

Direct observation of stacking disorder in a colloidal crystal

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Colloidal crystals of rhodamine labeled silica spheres dispersed in chloroform have been studied with fluorescence confocal scanning laser microscopy. We report the first determination of the three-dimensional crystalline stacking in the bulk of a concentrated dispersion. The structure was found to consist of a random stacking of close-packed planes. The results are compared with light scattering experiments. © 1995 American Institute of Physics.

INTRODUCTION

Significant interest exists in colloidal dispersions of monodisperse spheres forming colloidal crystals.^{1,2} Colloidal crystals have a number of characteristics that make them attractive for experimental studies: the lattice constant is of the order of the wavelength of visible light, allowing the use of light scattering and light microscopy; characteristic time scales for colloidal crystallization processes are easily accessible; and the interaction between particles can be tuned by selecting an appropriate combination of surface treatment and solvent. In addition to this, colloidal crystals can be used to model atomic crystals, since they are thermodynamically equivalent. Phenomena that have been studied include the kinetics of crystallization,^{3,4} phase diagrams involving both body centered cubic (bcc) and close packed structures,⁵ and stacking disorder in close packed structures.⁶ In this paper we report the direct observation, by microscope, of stacking disorder in a colloidal crystal.

The simplest model system to show crystallization is the hard sphere system.⁷ The thermodynamically stable crystalline phase for hard sphere crystals appears to be face centered cubic (fcc), although Frenkel *et al.*⁸ showed that the free energy for a hexagonal close packed (hcp) structure is only $2 \times 10^{-3} k_B T$ (thermal energy) per particle higher. In view of this small difference it is conceivable that disordered packings may also occur. A packing can be characterized with a stacking probability parameter α .^{9,10} An hcp lattice, consisting of an ABAB... sequence of close packed planes, has $\alpha=0$. An fcc lattice corresponds to an ABCA... sequence, and has $\alpha=1$. A random sequence of close packed planes has $\alpha=0.5$. Sanders¹¹ mentioned the possibility of random stacking of close packed planes in connection with gem opals, consisting of silica spheres, and Pusey *et al.*⁶ determined a random stacked close packed structure for a crystal of colloidal hard spheres using powder diffraction of light. Light scattering studies by van Duijneveldt *et al.*¹² indicated a random stacked close packed structure for a colloidal crystal of charged spheres formed in an expanding sediment.

So far, the structure of ordered dispersions has been studied successfully both by diffraction and by microscopic techniques. Hiltner *et al.*¹³ performed accurate light diffrac-

tion measurements on colloidal crystals. Williams *et al.*¹⁴ were the first to determine the crystal structure from the measured structure factor containing information on Bragg reflections of visible light, which can also be seen by eye as iridescent specks. Since then diffraction of light has been used successfully to determine the colloidal crystalline structure even for nonequilibrium structures.¹⁵⁻¹⁷ A limitation of diffraction techniques, which provide the average structure factor in reciprocal space, is that it is hard to obtain information about local structures such as vacancies, defects, and coexistence of different phases, so-called two-state structures.¹⁸

Direct observation with a microscope yields real-space information on the particle distribution in the dispersion. Scanning electron microscopy provides clear images of three-dimensional crystals with a resolution of only a few nanometers. However, for electron microscopy the sample has to be dried first which might distort the crystalline structure. Recently, many improvements in the area of freeze-fracture electron microscopy were made allowing the study of the structure of a sample which has been trapped in an ice matrix by rapid freezing (10^4 K/s), for example, nematic structures formed by tobacco mosaic viruses and blue phases exhibited by liquid crystals.^{19,20} Cohen *et al.*²¹ employed this technique to study the structure of polystyrene colloidal crystals, although their cooling rate was considerably lower (340 K/s). It is still not obvious that this rapid freezing process does not affect the actual structure.

