

## Second-type disorder in colloidal crystals

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**Abstract** – The presence of second-type disorder in self-organised colloidal crystals is demonstrated on the basis of confocal microscopy. The study is performed for crystals consisting of colloidal hard spheres and hard polyhedral colloids. Using confocal microscopy single-crystalline domains were imaged and the particle coordinates were retrieved using particle tracking routines. To distinguish different types of disorder present in the crystals the corresponding diffraction patterns were computed from the real-space coordinates. We show that second-type disorder is present in the crystals of *both* the spheres and the polyhedrals. The amount of second-type disorder is significantly larger in the crystal of the polyhedrals. This shows that colloidal crystals form an ideal model system to study various types of disorder since the analysis is possible in both real and reciprocal space. Simulating diffraction patterns from real-space coordinates therefore provides a useful route to a better understanding and interpretation of diffraction patterns.

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**Introduction.** – In an ideal crystal all atoms are located at perfectly periodically positioned lattice sites. However, in practice, crystals always contain various types of disorder. This is of considerable interest since crystal imperfections have important implications on the mechanical [1,2] and photonic properties of crystals [3,4]. In this work we distinguish three types of disorder following the classification of Guinier [5]: i) thermal motion of atoms (first-type disorder), ii) strain-induced lattice deformations (second-type disorder) and iii) finite-size effects. Diffraction is a powerful technique for structure determination and allows one to distinguish between these main types of lattice disorder [5]. The diffraction pattern of a perfect crystal consists of a set of delta-peaks. In three-dimensional crystals first-type disorder does not destroy the long-range correlation in the atomic positions [6] and, therefore, it does not affect the peak width. Instead, first-type disorder reduces the intensities of the higher-order reflections via the Debye-Waller factor [5]. In contrast, both second-type disorder and finite-size effects reduce the lattice positional correlation length and, therefore, broaden the diffraction peaks. Second-type disorder and finite-size effects can be distinguished by determining

the width of the higher-order reflections, which are more sensitive to slight lattice deformations. In the case of second-type disorder the reflection width increases with increasing length of the diffraction wave vector  $q$ , while in a powder or a mosaic of small perfect crystals the lattice is lost abruptly at the crystal boundaries and the peak broadening is independent of the length of  $q$ .

Although significant understanding of lattice disorder has been gained in the past [5], second-type disorder remains least studied. The simplest model allowing for a rigorous calculation of the structure factor  $S(q)$  and exhibiting second-type disorder is the one-dimensional gas of hard “spheres” as described by Zernike and Prins [7]. In this model non-interacting atoms with diameter  $d$  and linear number density  $n$  are randomly distributed on an infinite straight line. At very low densities the structure factor hardly exhibits any structure, while for  $nd \rightarrow 1$  sharp diffraction peaks appear that correspond to the formation of quasi-periodic structure. Since this system does not possess true long-range order, the width of the diffraction peaks at intermediate densities increases with increasing diffraction order, which is reminiscent of second-type disorder.

From the experimental side, it is difficult to study lattice imperfections in atomic crystals in real space.

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Colloidal crystals form an ideal model system to study disorder in crystals since the colloidal “atoms” can be made sufficiently large to allow the direct observation of the local crystal structure using optical microscopy [8–14]. At the same time, the long-range order can be accessed using diffraction of light [15–19] or microradian X-ray diffraction [20–23]. Due to size-polydispersity and slow dynamics, colloidal crystals possess a broad spectrum of defects at relatively high density [24–27], which induce various types of disorder. For example, small polydispersities may contribute to the presence of the first-type disorder in colloidal crystals. Larger polydispersities may induce various internal stresses in the colloidal crystal, which can deform the colloidal crystal possibly leading to second-type disorder as was suggested by high-resolution X-ray diffraction [22]. However, interpretation of diffraction patterns in terms of the local crystal structure models is not always straightforward. In this letter, we characterize lattice disorder using diffraction patterns computed on the basis of particle coordinates obtained with confocal microscopy. The study is performed for single-crystalline domains of colloidal crystals, that are spontaneously formed by spherical and polyhedral colloids [28]. Shape polydispersity of the latter frustrates the hexagonal symmetry of the lattice and leads to a hexatic-like structure of the crystal of polyhedrals [29]. In other words, the long-range translational order is destroyed by the shape of the particles, while the orientational order is preserved.

