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3D structure of nematic and columnar phases of hard colloidal platelets

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Abstract
We present small angle x-ray scattering data of single-domain nematic and columnar liquid crystal phases in suspensions of sterically stabilized gibbsite platelets. The measurements are performed with different sample orientations to obtain information about the three-dimensional structure of the liquid crystalline phases. With the x-ray beam incident along the director of the nematic phase a strong correlation peak is observed corresponding to the side-to-side interparticle correlations, which suggests a columnar nematic structure. Upon sample rotation this side-to-side correlation peak of the nematic shifts to higher \( Q \)-values, suggesting the presence of strong fluctuations of small stacks of particles with different orientations, while the overall particle orientation is constant. In the hexagonal columnar phase, clear Bragg intercolumnar reflections are observed. Upon rotation, the \( Q \)-value of these reflections remains constant while their intensity monotonically decreases upon rotation. This indicates that the column orientation fluctuates together with the particle director in the columnar phase. This difference between the behaviour of the columnar and the nematic reflections upon sample rotation is used to assign the liquid crystal phase of a suspension consisting of larger platelets, where identification can be ambiguous due to resolution limitations.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Suspended colloidal particles, such as rods and platelets, show rich phase behaviour involving isotropic (I), nematic (N), smectic (S) and columnar (C) lyotropic liquid crystalline states. In the I phase the particles do not possess order. In the N phase, particles possess orientational order but lack long-range positional ordering. In the S and the C phase the particles possess orientational ordering and additional positional order in one and two dimensions, respectively. The first observations of the N phase were made in 1925 by Zocher who studied spontaneously self-organizing ribbon-like vanadium pentoxide (\( \text{V}_2\text{O}_5 \)) particles [1]. Later, N phases were also found to occur in suspensions of tobacco mosaic virus [2, 3], goethite rods [4] and clay plate-like particles [5]. Nowadays a rich variety of different liquid crystalline phases are reported in suspensions of rod-like [6, 7], board-like [8, 9] and plate-like particles [10–19]. For the plate-like particles these include the observations of the I–N phase transition in suspensions of mixed metal hydroxides [14], F- Hectorite [15], nontronite [12] and beidellite [13], as well as the observation of the I–C phase transition in nickel hydroxides [10] and the occurrence of the I–S phase transition in extended sheet materials [11].

Starting with the seminal work of Onsager in the 1940s [20] it has been shown that this rich phase behaviour can be explained on the basis of the particle shape alone. With computer simulations Frenkel and co-workers predicted the formation of the N, S and C phase for anisotropic hard particles [21–23].

Several techniques are available to study liquid crystalline systems, ranging from polarized light microscopy [24], (cryo) transmission and scanning electron microscopy (cryoTEM/SEM) [25], NMR [11, 26] and neutron scattering [27, 28] to wide and small angle x-ray scattering (WAXS/SAXS) [29]. Of these methods, polarized light microscopy is most commonly used, as it reveals phase separation and indicates particle orientation. For structure
characterization in the range of approximately 5–500 nm, SANS has proven to be a powerful technique. Since the detailed atomic structure is irrelevant, scattering is sensitive only to the particle shape and their ordering.

Gibbsite (γ-Al(OH)₃) suspensions are a unique plate-like system as they display a well-defined I–N–C phase separation [18]. The system was extensively studied with polarized light microscopy and SANS for both sterically and charge-stabilized particles [18, 19, 25]. The hexagonally shaped disc-like particles have a thickness significantly smaller than the diameter. These can be synthesized with varied sizes using the seeded growth method [30] and it has been shown that 560 nm sized sterically stabilized gibbsite platelets are also able to form hexagonal columnar liquid crystals [31]. Larger particles have the advantage that they can be made visible with confocal microscopy but they are more challenging for x-ray scattering as resolution becomes an issue, due to disorder and size fractionation [19, 31, 32].

So far the SANS measurements are usually reported with a single orientation of the sample which often coincides with the particle normal, due to anchoring at the container wall. A more profound characterization of the three-dimensional (3D) structure can be achieved by studying large single-domain samples under various sample orientations. Moreover, for large particle systems this information is crucial for unambiguous phase identification.