Conventional light microscopy allows the study of colloidal crystals in dispersion, but its resolving power is much worse compared to electron microscopy, and because of the opacity of concentrated colloidal dispersions, it is hardly possible to study structures in the bulk. Consequently, light microscopy has been used successfully for two-dimensional colloidal crystals, for example, between two smooth glass plates²²⁻²⁴ or between glass and air.²⁵ For dilute dispersions of latex spheres in water, light microscopy has also been possible. Kose *et al.*²⁶ observed ordered structures close to the container wall using an inverse metallurgical microscope. At a volume fraction ≤ 0.1 vol %, they were able to visualize 30 crystal layers starting from the glass wall. However, in more concentrated dispersions the depth range was much more limited (3 layers at 8 vol %). Hachisu succeeded in elucidating super structures (AB_2 , AB_5 , and AB_{13}) in binary mixtures of latex dispersions at low volume fraction by im-

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aging various crystal planes with the inverse microscope.²⁷ Yoshida *et al.*^{18,28} compared results obtained by light diffraction and by light microscopy. Using a *fluorescence* microscope they were able to distinguish fluorescent particles of diameter of only 140 nm.¹⁸ Yoshida *et al.*²⁹ used a new type of light microscope, a confocal laser scanning microscope, which has an improved resolution compared to a conventional microscope. They were able to get deeper into the bulk of a 1 vol % polystyrene latex dispersion in water (40 μm away from the cover glass), because of the improved depth resolution. Although they measured a constant interlayer distance between close packed planes parallel to the glass wall and a constant interparticle distance between two neighboring particles at several heights in the dispersion, they did not report the type of stacking. Further, the high turbidity of latex spheres in water can result in image distortion in reflected light confocal microscopy.³⁰

Recently a new type of light microscope, a *fluorescence* confocal scanning laser microscope (CSLM) has been introduced into colloid science to study concentrated silica dispersions.^{31–33} These colloidal systems of sterically stabilized silica spheres dispersed in apolar solvents crystallize at high volume fractions into close packed structures. Structure analysis by conventional light microscopy is not convenient for these concentrated crystals, since the intensity of light is strongly reduced by scattering. Since a fluorescent dye was incorporated in the particles it became possible to use fluorescence CSLM.³² By designing the particles such that only the core contains dye, surrounded by a nonfluorescent shell, particles could be distinguished that were at surface–surface separation smaller than the resolution of the microscope. The fluorescence confocal microscope has been used to study colloidal crystals, for example, an equilibrium interface of a coexisting colloidal liquid and a colloidal crystal phase (two-state structure) and the dynamics of crystallization in a crystallizing system.³⁴ A preliminary determination of the crystalline stacking in four subsequent crystal planes in several crystallites indicated an hcp stacking.³¹

In this paper we present the three-dimensional structure of a colloidal crystal in a silica dispersion as determined with fluorescence CSLM. We relate our microscopy data to static light scattering data, obtained on the same system, in order to compare both techniques.

EXPERIMENT

Fluorescence CSLM (Ref. 35) has an improved resolving power compared to conventional light microscopy due to a diffraction limited excitation spot and a diffraction limited field of view. Both the incident laser beam, exciting the sample, and the emitted fluorescent light are imaged by the same lens, and are also forced to pass a pinhole. By scanning and digital data storage, micrographs of optical sections can be constructed. A series of optical sections at different heights in the bulk of the dispersion provides information on the crystalline stacking in three dimensions.

Recently, we have synthesized monodisperse colloidal silica spheres, with cores (diameter 200 nm) in which the fluorophore rhodamine isothiocyanate is chemically bound to silica, surrounded by a layer of plain silica (total diameter

