

## High-Resolution Small-Angle X-Ray Diffraction Study of Long-Range Order in Hard-Sphere Colloidal Crystals

A. V. Petukhov,<sup>1,\*</sup> D. G. A. L. Aarts,<sup>1</sup> I. P. Dolbnya,<sup>2</sup> E. H. A. de Hoog,<sup>1,†</sup> K. Kassapidou,<sup>1,‡</sup> G. J. Vroege,<sup>1</sup> W. Bras,<sup>2</sup> and H. N. W. Lekkerkerker<sup>1</sup>

<sup>1</sup>*van 't Hoff Laboratory for Physical and Colloid Chemistry, Debye Institute, University of Utrecht, Padualaan 8, 3508 TB Utrecht, The Netherlands*

<sup>2</sup>*DUBBLE CRG/ESRF, The Netherlands Organisation for Scientific Research, ESRF BP220, F-38043 Grenoble Cedex, France*  
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The long-range order parameters in single crystals of hard colloidal spheres grown in sediments of colloid-polymer mixtures are determined using synchrotron small-angle x-ray diffraction with a resolution of  $10^{-6}$  of the wave vector. The interplanar positional order derived from the width of lattice reflections extends over at least 500 lattice planes. The lattice planes are orientationally correlated within  $\sim 0.1^\circ$  throughout the crystals, whereas the stacking of hexagonal planes remains random.

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Suspensions of hard-sphere colloids display an entropy-driven fluid-crystal transition. This remarkable phenomenon widely serves as a simple model of crystallization in atomic systems [1–3]. Recently, colloidal crystals are also attracting significant attention for their high potential as photonic band gap materials [4]. For these applications the emphasis is on the preparation of large single crystals possessing long-range order, with a low density of defects and small fluctuations of the particle positions. The growth of millimeter-large colloidal crystals has been reported by many researchers [1,2], while the actual order parameters are hardly ever addressed. The elongated shape of the reflections in an earlier synchrotron x-ray diffraction experiment [5] on charge-stabilized single colloidal crystals clearly indicates that these crystals have a mosaic structure consisting of many orientationally correlated but positionally independent fragments. In this Letter the characterization of long-range order parameters in hard-sphere crystals is performed using high-resolution small-angle x-ray diffraction.

The challenge of x-ray diffraction to characterize long-range order in colloidal crystals stems from the very large difference between the typical lattice period  $a$  and the x-ray wavelength  $\lambda$ ; their ratio  $\epsilon = \lambda/a$  is typically of the order  $10^{-3} \ll 1$ . The length  $\Lambda$  over which the positional order is preserved manifests itself in the width  $\delta q$  of the reciprocal lattice reflections [6,7]. For  $\Lambda$  as large as  $\sim 10^3 a$ , the width  $\delta q$  is of the order of  $10^{-6}$  of the x-ray wave vector  $k_0 = 2\pi/\lambda$ . To resolve it, one needs to fulfill conditions of coherent interference of diffracted waves over distances larger than  $\Lambda \sim 10^6 \lambda$ .

In the transverse direction the coherence length  $l_{tr} = \lambda/\vartheta$  [8] is mostly governed by the angular size  $\vartheta$  of the radiation source seen from the position of the sample. Parts of the crystal separated in the transverse direction by more than  $l_{tr}$  are irradiated by waves with different and uncorrelated phases. The positional order in the transverse direction can thus be resolved only on a distance of

$$N_{tr} = l_{tr}/a = \epsilon/\vartheta \quad (1)$$

lattice periods.

In the longitudinal direction the coherence length  $l_{long} = \lambda^2/\Delta\lambda$  is mostly restricted by the spectral width  $\Delta\lambda$  of the radiation source. The waves diffracted at the front and back faces of the sample are coherent if the length of their path from the source to the detector differs by less than  $l_{long}$ . This condition is fulfilled if the sample thickness is smaller than  $l_{long}/(1 - \cos 2\theta) = l_{long}/(2 \sin^2 \theta)$ , where  $2\theta$  denotes the scattering angle. For an  $n$ th order reflection from a periodic lattice with period  $a$  the scattering angle  $2\theta$  is given by  $\sin \theta = n(\lambda/2a)$  and the positional order over

