ESRF

Experiment title:
The Structure of Photonic Colloidal Crystals

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SC- 165

Beamline:
BL4/ID2

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Report:

On January 24-28, 1996, we have done a small angle x-ray scattering (SAXS) study of colloidal crystals with lattice parameters on the order of optical wavelengths. Our research interest is to use these crystals as nanostructured materials, especially for so-called photonic crystals [1], hence they are optically as multiply scattering as possible. Our main results are i) we have managed to do SAXS on a single crystal, ii) we have succeeded in resolving the crystal structure of dense charge stabilized crystals, iii) the data from our experiments have proven to be essential for the interpretation of our optical experiments, and iv) the form factors of the particles reveal a wealth of information on the internal structure of the colloids. Thus, synchrotrons SAXS turns out to be a very powerful tool to study colloids, even at optical length scales.

Before describing the results, we stress the necessity for using synchrotrons SAXS on BL4/ID2: Optical techniques probe too little reciprocal space to determine the structure of the crystals. Moreover, the large optical multiple scattering effects seriously impede structure determination [2]. The high brilliance of BL4/ID2 allows to study samples that are weakly scattering, e.g. the ubiquitous system of latex particles suspended in water. The narrow focus of the beam allows us to for the first time study single crystals, while maintaining sufficient signal. Note that this is an important advantage over small angle neutron scattering.

We now summarize our results, that are described in papers in the international scientific literature [3-6], and that have been presented on major international conferences [8].

i) We have grown crystals large enough to be probed individually by the X-ray beam. By using a 2D detector and rotating the samples, we have been able to literally sweep through reciprocal space. Clear sharp spots are immediately observed in the structure factor. We have resolved a great number of diffraction peaks, that are consistent with fcc single crystals. The orientation is usually such that the 111 direction is perpendicular to the cell wall, and $10\underline{1}$ is parallel to the long axis of the capillaries. Reflections down to -30 nm indicate that the crystals have a very low Debye-Wailer factor. We are currently analyzing the intensities along the c-axis rods, that are expected to provide highly detailed information on crystal defects. The results confirm that “self-organizing colloidal crystals are suitable building blocks for optical photonic matter [6].

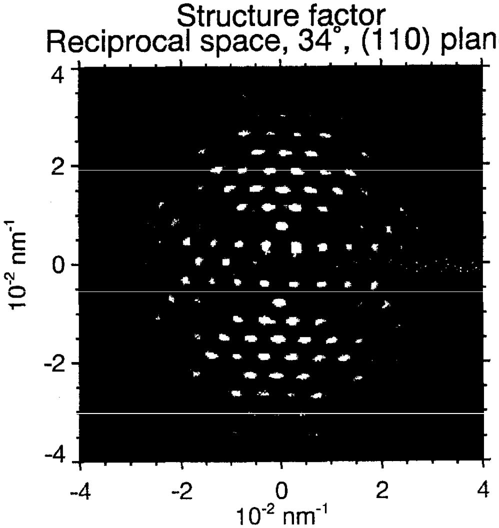

Fig. 1. Structure factor of an fcc colloidal single crystal (a= 366nm), looking down the 110 axis.

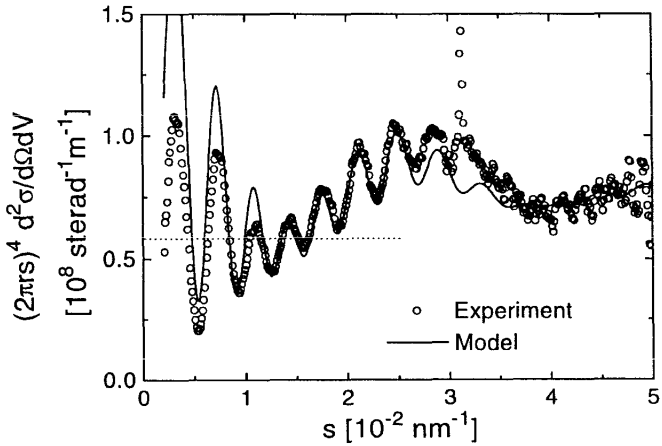

Fig. 2. Porod plot of the form factor of silica colloids with a core of radius 101 nm and a shell of 37 nm thick.

ii) Charge stabilized colloidal crystals have the very useful feature that the lattice parameter can be tuned by varying the ionic strength. Unfortunately however, the structure is unclear at the high densities of interest to applications: fcc is expected, but previous studies revealed vitrification beyond -25 vol% [7]. Glass formation can be overcome by applying a shear-field, but this results in random stacks of (hexagonal) close packed planes (rscp) [8]. Our experiments on samples of latex colloids suspended in water up to volume fractions of 60 vol%, however, reveal the fcc structure [4,6]. We note that the symmetry of fcc is more conducive for optical applications than rscp, leave alone glass.
iii) The information on the structure and orientation of crystals obtained by SAXS turn out to be essential to interpret optical transmission experiments. Such experiments probe the optical stop bands that are precursors to the hotly pursued complete optical band gaps [1]. The excellent agreement between the measured lattice spacings (SAXS) and optical stop band frequencies validates a model for the average refractive index of photonic crystals [3]. Moreover, we have been able to show that the width of optical stop bands has an optimum as a function of the volume fraction of scattering particles (the colloids) [3],
iv) The form factors of the colloidal particles are essential to interpret the crystal structure factors from the scattering patterns. However, the form factors also yield an unprecedented look at the structure of the colloidal particles themselves, because we use particles with a narrow size distribution (a few %) [4,5]. First of all, the form factors provide *in-situ* information about the size distribution, that is usually characterized *ex-situ* by e.g. electron microscopy. Moreover, the oscillations of the form factor far into reciprocal space put a sharp upper bound on the fuzziness of the surfaces of the particles, of less then 1% of the particle radius. Last but not least, the scattering pattern provide information about the internal structure of the particles, such as a core-shell structure that occurs during synthesis [5].

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