430 nm).³⁴ The polydispersity was 5.6% (standard deviation divided by mean diameter). The spheres were coated with a stabilizing layer of *n*-octadecyl chains, allowing the spheres to form stable dispersions in apolar, refractive index matching solvents such as chloroform. Due to this refractive index matching, light scattering is reduced and we were able to study dispersions at high volume fractions under the fluorescence confocal microscope by detecting the intensity of the wavelength emitted by the dye. Dispersed in chloroform (Baker), these spheres formed charge induced colloidal crystals at volume fractions around 7%, which was in the coexistence region of colloidal liquid and colloidal crystal. These colloidal crystals were excellently suited to be studied with fluorescence CSLM, because the surface charge increased the interparticle distance allowing the separate visualization of neighboring particles in a close packed crystalline array. The reason why these spheres, dispersed in chloroform, carry charge is not understood, and in fact rather unexpected, since the dielectric constant of the solvent is only 4.8. It was observed that the glass vessel containing the dispersion influenced the crystallization behavior of this system. It appeared to be much harder to grow crystals in cylindrical cuvettes with a diameter of 5 mm (used for static light scattering), than in flat capillaries with diameters up to 400 μm (used for CSLM). In these capillaries crystals grew rapidly at various volume fractions (5–16 vol %). Moreover, the crystallization rate decreased over months, and a 7 vol % dispersion in chloroform would not crystallize over the whole volume anymore several months after preparation, but was in equilibrium with a distinct fraction of colloidal liquid. Probably the melting and freezing volume fractions for this system had changed in time. We assume that the surface charge observed on *n*-octadecyl coated silica spheres in chloroform is related to the observed changes in crystallization behavior. This will be discussed later.

Confocal micrographs of colloidal crystals in a 7 vol % dispersion, filling the whole volume with crystals, have been obtained with a Biorad MRC 600 microscope mounted on a *Zeiss* Axioplan equipped with a combined krypton/argon mixed gas laser. We used a 40 \times , 1.3 N.A. oil immersion objective lens, and a YHS filter block (Biorad) which excited the dye at 568 nm and which detected the fluorescence above 585 nm. The resolution perpendicular to the laser beam was 200 nm and in the direction of the laser beam 650 nm. Images of transverse cross sections were obtained by optical scanning and the *z* axis drive from Biorad was modified to drive the focus of the stage. Micrographs of 512 by 768 pixels were constructed digitally in about one second by scanning. The colloidal crystalline dispersion was measured in a flat capillary (Vitro Dynamics, 200 μm thick and 2 mm wide, 10 cm long), sealed off by melting.

Static light scattering measurements were performed with an optical multichannel analyzer as described by^{4,36} (one-dimensional detection) with a resolution of one degree and thermostatted at 20 °C with a 5 mW helium–neon laser at a wavelength of 632.8 nm. This wavelength had been chosen such that the rhodamine labeled silica spheres did not absorb light. In order to obtain a proper average we used a cylindrical cuvette (diameter 5 mm). The 7 vol % sample

was in the coexistence region of colloidal crystal and colloidal liquid, and crystallization took about 12 h. The crystallites were larger than those studied by confocal microscopy (about 1 mm). Due to the large size of the crystallites, it was difficult to obtain a well-orientationally averaged structure factor ("powder diffraction"). The cuvette was rotated manually between scans, and the scattering volume was maximized to $1.5 \text{ mm} \times 1 \text{ cm} \times 0.5 \text{ cm}$ by expanding the laser beam and passing it through a slit to obtain a rectangular light source. The structure factor was obtained by correcting the measured scattered intensities for the solvent scattering and the form factor of the particles.

RESULTS

In order to determine the crystalline stacking of the colloidal crystal with fluorescence CSLM, we studied the 7 vol % dispersion in which crystals formed homogeneously throughout the whole volume. Iridescent spots could be observed by eye and an average size of a crystallite of less than 1 mm was estimated. A series of 13 confocal micrographs was recorded of the same lateral position in the dispersion, taken at depths $0.4 \mu\text{m}$ apart (average depth of this series was approximately $20 \mu\text{m}$ below the glass wall). In order to determine the stacking we looked for hexagonally packed layers in focus of the microscope. It was not trivial to find close packed crystal planes in the bulk of the dispersion along the required direction, which indicates that the glass wall has no large influence on the orientation of the crystallites in the bulk. Figure 1 shows two of these micrographs of optical sections taken $0.4 \mu\text{m}$ apart imaging polycrystalline crystals with close packed planes in the focal plane. The particles in the colloidal crystal did not diffuse anymore since the different optical sections each superimpose accurately as could be checked by comparing the position of particles which were easily recognized in subsequent micrographs (for example, dust or dumbbell particles). We determined a center-to-center distance in the hexagonally close packed plane of 850 nm which is considerably larger than the diameter of the particles, due to surface charge. This center-to-center distance corresponds to a distance between close packed lattice planes of 700 nm . As can be seen, for instance, in the upper right corner of Fig. 1(b), it is possible to see two subsequent crystalline layers in each optical section. This can be understood by comparing the interplane distance, 700 nm , and the resolution in the direction parallel to the laser beam, 650 nm . The fact that the particles in two subsequent layers were visible in one optical section allowed us to identify particles in the subsequent micrographs. Therefore, we were able to determine the actual position of the spheres in each crystal layer. In the set of thirteen micrographs eight, and in some cases, nine hexagonally packed crystal planes could be recognized. This can be understood since this set of thirteen micrographs covers a depth of $12 \times 0.4 \mu\text{m} + 0.65 \mu\text{m}$, taking the axial resolution of the microscope into account, yielding a depth of $5.45 \mu\text{m}$. As the interplane distance in this colloidal crystal was 700 nm , it should be theoretically possible to observe the stacking of nine crystal planes. Our measurements were hardly disturbed by the refractive index mismatch as described by Visser *et al.*,³⁷ who use a simple