**Experimental.** – The experimental details are described only briefly here. More details can be found in refs. [14,29]. The polyhedral colloids are fluorescently labeled crosslinked polymethyl methacrylate (PMMA) particles that are monodisperse in size (diameter  $d = 2.23 \pm 0.09 \mu\text{m}$ ), but exhibit a small random perturbation in shape [14,28,29]. As spheres we used monodisperse fluorescent PMMA particles with a similar size and size-polydispersity ( $d = 2.33 \pm 0.07 \mu\text{m}$ ) [30]. Both systems were dispersed in a solvent mixture consisting of *cis*-decalin, tetralin and carbontetrachloride, which simultaneously matches the refractive index and almost the mass density of the particles [31]. In this solvent the particles interact as hard spheres [32]. The particles in the first layer at the bottom glass wall of the sample were imaged using a Nikon TE 2000U inverted microscope with a Nikon C1 confocal scanning laser head. Samples with a volume fraction  $\phi \approx 0.40$  were prepared as described in refs. [14,29]. As sedimentation slowly proceeded, the samples crystallized with the (111)-plane orientated along the wall. After sedimentation had completed, we studied single-crystalline domains in the first (two-dimensional) layer of the three-dimensional system [29]. The centers of the particles were found using standard tracking software [33] and we verified that the polyhedral particle shape did not significantly affect particle tracking.

**Results and discussion.** – Typical confocal microscopy images of the structures formed by the

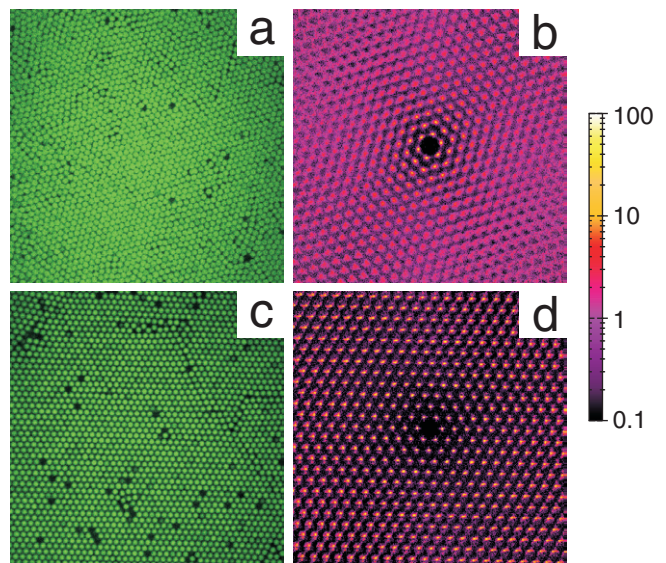


Fig. 1: Typical confocal microscopy images ( $100 \times 100 \mu\text{m}^2$ ) and the corresponding two-dimensional pair correlation functions  $g(\mathbf{r})$  ( $50 \times 50 \mu\text{m}^2$ ) for the polyhedral colloids (a and b) and the spheres (c and d).

polyhedrals and the spheres are shown in respectively fig. 1a and c. Before we switch to reciprocal space to study second-type disorder, we shortly recapitulate the real-space structure of the colloidal crystals as was reported in [29] by calculating the two-dimensional pair correlation function  $g(\mathbf{r})$  (being proportional to the probability of finding a pair of particles separated by a vector  $\mathbf{r}$ )

$$g(\mathbf{r}) = \frac{1}{\rho} \left\langle \sum_{j \neq i} \delta(\mathbf{r}_i - \mathbf{r}_j - \mathbf{r}) \right\rangle_i, \quad (1)$$

with  $\rho$  the average number density. The indices  $i$  and  $j$  run over all particles. The resulting  $g(\mathbf{r})$  patterns for the polyhedral and the spheres are presented in, respectively, fig. 1b and d. While in both cases the presence of sixfold symmetry is obvious, the difference in terms of long-range order is more striking. Whereas for the spheres relatively sharp peaks are observed for the whole  $g(\mathbf{r})$ , the peaks of the polyhedrals are significantly broader and their sharpness decays much faster [29].

