DUBBLE	**Experiment title: Depletion-assisted wall crystallisation of colloidal hard spheres for photonic applications**	**Experiment number**: **26-02-138**
Beamline: BM-26 "DUBBLE"	**Date(s) of experiment**: From: 07-10-2002 To: 10-10-2002	**Date of report**: 19 - 10 -2002
Shifts: 9	**Local contact(s)**: Igor Dolbnya	

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Samples. One of the series of samples was prepared as illustrated in Fig.1. A flat glass platelet (with thickness of 0.22 mm, covered with stearyl alcohol) was inserted vertically into a glass vial with a colloid-polymer mixture. To avoid evaporation of cyclohexane, the vial was fixed at the bottom of a larger sealed bottle containing pure cyclohexane. In the samples with optimal polymer concentration (in our case ~ 0.2 volume fraction of polymer penetrable random coils) one could see very strong green Bragg reflections of light from the platelets as shown in Fig.1 after a couple of days. Since in this case the *in situ* structure evaluation with x-rays was impossible (too thick glass walls), these platelets were dried and investigated *ex situ*. Another series of samples was prepared in flat glass capillaries (internal pathlength and wall thickness of about 0.2 mm). The inner surface of the capillaries was also treated with stearyl alcohol to avoid any interaction with colloidal particles or polymer molecules at any distance beyond their direct contact. These samples were subjected to x-rays at DUBBLE for *in situ* study of the crystal structure. The second series is very important for our study since the dried samples have experienced huge capillary forces, which may have affected the structure. In contrast, in the *in situ* study only the entropy-induced depletion forces are governing the structure.

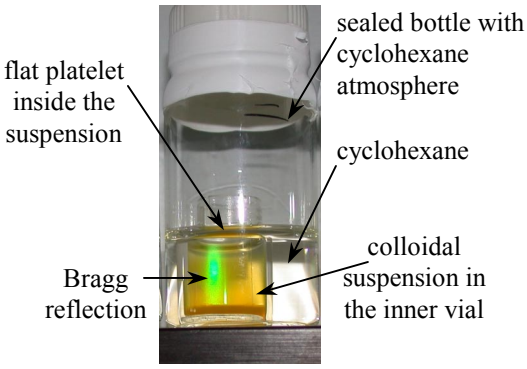

Fig. 1(**colour**). Green Bragg reflections of light from a depletion-induced colloidal crystal on a flat wall inside the

X-ray diffraction set-up. Diffraction of a 12.38 keV x-ray beam (wavelength $\lambda = 0.1$ nm, beam size of about 0.1×0.1 mm^2 at the sample) was registered at 8 meters distance by a two-dimensional gas-filled detector. The samples were mounted on a computer-controlled goniometer allowing for rotations around two axes orthogonal to the beam.

Results. In Fig.2 we show diffraction patterns measured *in situ* at three different positions in a flat capillary. The left pattern clearly originates from a large enough (≥ beam size) single crystal. In the central pattern the x-ray beam hits a few domains while the right picture is produced by many domains forming a 2D texture. The hexagonal planes in these domains are parallel to the flat substrate while their azimuthal orientations are different.

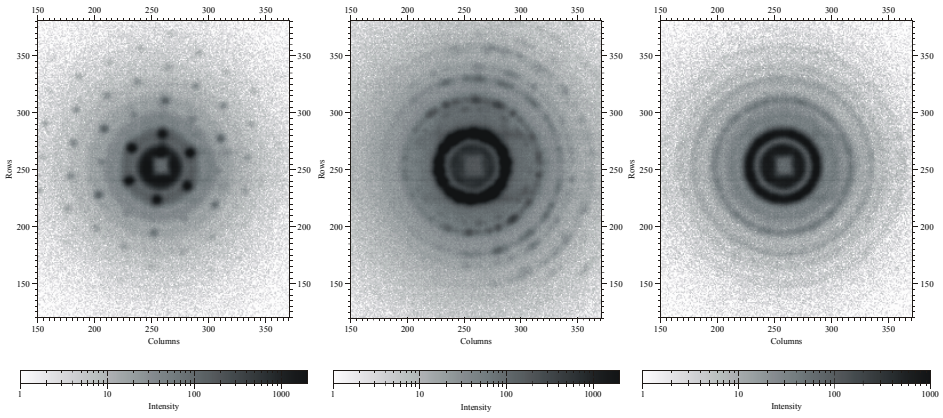

Fig.2 Diffraction patterns from depletion-induced crystals at the wall of a flat capillary at three different positions.

The intrinsic reciprocal lattice of a close-packed crystal is schematically depicted in Fig.3. The diffraction is observed at wave vectors $\boldsymbol{q} = h\,\boldsymbol{b}_1 + k\,\boldsymbol{b}_2 + l\,\boldsymbol{b}_3$, where h and k must be integers due to in-plane periodicity. For $(h - k)$ divisible by 3 the reflection does not depend on the stacking order and is only observed at integer values of l. For $(h - k)$ not divisible by 3 the diffraction intensity is continuously distributed along the $\boldsymbol{b}_3$ vector in random-stacking hexagonal close-packed (rhcp) crystals leading to the so-called Bragg scattering rods [1,2]. The reciprocal lattice of the 2D texture can be obtained from the single-crystal lattice by performing radial smearing around the axis normal to the substrate surface (vertical axis in Fig.3). Sharp stacking-independent Bragg reflections then lead to Bragg circles while the Bragg rods end up in Bragg cylinders. In Fig.3 we illustrate that by showing the (111), (110) and (11-1) Bragg circles and the (10l) Bragg cylinder. Only the (00l) reflections remain localised. The optical green Bragg reflection in the photo of Fig.1 is caused by the sharp (001) node of the reciprocal lattice.