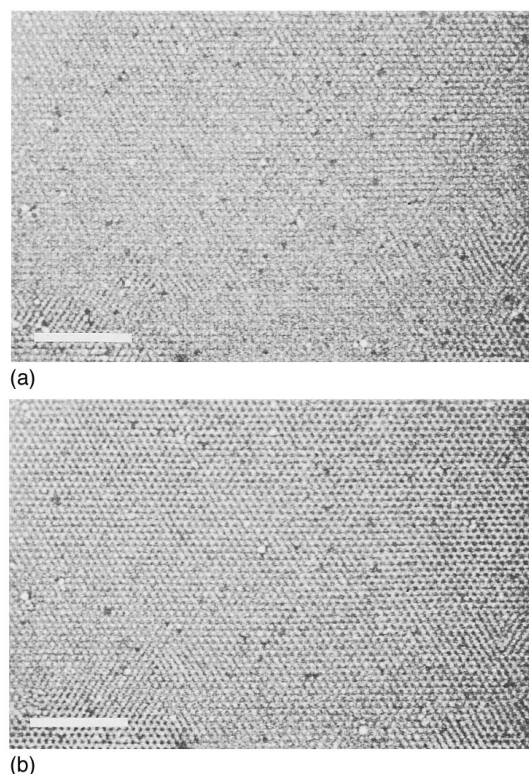


FIG. 1. Confocal scanning laser micrographs of a polycrystalline optical section in a 7 vol % dispersion of rhodamine labeled silica spheres in chloroform. (a) Micrograph taken at a depth of about $20 \mu\text{m}$ below the glass wall. (b) Micrograph taken $0.4 \mu\text{m}$ below the previous one. bar = $10 \mu\text{m}$.

geometric marginal ray model, and by Hell *et al.*,³⁸ who take the vectorial properties of light into account. They show that for objects immersed in a solution with a lower refractive index than the oil immersion lens, the apparent axial distance is larger than the actual axial distance. In our dispersions in chloroform ($n_D \approx 1.45$) this would give a decrease in axial displacement of, at most, 5% compared to the apparent displacement.

The particle positions are presented in Table I. From the sequence of particle positions in the stacked layers the stacking probability α was determined by assigning to each triplet of consecutive layers an appropriate value ($\alpha = 0$ or 1) and averaging these values to obtain the α as indicated in Table I.

The average stacking probability was calculated to be 0.4 ± 0.2 . The relatively large uncertainty is due to poor statistics related to this method of studying crystal structures, since we only obtain information about a few crystal layers in a crystallite. It should be emphasized that we found a *random* stacking of hexagonal planes by direct observation. We consider it rather unlikely that the observed random stacking is part of a large complex unit cell extending over more than nine crystal planes. We are not aware of earlier indications for random stacked close packed planes in spontaneously formed crystals in dispersions of slightly charged particles. van Duijneveldt *et al.*¹² observed for charge-stabilized particles, generally crystallizing in an fcc like structure, that after centrifugation for 30 min at 500 g, ran-

TABLE I. Particle positions and stacking probability α as determined for a polycrystalline crystal in a 7 vol % dispersion in chloroform measured by fluorescence CSLM.