To elucidate how these features are reflected in reciprocal space, we computed the two-dimensional structure factor  $S(\mathbf{q})$  on a 2D grid of  $\mathbf{q}$ -values with the sampling rate of  $\pi/L$ , where  $L$  is the size of the microscope image:

$$S(\mathbf{q}) = \frac{1}{N} \left| \sum_{n=1}^N \exp(i\mathbf{q} \cdot \mathbf{r}_n) \right|^2. \quad (2)$$

Here  $\mathbf{r}_n$  are the coordinates of the particle centres and  $N$  is the total number of particles. Every  $S(\mathbf{q})$  pattern contains speckle-like random noise and the horizontal and

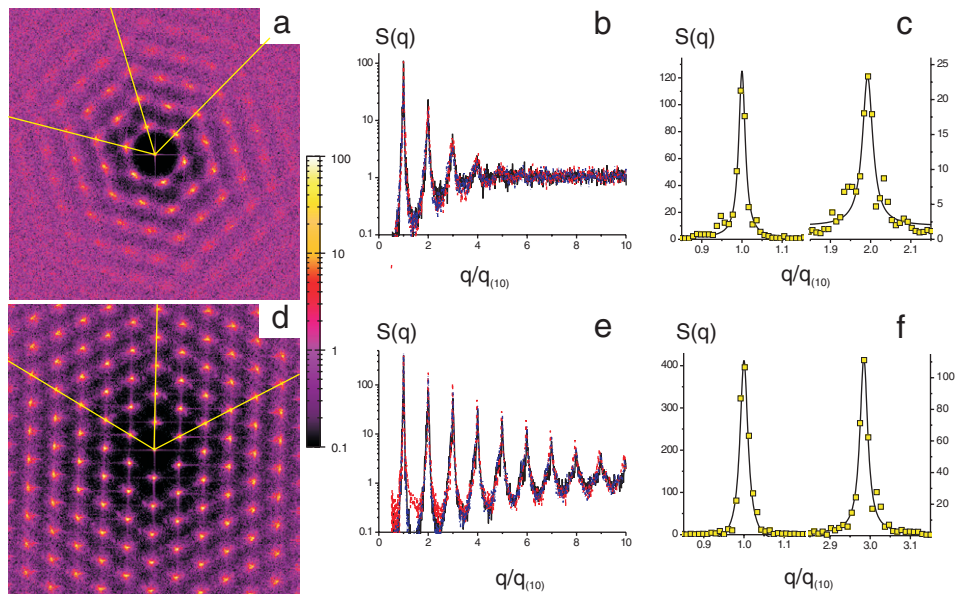


Fig. 2: Left column: the structure factor  $S(\mathbf{q})$  for (a) the polyhedrals and (d) the spheres. Central column: the radial profiles of  $S(\mathbf{q})$  corresponding to the three different directions as indicated by the lines in the left column (a and d) for (b) the polyhedrals ( $\delta\phi = 5^\circ$ ) and (e) the spheres ( $\delta\phi = 2^\circ$ ). Right column: (c) the (10) and (20) peaks for the polyhedrals and (f) the (10) and (30) peaks for the spheres. The profile of the ( $h0$ ) peaks were fitted by a Lorentzian lineshape. Note the different vertical scales for the ( $h0$ ) peaks in (c) and (f).

vertical stripes in the structure factors are due to the finite-size effects. Note that structure factor profile  $S(\mathbf{q})$  and the  $g(\mathbf{r})$  profile are two related but distinctly different representations. As will be shown in more detail below, the  $S(\mathbf{q})$  is more convenient for quantitative characterization of various types of *long-range* positional disorder, which is “hidden” in the details of the decay of the higher-order peaks of  $g(\mathbf{r})$ . More importantly, the distinction between the finite-size effects (abrupt loss of the positional order) and the second-type disorder (monotonic deformation of the lattice) is extremely difficult on the basis of  $g(\mathbf{r})$  but is easily obtainable from  $S(\mathbf{q})$ .