$$N_{long} = l_{long}/(2a \sin^2 \theta) = 2\lambda/(n^2 \epsilon \Delta\lambda) \quad (2)$$

lattice periods can be resolved. Thus, for a small-angle diffraction experiment on mesoscopic colloidal spheres, the smallness of the  $\epsilon = \lambda/a$  ratio makes it difficult to resolve the positional order in the transverse direction ( $N_{tr} \propto \epsilon$ ) while it, in fact, helps to resolve the positional correlation in the longitudinal direction ( $N_{long} \propto 1/\epsilon$ ). As it is shown below, the latter factor allows one to easily resolve the long-range order over about a thousand lattice constants in a single-crystal diffraction scheme.

Samples are prepared in flat glass capillaries of internal path length 0.2 mm filled with a dilute 5% volume fraction colloid suspension. The silica spheres [9] of 224 nm diameter and 4.1% size polydispersity have been covered with 2 nm thin hydrocarbon layers to prevent their agglomeration in solvent cyclohexane (steric stabilization). The fraction of dumbbells is 3.6%. The crystals grow in the concentrated sediment within 1–2 weeks after sedimentation from the top of the sediment. Osmotic compression by adding nonadsorbing polymer (polydimethylsiloxane, 14 nm radius of gyration, at volume fractions  $\phi_p \sim 10\%–15\%$  around the phase boundary [10]) to the suspension is observed to accelerate crystallization and to

give large high-quality crystals, which have been selected for the present study. In addition, reference samples without polymer have also been used.

Small-angle x-ray diffraction measurements have been performed at the Dutch-Flemish bending magnet BM26 "DUBBLE" beam line at the European Synchrotron Radiation Facility (E.S.R.F.) in Grenoble. Scattering of a 10 keV x-ray beam (wavelength  $\lambda = 1.24 \text{ \AA}$ , bandpass  $\Delta\lambda/\lambda = 2 \times 10^{-4}$ , size  $0.1 \times 0.1 \text{ mm}^2$  at the sample) is registered at 8 m distance by a two-dimensional ( $512 \times 512$  pixels) gas-filled detector. The samples have been mounted on a goniometer head, which allows for careful orientation around three orthogonal axes. A more detailed discussion of the longitudinal and transverse coherence within the optical setup will be published elsewhere. In brief, the transverse coherence is characterized by  $l_{tr} \approx 10 \text{ \mu m}$ , i.e., only  $N_{tr} \approx 40$  times larger than the nearest neighbor distance. This value is sufficient to obtain clear diffraction patterns but is far too small to determine the long-range order in the transverse direction. On the other hand, the narrow spec-

tral width leads to  $N_{long} \approx 10^4$  even for the highest order reflections falling on the detector with  $\sin\theta = 20(\lambda/2a)$ .

A carefully oriented sample gives a diffraction pattern as in Fig. 1(a). The diffracted intensity

$$I(\mathbf{q}) = S(\mathbf{q})F(q) \quad (3)$$

can be written as a product of the structure factor  $S(\mathbf{q})$ , which is the result of the diffraction on the periodic lattice of a single crystal, and the form factor  $F(q)$  representing the intraparticle scattering. 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. The weaker spots in between are discussed later, but depend upon the stacking of consecutive planes in the crystal. Figure 1(b) illustrates the extreme sensitivity of the diffraction pattern to the sample orientation (rotations by less than  $0.1^\circ$  can easily be detected). We observed that the pattern does not change noticeably upon translating the sample vertically and horizontally indicating a very high degree of orientational