Number	Particle Position									Stacking probability α
	1	2	3	4	5	6	7	8	9	
I	A	C	A	C	B	C	B	C		$\frac{1}{6}$
II	A	B	A	B	C	A	C	A	C	$\frac{2}{7}$
III	A	C	B	A	B	C	A	C	A	$\frac{4}{7}$
IV	A	B	A	B	C	B	A	B	C	$\frac{3}{7}$
V	A	C	B	A	B	C	A	C	A	$\frac{4}{7}$
VI	A	C	A	C	B	C	B	C		$\frac{1}{6}$
VII	A	C	B	C	A	B	A	C	A	$\frac{4}{7}$
Average										0.4 ± 0.2

dom stacked crystals were formed in the top of the expanded sediment.

These results illustrate the potential of fluorescence CSLM to study bulk properties in a concentrated dispersion. The question remains if the glass wall somehow affects the bulk structure, since the microscopic setup always forces us to study optical sections parallel to the glass wall. For three-dimensional studies, such as this attempt to elucidate the crystalline stacking in three dimensions, we have to realize that we observe cross sections parallel to the glass wall, and possibly the studied crystal planes might even have grown, starting from the glass wall as was discussed by Yoshida *et al.*²⁹ This is especially valid for small containers such as the capillaries used for these CSLM studies. Another important effect is that both the injection procedure for filling our capillaries and the homogenization of the dispersion by shaking may produce shear-induced crystalline structures.³⁹ The shear, resulting from the flow in the capillary, is thought to yield ordering of the spheres in hexagonal layers parallel to the flow vector which is, in our case, also parallel to the container wall. This induced shear can be effective in containers of dimensions comparable to our capillaries, but not in thicker geometries, and this might explain the observed difference in crystallization behavior for dispersions in thin capillaries and thicker cuvettes. However, in earlier work we presented confocal images of an equilibrium coexistence between a colloidal liquid phase and two colloidal crystal phases in a capillary, that exposed different crystal planes.³⁴ Moreover, most of the crystallites did not have their close packed plane parallel to the glass wall. Both are strong indications for the fact that the glass wall did not influence the bulk structure in small capillaries.

Consequently, it was interesting to compare the information obtained by confocal microscopy with the average structure as measured by static light scattering. Figure 2 shows the structure factor vs the normalized wave vector K^* (wave vector divided by position of first peak = $1.0 \times 10^7 \text{ m}^{-1}$: this corresponds to a scattering angle of 41°) for this system. The dispersion contained both colloidal liquid and large colloidal crystallites, which settled under gravity into a sediment.

Measurements were performed in the upper part of this sediment. The scattering pattern does not show many details, considering the instrument resolution of 1° . We speculate that this is due to scattering from colloidal liquid between the crystallites, concealing details of the crystal scattering pattern. We concentrated on Bragg peaks occurring at wave vectors up to $K^* \approx 2$, the first minimum of the form factor. The first peak, corresponding to either the (111) reflection of an fcc stacking or a (002) reflection of an hcp stacking was always the most intense. Based upon the value for the wave vector corresponding to this Bragg reflection we calculated an interparticle distance in close packed planes of 840 nm immediately after preparation, while a few months later this distance had decreased to 770 nm. Although both values for the interparticle distance are of the same order of magnitude as the one measured with CSLM (850 nm) the latter is distinctively smaller. This difference might be correlated to the fact that the crystallization behavior had changed in time, which may be due to a decrease of surface charge on the particles.