The structure factors are presented in fig. 2a and d for, respectively, the polyhedrals and the spheres. The difference between the long-range order in the polyhedrals and the spheres is again obvious. This is observed more clearly by the radial profiles, which were determined by averaging  $S(\mathbf{q})$  over short arcs with an opening angle  $\delta\phi$  and a radius  $q$ . Figure 2b (polyhedrals) and e (spheres) show the profiles along the three different directions marked by the thin lines in fig. 2a and d. While for the polyhedral only the first four diffraction orders are observed, the radial profiles of the spheres exhibit more than ten diffraction peaks. The decay of the area under the diffraction peaks can be assigned to the Debye-Waller factor, which originates from first-type disorder [5,34]. Note that the amplitude of the peaks in the  $S(\mathbf{q})$  of the polyhedrals is smaller and decays considerably faster than that of the spheres, which suggests a much higher degree of first-type disorder in the crystals of polyhedral colloids. To show the presence of second-type disorder, we analyzed

the radial width of the diffraction peaks for increasing diffraction order, as shown in fig. 2c and f. In these panels the (10) and (20) peaks for the polyhedrals (c) and the (10) and (30) peaks of the spheres (f) are presented. The data are fitted to a Lorentzian lineshape. The peakwidth is defined as the full-width-at-half-maximum  $\delta q$  of the fit. For the first-order diffraction peak the difference between the spheres and the polyhedra is not very striking. A much more significant distinction between the two cases is found in the dependence of  $\delta q$  on the diffraction order. For the spheres the relative width  $\delta q/q_{(10)}$  of the (10) peak is 0.018 and increases to 0.033 for the (30) peak. Hence, this suggests that there is some second-type disorder present in the crystal consisting of the spheres. However, the effect dramatically increases for the polyhedrals: here  $\delta q/q_{(10)}$  increases from 0.030 to 0.19 from (10) to (30) peaks, suggesting that the amount of second-type disorder in the polyhedral system is much larger.

To verify our results and analysis for possible artefacts caused by, *e.g.*, finite size of the microscopy images, we used the experimental coordinates to generate a “reference lattice”. To this end, we first mapped a perfect hexagonal lattice to the coordinate sets permitting the presence of vacancies in the lattice [29]. Subsequently, we introduced first-type disorder by shifting the particle positions by a randomly chosen distance  $\delta r$  in a random direction  $\phi$  around their lattice positions as given by the underlying perfect lattice. An example of such a “reference lattice” is shown in fig. 3a. Here,  $\delta r$  and  $\phi$  were uniformly distributed over the ranges  $[0, 0.2 \mu\text{m}]$  and  $[0, 2\pi]$ , respectively. Note that the reference lattice contains various types of

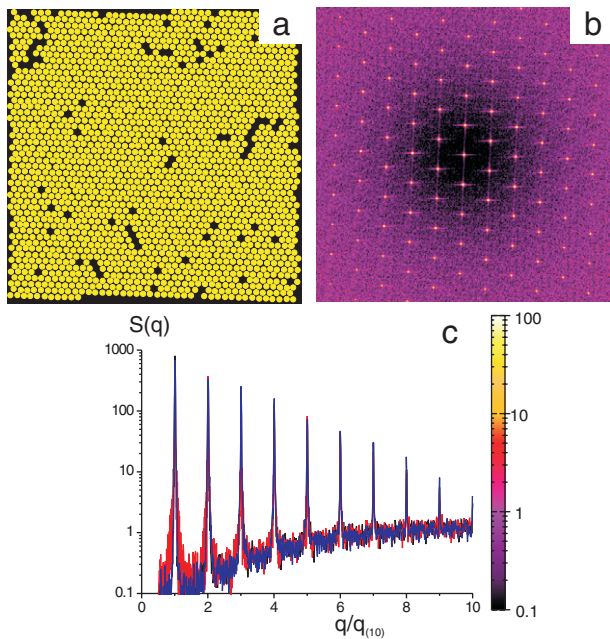


Fig. 3: (a) An example of a “reference lattice” (corresponding to fig. 1c). (b) The corresponding 2D structure factor and (c) the radial profiles, which were determined in exactly the same way as those in fig. 2 ( $\delta\phi = 2^\circ$ ).

disorder such as vacancies, finite-size artefacts and first-type disorder, but *no second-type disorder*. The corresponding 2D structure factor  $S(\mathbf{q})$  is shown in fig. 3b and the radial profiles in fig. 3c ( $\delta\phi = 2^\circ$ ). The radial profiles clearly show that the structure factor consists of sharp peaks indicating the presence of long-range order. Similar results were obtained for a reference lattice generated from the particle coordinates in the crystals of the polyhedral colloids.