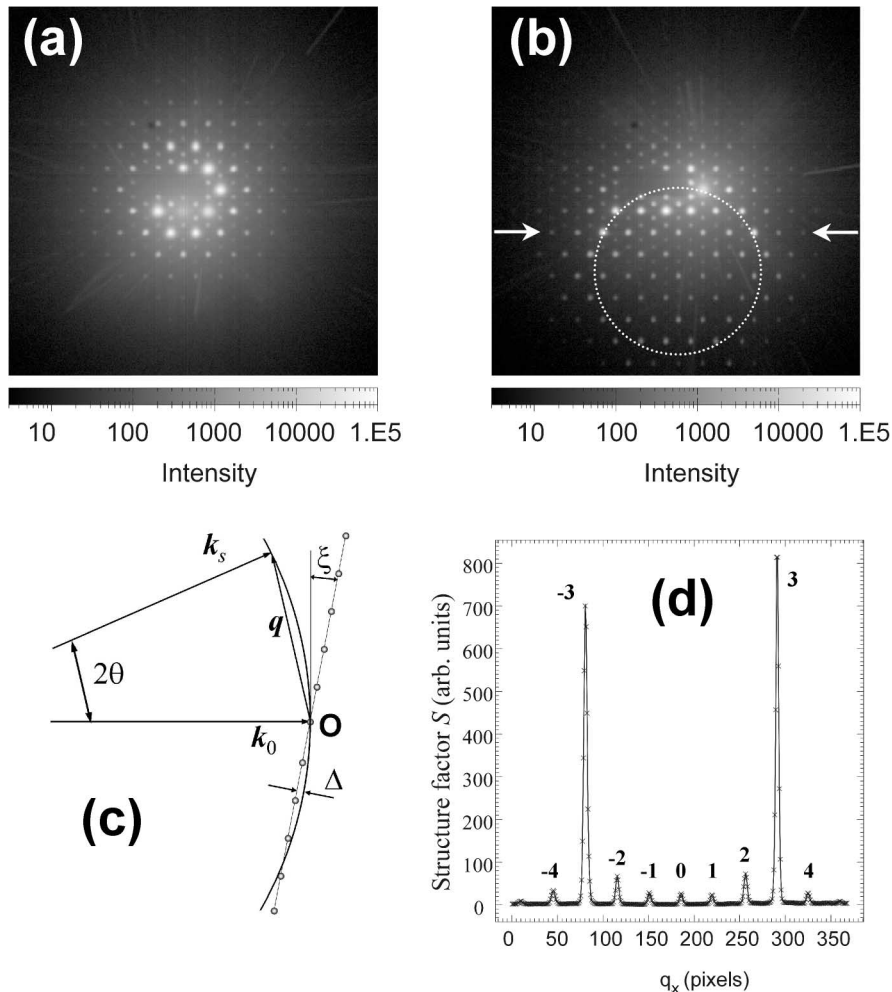


FIG. 1. Diffraction patterns measured when the hexagonal planes of the crystal are normal to the incident x-ray beam (a) and after rotating the sample around the horizontal  $x$  axis (normal to the beam) by  $\zeta = 0.2^\circ$  (b). (c) Sketch of the intersection of the Ewald sphere through a set of reflections in reciprocal space for a tilted sample.  $\text{O}$  denotes the origin of the reciprocal space. The curvature of the Ewald sphere is greatly enhanced for clarity. (d) Variation of the structure factor along the line, indicated by arrows in (b).

order within this single crystal area of size  $0.5 \times 0.2 \times 2 \text{ mm}^3$ , surrounded by crystals with other orientations. This extraordinary orientational order suggests a high rigidity of the crystal planes, which are flat within a sphere diameter over a distance comparable to the crystal size.