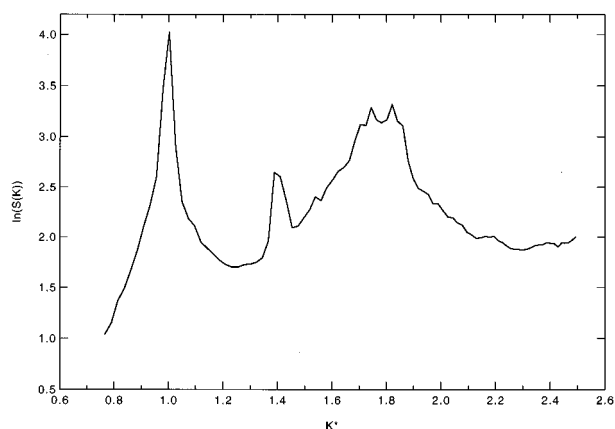


FIG. 2. Structure factor vs normalized wave vector (divided by position of first peak = $1.0 \times 10^7 \text{ m}^{-1}$) for a polycrystalline colloidal crystal in a 7 vol % dispersion of rhodamine labeled silica spheres in chloroform.

Of the other Bragg peaks just the peak at $K^*=1.4$ was recognizable. This value is not present in an fcc stacking, but it can be attributed to the (102) reflection of an hcp stacking. This peak could also be explained resulting from a (110) reflection of a body centered cubic (bcc) stacking. This seems unlikely, however, in view of the CSLM results which clearly show close packed planes. Moreover, bcc ordering is typically found at lower volume fractions than those studied here.⁵

In a case where we have a random stacked close packed crystal, as was concluded from CSLM, sharp peaks in the structure factor are solely predicted at those wave vectors where both fcc and hcp lattices yield a Bragg reflection.¹⁰ Therefore, we conclude that our static light scattering results indicate an hcp like character of the colloidal crystal. However, then the question that arises is why the (100) and (101) reflections of hcp are not being observed, which would be expected at $K^*=0.94$ and 1.06. Although, as mentioned before, the structure factor does not contain many details these reflections should at least broaden the first intense peak around $K^*=1$. An explanation why this is not the case might be the poor statistics of the experimental powder diffraction pattern. The observed crystallites are rather large (and, consequently, their number in the scattering volume rather small) and, moreover, the crystallites might be preferentially orientated after settling. Since we have one-dimensional detection, only those reflections in the scattering (horizontal) plane can be detected. This might explain that certain reflections cannot be observed. Since we clearly observe the reflection of the close packed planes we might assume that these planes have preferably settled with their normals in the scattering plane. In that case other crystal planes have their normals tilted compared to the scattering plane, resulting in reflections out of the plane of detection. This might explain why the (100) and (101) reflections of an hcp lattice, which make angles of 90° and 62° with the close packed planes, are not observed in this one-dimensional detection geometry. This hypothesis does not account for the presence of a (102) hcp reflection, since the angle between this crystal plane and the close packed plane is 43°. Therefore, although we establish the presence of a reflection from close packed planes and of a reflection indicating the presence of hcp (102) planes, we cannot give an unambiguous explanation for the absence of other hcp reflections in the measured structure factor. Apparently the colloidal crystals studied with static light scattering and with fluorescence CSLM possessed different kinds of structures, even though they were obtained from the same system. It is interesting to compare our results with those of Pusey *et al.*⁶ who also found different structures for colloidal crystals formed in a dispersion of nearly hard spheres. They observed a correlation between the crystallization rate and the observed stacking. A crystallizing colloidal dispersion stacked in a random way when the crystallization rate was fast, but it stacked with a tendency towards fcc stacking when the crystallization rate was slow. They explained these differences in crystallization behavior by assuming that a fast crystallizing system has no time to obtain its equilibrium structure, while a slower crystallizing system can reach its equilibrium structure. This explanation corresponds with the

observations made for our colloidal crystal since we already mentioned that in thin capillaries used for CSLM the crystallization rate was faster than in thicker cuvettes used for light scattering.

CONCLUSION

Summarizing, with fluorescence CSLM we have directly observed the three-dimensional crystal structure of a colloidal crystal in the bulk of a dispersion. The stacking of hexagonally close packed planes appeared to be disordered. As far as we know, such a random stacking has not yet been observed directly, for a colloidal crystal. Light scattering experiments, performed on a similar colloidal crystalline sample, but a few months later, indicated a tendency towards hcp stacking. We assume that the crystalline behavior of the dispersion has changed in time.

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