In fig. 4 we show the peak widths as a function of the diffraction order for the polyhedrals, the spheres and the “reference lattice”. The widths  $\delta q_{i,j}$  are determined for all images ( $N_{\text{images}}$ ) of the polyhedrals and the spheres and in three different directions ( $1 \leq i \leq 3$ ):

$$\frac{1}{\delta q} = \frac{1}{3N_{\text{images}}} \sum_{i=1}^3 \sum_{j=1}^{N_{\text{images}}} \frac{1}{\delta q_{i,j}}. \quad (3)$$

Physically, this averaging procedure is analogous to averaging the positional correlation length, which is inversely proportional to the peak width. The error bars are evaluated as a standard error in the average value from the spread of the values in  $1/\delta q_{i,j}$ . First of all, we observe that the widths of the diffraction peaks corresponding to the “reference lattice” are constant as a function of the diffraction order, which confirms the absence of second-type disorder and verifies our analysis. The width of the diffraction peaks is in fact determined by the finite size of the microscopy images. Secondly, it is observed that the peak width in colloidal crystals is increasing with the diffraction order, which confirms the presence of the

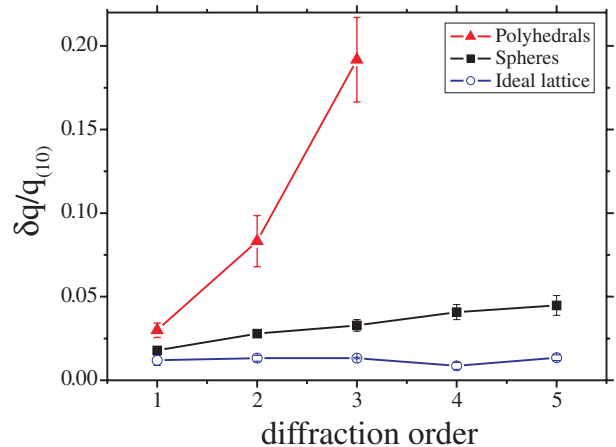


Fig. 4: The relative full-width half maximum (FWHM) peak widths  $\delta q/q_{(10)}$  as a function of the diffraction order  $q/q_{(10)}$  for the crystals of the polyhedrals (triangles), the spheres (squares) and the “reference lattice” (circles).

second-type disorder in *both* colloidal systems. However, as was already suggested by fig. 2, there is a large difference between both systems in terms of the amount of second-type disorder. While the width only slowly increases with the diffraction order for the spheres (slope  $\approx 0.7$ ), it dramatically increases with the diffraction order for the polyhedrals (slope  $\approx 7$ ). This order-of-magnitude difference in slope, confirms the enormous increase of second-type disorder in the crystal of the polyhedral colloids with respect to the crystal of the spherical colloids. A similar increase of the width of the diffraction peaks with the diffraction order was reported for the hexatic columnar liquid crystal phase in polydisperse colloidal platelets [35]. The presence of second-type disorder in the colloidal crystal of the spheres is in agreement with results from high-resolution X-ray diffraction [22].

**Conclusions.** – We have shown that various types of disorder in colloidal crystals can be characterized by computing diffraction patterns from real-space coordinates which are obtained from confocal microscopy images. First-type disorder can be quantified from the Debye-Waller factor, which describes the decay of the area under the diffraction peaks as a function of  $q$  [5,34]. The divergence of the radial peak width  $\delta q$  with the diffraction order is related to the amount of second-type disorder. We demonstrate the presence of second-type disorder in colloidal crystals formed by *both* spherical and polyhedral colloidal particles. The amount of second-type disorder in the crystal of the polyhedral is significantly larger than in the crystal of the spheres. The possibility of investigating colloidal systems both in real and reciprocal space, makes them an important playground to study various types of disorder in crystals, especially as specific particle properties as shape and size polydispersity [29,35] can strongly influence the amount and character of disorder in colloidal crystals. Therefore, analyzing diffraction patterns



from real-space microscopy data is useful to the understanding and interpretation of scattering studies.

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