The size of the diffraction pattern spots is dominated by the detector resolution and the above-mentioned limited coherence in the transverse direction. However, our results shown in Fig. 1 do allow evaluation of the positional order in the longitudinal direction. The diffraction patterns can be understood by a consideration in reciprocal space schematically shown in Fig. 1(c). The scattering vector  $\mathbf{q} = \mathbf{k}_s - \mathbf{k}_0$  must lie on the so-called Ewald sphere [6] since the wave vectors,  $\mathbf{k}_0$  and  $\mathbf{k}_s$ , of the incident and scattered waves have the same length of  $2\pi/\lambda$ . Diffraction is observed only 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 Fig. 1(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 plane of reciprocal lattice reflections along a circle. The center of this circle is at  $2\theta = \zeta$  (see Fig. 1c), where for  $\zeta = 0.2^\circ$  the Ewald sphere deviates from the plane by as little as  $\Delta = (1 - \cos\zeta)k_0 = 6 \times 10^{-6}k_0$ . 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 Fig. 1(d) the profile of the structure factor  $S(\mathbf{q})$ , obtained after dividing out the form factor  $F(q)$  according to Eq. (3), along a line of diffraction peaks. Two very strong reflections (denoted 3 and  $-3$ ) are closest to the Ewald sphere for this sample orientation. For the neighboring reflections  $\pm 2$  and  $\pm 4$  the mismatch from the Ewald sphere amounts to  $2 \times 10^{-6}k_0$  and  $3 \times 10^{-6}k_0$ , respectively. They are seen in Fig. 1(d) to be weaker than the brightest  $\pm 3$  reflections by at least 1 order of magnitude indicating that the width of the reciprocal lattice spots  $\delta q$  is smaller than  $10^{-6}k_0$ . The inverse of this width  $\Lambda = 2\pi K/\delta q$ , where  $K$  is a constant of order 1, translates into a positional correlation [7,6] between at least 500 crystal layers along the beam. We thus find high positional order, possibly ranging from wall to wall (the thickness of the capillary allows it to accommodate 1000 layers). Although the data do not allow a similar determination of the in-plane positional correlations (in the transverse direction), the combination of high orientational and interplanar positional order suggests a high in-plane positional order as well.

Above, the spatial extent  $\Lambda$  of the positional order is evaluated by comparing the diffraction intensity of peaks of different order within one diffraction pattern. A similar estimate of  $\Lambda$  can be obtained by measuring the rocking

curve, i.e., the dependence of the intensity of a particular reflection on the sample tilt angle  $\zeta$ . A third way of evaluation  $\Lambda$  is to use the results presented below and to compare the intensity of diffraction originating from the intersection of the Ewald sphere with a bright spot and a scattering rod, respectively. While the maximum diffraction intensity in a spot is proportional to  $\Lambda$ , in a rod it is independent of  $\Lambda$ . All three estimates yield similar results.

In Fig. 2(a) the generic reciprocal lattice [9] is sketched for close-packed crystals which consist of stacked hexagonal layers. The diffraction vector  $\mathbf{q}$  can be written in terms of three basis vectors  $\mathbf{q} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$  introduced in the figure. Because of the periodicity within the hexagonal layers the diffraction is observed only for integer values of  $h$  and  $k$ . For  $h - k$  divisible by 3, diffraction is independent of the stacking order and is observed only for integer values of  $l$  (spots in Fig. 2a). For other values of  $h - k$  the diffraction intensity sensitively depends on the probability  $\alpha$  of finding an  $ABC$  stacking sequence among three consecutive layers within the crystal, where  $A$ ,  $B$ , and  $C$  denote the three possible lateral positions. The intensity may be concentrated at new spots [for truly regular stacking like the  $ABCABC$  stacking of the face centered cubic (fcc) crystal:  $\alpha = 1$ ; or the  $ABABAB$  stacking for the hexagonal close packed (hcp) crystal:  $\alpha = 0$ ] or may be distributed continuously for intermediate values of  $\alpha$  [9]. The results presented in Fig. 1 correspond to  $l \approx 0$ . Larger rotations of the sample give different intersections (at larger  $l$ ) between the reciprocal lattice and the Ewald sphere, which allows us to measure the intensity profile along the rods and, thus, to determine the stacking order of consecutive hexagonal planes.

In Fig. 2(b) the structure factor at  $9.5^\circ$  is shown. The corresponding Ewald sphere cuts through the origin  $\mathbf{O}$  in

