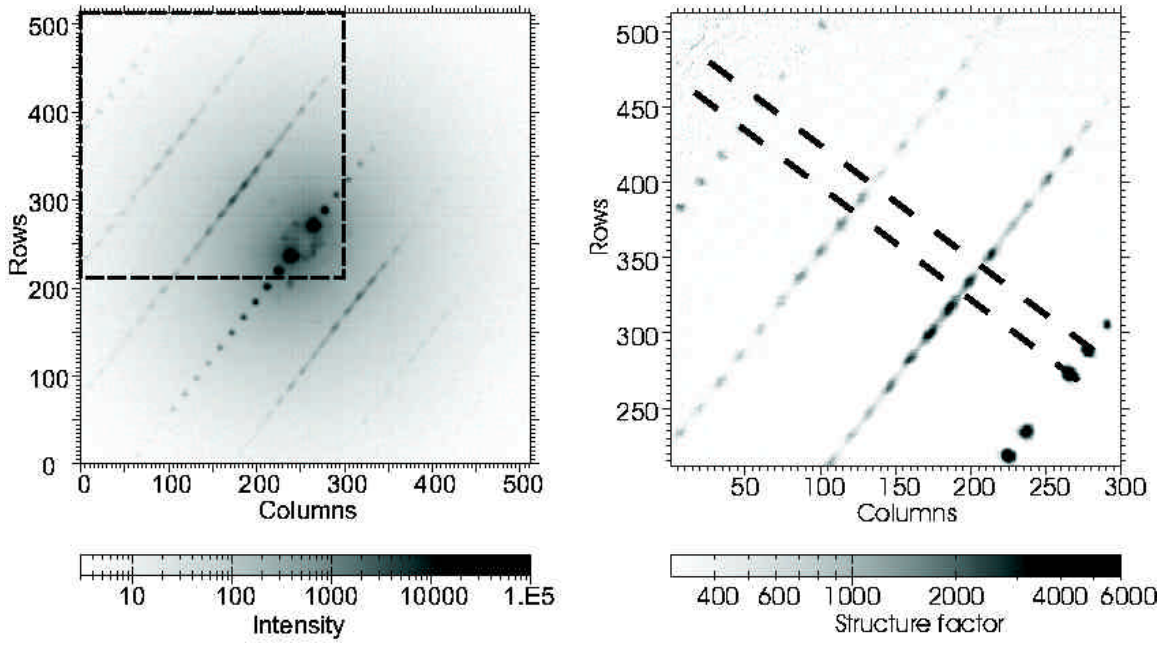

Figure 3. The same as in Fig. 2 but for another crystal orientation. The dashed lines in the right panel display the position of the shadowed planes of Fig. 1a.

assign this effect to multiple scattering: the incoming X-ray wave can be first scattered into a rod and then be re-scattered again. Note that these multiple scattering events always lead to scattering along the same lines on the detector, which are equally spaced.

To reduce the effect of multiple scattering, a new crystal orientation has been chosen. The incident X-ray beam is again parallel to the hexagonal planes of the crystal but the Ewald sphere intersects the reciprocal lattice differently, as sketched in figure 1a by the dashed line. In this case the Ewald sphere misses many rods of low order but does cross a few of them at larger diffraction vectors $\boldsymbol{q}$. The scattering into the rods is then very much weaker, mainly due to the rapid decay of the form factor $F(q)$ of spherical particles. The probability of multiple scattering via scattering rods is very much reduced and the lines of diffraction spots are clearly visualised and free of the scattering between them.

The scattering rods in Fig. 3 are seen to be distinctly different from the lines of spots. The diffraction intensity here is smoothly varying along the rod and displays a periodic modulation. At the points where the rods cross the imaginary shadowed planes of figure 1, the structure factor $S(\mathbf{q})$ possesses minima while broad maxima appear in between them. This profile of the structure factor along the rod is typical for a random-stacking crystal with stacking parameter $\alpha \approx 0.5$. Simulations show that for $\alpha < 0.4$ the maxima are narrower and new maxima develop on the rods where they cross the shadowed planes of Fig. 1a. For $\alpha > 0.6$ the broad maxima split into two.

In addition to the careful analysis of the stacking order, which is described above, we have performed several other experiments. We did try to address the crystallisation dynamics of our colloidal hard spheres but a too short beam time granted for this experiment (9 shifts instead of 15) did not allow to completely fulfil this task. Instead, we have succeeded to perform a preliminary experiment on the dynamics of the structure modification during a ‘reverse’ transition induced by sample drying. This study is of importance since dried crystals possessing higher contrast are more suitable for photonic applications. The enormous pressure applied to the crystal by the capillary force is found to break the single crystal into smaller crystallites. This experiment with more detailed analysis was repeated in our recent session (26-02-111) in March 2002 and the results will be described in more detail in a forthcoming report.