In this paper, we show that characterization of the full 3D structure is an effective method to distinguish between different liquid crystalline phases especially when the resolution becomes an issue. In a system with small (≈200 nm) platelets the N phase with columnar nematic (N_{col}) structure and the C phase are studied in three dimensions. In the N_{col} structure small particle stacks are formed which have a stack axis that can fluctuate while the average particle normal remains constant. This decoupling causes a characteristic increase in the scattering vector \( \mathbf{Q} \) upon rotation. In the C phase there is no decoupling, hence \( \mathbf{Q} \) remains constant when the sample is rotated. With the obtained information the technique is then applied to a system of larger platelets (≈400 nm) and used to determine its 3D liquid crystal structure.

### 2. Experimental details

#### 2.1. Materials

Two different particle suspensions were used, one consisting of small and one of larger sterically stabilized gibbsite platelets referred to as system 1 (S1) and system 2 (S2), respectively. The S1 hexagonal colloidal gibbsite platelets (γ-Al(OH)₃) were prepared from an acidic aqueous aluminium alkoxide solution, according to the procedure of Wijnhoven et al [33]. The particles were subsequently grafted with end-functionalized polyisobutene and were dispersed in toluene [34]. For S2, large particles were synthesized via the seeded growth method from small gibbsite platelets; a detailed description of the procedure is described elsewhere [31]. The particles obtained after five growth steps were grafted with polyisobutene and suspended in tetralin.

Transmission electron microscopy (TEM) was used to determine the surface area of over 200 particles for both systems. The particle diameter \( D \) was determined to be 232 nm for S1 and 411 nm for S2 with a polydispersity of 20% and 10%, respectively. In solution the thickness of the stabilizing layer is expected to be 2–3 nm, giving effective diameters \( D_{\text{eff}} \) of 237 nm for S1 and 416 nm for S2 (table 1).

#### 2.2. Sample preparation

To promote the formation of large single columnar crystals, non-adsorbing polymer (poly-dimethylsiloxane, \( M_w = 423 \) kDa) was added at a concentration of 0.8 g l⁻¹ to a dispersion of S1 with a volume fraction of 0.38 [19, 35]. The suspension was placed in a flat capillary with internal dimensions of 0.3 mm \( \times \) 3 mm. For S2 a home made flat capillary consisting of two coverslips (24 mm \( \times \) 50 mm \( \times \) 0.15 mm and 24 mm \( \times \) 24 mm \( \times \) 0.15 mm) glued together with internal dimensions of 0.15 mm \( \times \) 20 mm was made and filled with a highly viscous suspension of S2. The capillaries were stored upright for a period of one year for S1 and 40 days for S2, which allowed the establishment of a gravity controlled profile of osmotic pressure in the samples. In figure 1(a) a schematic representation of the sample cells and

#### Table 1. Properties of the two different platelet systems.

<table>
<thead>
<tr>
<th>System</th>
<th>Effective particle diameter ( D_{\text{eff}} ) (nm)</th>
<th>Polydispersity ( \sigma ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>237</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>416</td>
<td>10</td>
</tr>
</tbody>
</table>

![Figure 1](image)
the sedimentation profiles as observed between cross polarizers is shown. In S1 the I–N–C phase transitions were observed, as indicated with the dotted lines. In S2 birefringence was observed but the liquid crystal phase was unassigned.

2.3. Small angle x-ray scattering

X-ray studies were performed at the Dutch–Belgian beamline BM-26 DUBBLE [36] of the European synchrotron radiation...
positions, one in the domain determined to be nematic and one in the domain determined to be columnar at positions marked in figure 1(a). In the capillary the platelets will align flat against the glass wall; hence the x-ray beam is parallel to the platelet normal for $\alpha = 0^\circ$.

In figure 2 the SAXS diffraction patterns, as well as the corresponding horizontal and vertical intensity profiles measured in the N domain, are shown for $\alpha = 0^\circ$, $30^\circ$ and $50^\circ$. Intensity profiles are obtained by integration of the pattern over the area between the black and red lines, as shown in figure 2(a). The diffraction pattern measured at $\alpha = 0^\circ$ (figure 2(a)) shows a broad ring-like reflection with a maximum at scattering vector $Q = 0.024\, \text{nm}^{-1}$ (figure 2(d)). This corresponds to a distance in real space of 262 nm, which is in the order of $D$. This broad and strong reflection indicates the presence of pronounced side-to-side correlations, which is a signature of the columnar nematic structure ($N_{\text{col}}$) [39]. In this phase the platelets form short stacks that, in turn, display nematic ordering. As illustrated in figure 3(a), in these short stacks the lateral correlations between the particle positions give rise to a stack axis $\Xi$ parallel to the particle normal $\xi$. This leads to strong side-to-side correlations and hence an intense scattering peak.