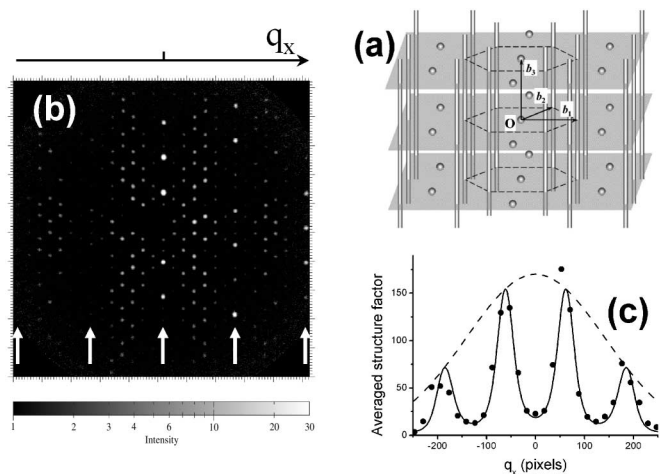


FIG. 2. (a) Reciprocal lattice of a random-hexagonal-close-packed crystal, which consists of localized spots and rods. The shadowed planes are for illustration purposes only. (b) Structure factor after the sample is rotated by  $9.5^\circ$  around the vertical axis relative to its orientation shown in Fig. 2(a). (c) Horizontal variation of rod intensities in (b). The solid line displays the result of calculations [6] for  $\alpha = 0.55$  multiplied by a Debye-Waller factor (shown by the dashed line).

Fig. 2(a) and intersects 5 planes of spots corresponding to  $l = 0, \pm 1, \pm 2$  [at  $q_x$  indicated by arrows in Fig. 2(b)] within the range of scattering angles presented at the detector, leading to vertical lines of bright diffraction peaks. Again, note the asymmetry (stronger on the right, vanishing on the left) of the intensity of these peaks. The additional pattern is formed by intersections with rods. This pattern is symmetric since the curvature of the Ewald sphere does not play any role here; it only imperceptibly shifts the point of intersection along the rod. By vertically averaging the intensities of the rod pattern we get a representation of the intensity variation along the length of the rods, which corresponds closely to a stacking parameter  $\alpha = 0.55 \pm 0.05$  as shown in Fig. 2(c); i.e., the crystal possesses no stacking order. In fitting Fig. 2(c) the true theoretical variation [9] was multiplied by an additional Gaussian function. This corresponds to the usual Debye-Waller factor in crystals, which accounts for the fluctuations in the particle positions around perfect lattice positions [11]. We consistently found a fluctuation of about 2% of the sphere diameter, which should be compared to the average nearest neighbor distance of about  $(3 \pm 1)\%$  larger than the sphere diameter as determined from our diffraction patterns. Within 1% accuracy we find the same nearest neighbor distance at all heights.

With the same series of samples two similar x-ray diffraction studies have been performed, two weeks after crystallization and a year later. The results shown in Figs. 1 and 2 have been obtained in the second measurement session. The earlier experiment indicated the presence of high positional order already at an early age of the crystals. No variation of the stacking disorder was seen within one year. A similar study has been performed on reference samples without polymer. Except for a smaller typical crystal size leading to difficulties in exploring the three-dimensional reciprocal properties by crystal rotation, the results are similar and also suggest the presence of long-range positional order and stacking disorder in the polymer-free samples.

To summarize, a resolution in reciprocal space of order  $\delta q = 10^{-6}k_0$  is demonstrated with synchrotron small angle x-ray diffraction on colloidal crystals. Our use of the single crystal diffraction is crucial in obtaining such a resolution, which is much more difficult to achieve in the powder diffraction [12] scheme. It is remarkable that it can be achieved at a bending magnet station of a synchrotron and does not necessarily require higher quality and brighter beams from an undulator. The data allow for accurate characterization of various long-range order parameters and clearly reveal that the inherent size polydispersity [13–17] of colloids does not prevent the formation of high-quality large single crystals possessing long-range orientational and positional order. Theory predicts [18] that for monodisperse hard spheres the face-centered cubic structure is the most stable. However, a random stacking structure is found, which is also commonly observed in other hard-sphere systems [3,19].

The present results suggest that the stacking disorder has an extremely long lifetime (much longer than a year) or even becomes stable due to, e.g., the sphere polydispersity. It is interesting to note that the structure displayed by our hard-sphere crystals distinctly differs from the structure of charge-stabilized colloidal crystals [5,12]. Although the latter have a mosaic structure with a much shorter extent of the positional order [5], they do display a high degree of the fcc stacking order [5,12].

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\*Corresponding author.

Email address: a.v.petukhov@chem.uu.nl

†Present address: NIZO Food Research, Kernhemseweg 2, 6718 ZB Ede, The Netherlands.

‡Present address: Department of Materials Science and Technology, University of Crete, P.O. Box 2208, 71003 Heraklion, Crete, Greece.

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