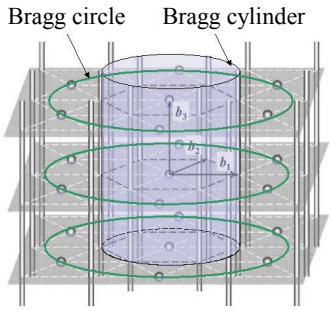

Fig.3. Reciprocal lattice of close-packed 2D texture at a flat wall.

Fig.4 presents the diffraction pattern obtained *ex situ* with the x-ray beam (nearly) normal to the surface of dried glass plate with 2D texture. At this orientation the Ewald sphere is close to the $l = 0$ plane of the reciprocal lattice. Many sharp rings are clearly visible and most of them originate from the Bragg circles. The (300) circle is missing since it falls into the minimum of the form factor $P(\boldsymbol{q})$. The closely-spaced (520) and (600) circles are not resolved from each other and lead to a slightly thicker ring on the detector. Because the structure factor in the Bragg cylinders has a minimum at $l \approx 0$, only the low-order (10l) and (21l) Bragg cylinders with the largest $P(\boldsymbol{q})$ are visible. The (20l) cylinder is too close to the strong (110) circle and is not resolved.

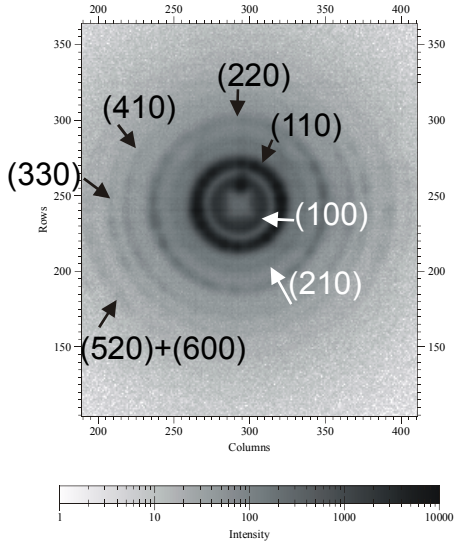

Fig.4. Diffraction pattern from a dried 2D texture on a glass substrate. Assignments to the Bragg circles are shown in black while the white arrows label rings originating from the Bragg cylinders.

Rotating the sample allows for a different intersection of the reciprocal lattice by the Ewald sphere. Both panels of Fig.5 present the same diffraction pattern measured after rotating the sample by 19.5° around the vertical axis. The Ewald sphere crosses through the $l = 0, \pm 1$ planes along the vertical lines labelled in the left panel. Sharp features, which are visible along those lines, originate from the Bragg circles crossing the Ewald sphere. Their assignment is shown in the right panel. At this angle the Ewald sphere only touches the (301) circle, leading to a 'stripe' on the detector. The form factor $P(\boldsymbol{q})$ of this circle is much higher than the one of the (300) circle because of a slightly longer wavevector. On the other hand, the intersection with the (411) circle is invisible since it falls into another minimum of $P(\boldsymbol{q})$. Much broader features can also be seen where the Ewald sphere crosses the semi-integer values of $l = \pm ½$. These features are induced by the broad maxima in the structure factor along the Bragg rods, which are typical for rhcp crystals with the stacking probability $\alpha \approx 0.5$ [1,2]. Assignment of some of them is also given in the right panel.

To summarise, we have performed a detailed structural characterisation of photonic colloidal crystals formed on flat substrates due to the entropy-driven depletion interactions in colloid-polymer mixtures. The crystals are found to consist of randomly stacked hexagonal planes parallel to the substrate. The size of single crystalline domains significantly varies; it can be larger or much smaller than the beam size ≈100 microns. Unfortunately, the too poor resolution of the gas-filled detector does not allow for a more precise evaluation of the size of the domains along the substrate from the width of the reflections. However, we did measure the width of the reflections in the longitudinal direction (along the beam) [1], which allows for evaluation of the thickness of the crystalline layer on the substrate (detailed analysis is in progress).

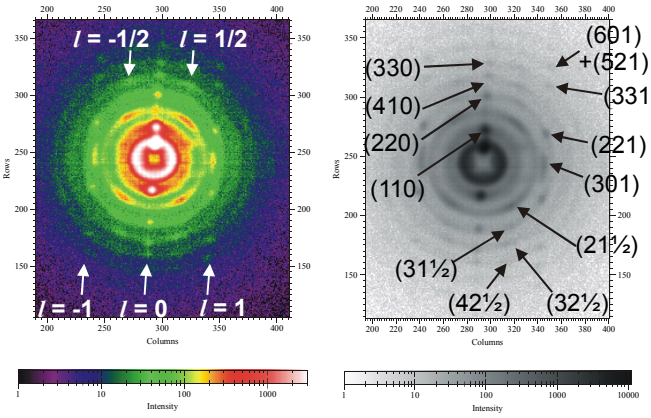

Fig.5. Diffraction pattern in colour and grey scale obtained from a dried 2D texture on a glass substrate after rotating by 19.5°. See text for further details.

[1] A.V.Petukhov *et al*., Phys. Rev. Lett., 208301 (2002).
[2] A.V.Petukhov *et al*., submitted; reports of experiments 26-02-90; 26-02-101.