The patterns measured at $\alpha = 30^\circ$ and $50^\circ$ (figures 2(b) and (c), respectively) both show elongation of the ring-like pattern and a decrease in intensity in the horizontal direction. As expected, the peak position in the vertical direction (along the rotation axis) remains the same, as is confirmed by the intensity profiles shown in figures 2(d) and (e).

The increase in $Q$ suggests the presence of an apparent correlation length shorter than $D$ when the structure is seen at an angle. This can be understood as follows: the stacks in the $N_{\text{col}}$ phase can also be formed by platelets that are slightly shifted with respect to each other, as illustrated in figure 3(b). While the average particle normal $\xi$ is constant and approximately perpendicular to the capillary wall, the stack axis $\Xi$ fluctuates and is as a result decoupled from $\xi$. When the structure is seen at angle $\alpha$, the apparent side-to-side distance will then be $D\cos \alpha$.

Figure 3(c) illustrates how the variation in the axes of the stacks $\delta \Xi$ broadens the side-to-side reflections in reciprocal space leading to an increase in $Q$ via $Q_\alpha = Q_0 / \cos \alpha$, with $Q_0$ and $Q_\alpha$ the scattering vectors measured at $\alpha$ and $\alpha = 0^\circ$, respectively. The expected peak positions for $\alpha = 30^\circ$ and $50^\circ$ are marked with a blue cross in the intensity profiles in figures 2(e) and (f), and correspond well to the measured peak maxima.

The SAXS pattern and corresponding intensity profile in the horizontal directions obtained in a large single columnar domain of approximately 8 mm in sample S1 at $\alpha = 0^\circ$ are shown in figures 4(a) and (d). Strong Bragg reflections can be observed at $Q = 0.029$ and $0.058\, \text{nm}^{-1}$. These values relate to each other as 1:2, confirming that they originate from the (10) and the (20) reflections of the hexagonal columnar structure. The (11) and (21) reflections can also be observed but these are not discussed here as the horizontal part of the pattern is integrated as indicated by the black lines in figure 4(a).

The patterns measured at $\alpha = 30^\circ$ and $50^\circ$ (figures 4(b) and (c)) and the corresponding intensity profiles (figures 4(d).
Figure 4. High resolution SAXS patterns of the S1C phase at $\alpha = (a) 0^\circ$, (b) 30$^\circ$ and (c) 50$^\circ$, with (d) accompanying intensity profiles. (e) Decrease in intensity for increasing $\alpha$ of the (10) and the (20) columnar reflections. Dots represent experimental data, lines are a guide for the eye. (f) Positions of $Q(10)$ as determined for $\alpha$ and the expected position for a N$_{col}$ structure. Black lines in (a) show the area over which intensity profiles were taken. The direct beam was absorbed by a square-shaped lead beamstop.

and (e)) show a decrease in intensity in the horizontal direction, whereas the peak positions remain constant. In the highly ordered hexagonal C phase the particles are stacked into perfect columns which, in turn, order in a hexagonal structure. The result is a column axis coupled to the average particle orientation (which is determined by the glass wall), hence $\Xi = \xi$ and the Bragg reflections will be sharp point-like features in the 3D reciprocal space. It is therefore expected that the (10) and (20) reflections are only visible at $\alpha = 0^\circ$. However, our results do show some of the (10) and
Figure 5. High resolution SAXS-patterns of S2 at $\alpha = (a) 0^\circ$, (b) 30$^\circ$ and (c) 45$^\circ$ with (d)-(f) accompanying intensity profiles for vertical and horizontal directions. Black and red lines in (a) show the areas over which intensity profiles were taken in the vertical and horizontal direction, respectively. The blue crosses mark the $Q$-values of the expected peak positions for $N_{col}$. The direct beam was absorbed by a wedge-shaped tantalum beamstop.

(20) reflections upon rotation. This indicates the presence of domains with slightly different column orientations where the directions of both $\Xi$ and $\xi$ can fluctuate. However, the fact that the value of $Q$ is constant upon rotation indicates that here the coupling between these $\Xi$ and $\xi$ still holds: $\Xi = \xi$. Figure 4(e) shows the angular dependence of the (10) and (20) intensity
and indicates that most fluctuations of $\Xi$ and $\xi$ occur over a range of $20^\circ$ with a maximum of $30^\circ$. These domains are most likely situated in the centre of the capillary where the influence of the glass walls is expected to be smallest. Figure 4(f) emphasizes the drastic difference in the $\alpha$-dependence of the (10) peak positions for the C phase when compared to the expected position for the N$_{col}$ structure.

3.2. System 2

In S2 the liquid crystal phase could not be determined from polarization microscopy experiments. Due to the large dimensions of the platelets in sample S2, it is challenging to determine the intrinsic width of the reflections, which occur at considerably lower $Q$-values. Another complication is that in liquid crystals consisting of large platelets (columnar) reflections can be seriously broadened by disorder of different types [19, 31] and by the presence of size fractionated crystals [32]. To determine the liquid crystal structure the sample was therefore measured with SAXS along its $z$-axis and 3D SAXS was performed at the marked position in figure 1(b).

Figure 5(a) shows the SAXS pattern measured at $\alpha = 0^\circ$. A circular pattern with strong side-to-side correlations with a maximum at $Q = 0.0136$ nm$^{-1}$ and a much weaker reflection at $Q = 0.028$ nm$^{-1}$ observed. These might be assigned to (10) and (20) reflections, as observed in the C phase in S1, but they are relatively weak and broad. It is thus ambiguous to assign the liquid crystal phase based on this alone.

In figures 5(b)-(f) the SAXS-patterns and the accompanying intensity profiles measured at $\alpha = 30^\circ$ and $45^\circ$ are shown. Here the elongation in the horizontal direction with an increase in $Q$ can be observed. Since this is specific for the N$_{col}$ structure the phase can be unambiguously identified as such.

However, in figures 5(e) and (f) it can be seen that the increase in $Q_{\text{max}}$ is not as high as expected according to the dependence $Q_{\text{max}} = Q_0/\cos \alpha$ observed in the N phase of S1. Thus, the results obtained in S2 are in between those seen in the N phase ($\Xi$ fluctuates, $\xi$ is constant on average) and the C phase (both $\Xi$ and $\xi$ fluctuate keeping $\Xi = \xi$ on average) of S1. This points to the presence of significant fluctuations of not only the axes $\Xi$ of the stacks, but also the average particle orientation $\xi$. It is the combination of the fluctuations of both $\Xi$ (broadening the reflections along a line orthogonal to $Q$) and $\xi$ (broadening the reflections along an arc) that leads to the observed shape of the side-to-side reflections, which is illustrated in figure 6.

The fluctuation of $\xi$ can have several causes. First of all, the larger particle size leads to a shorter sedimentation time. As a result, the particles have less chance to reorient themselves. Secondly, the difference in the sample age can also be an important factor [25]. Thirdly, there is no non-absorbing polymer added in S2, which in S1 could have caused stronger anchoring at the capillary wall.

The information obtained on the 3D structure of S2 clearly shows that the sample has an N phase with a N$_{col}$ structure, with several domains where both $\Xi$ and $\xi$ fluctuate and are decoupled. The expectations are that after some time the particles in the S2 system will align better with the walls, resulting in a single N$_{col}$ domain.

4. Conclusions

We have studied and identified different liquid crystal phases of suspensions of small and large gibbsite platelets using SAXS measurements. By rotating the samples around the vertical axis by an angle $\alpha$, information about the 3D structure of the N and C phase was obtained. For the N phase in a suspension of 237 nm sized platelets a N$_{col}$ structure is found, where fluctuations of the stack axes $\Xi$ are decoupled from a constant overall particle normal $\xi$. This led to an apparent decrease in the side-to-side correlation distance with $\alpha$.

On the contrary, in the C phase $\Xi$ and $\xi$ are coupled, causing the side-to-side correlation and hence $Q$-values to remain constant. With this information the liquid crystal phase of a gibbsite dispersion consisting of large (416 nm) platelets was studied and the structure was identified as N$_{col}$ with several domains. This conclusion could not have been based on a scattering pattern at $\alpha = 0^\circ$ alone and illustrates the importance of exploring the 3D reciprocal space for unambiguous identification of the liquid crystal structure. With the obtained knowledge we would like to take the 3D research further in the future by measuring a range of angles, so that the full 3D reciprocal space can be reconstructed as was, for example, done in [40, 41] for a system of hard colloidal spheres.

Acknowledgments

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