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Direct observation of columnar liquid crystal droplets†

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While the columnar liquid crystalline phase in suspensions of plate-like colloids is by now well-established, little is known about the pathway leading to the formation of this highly ordered, self-assembled structure. Here, we present direct observations of the morphology and structure of micrometer-sized droplets of the columnar phase formed in the nematic phase in suspensions of colloidal gibbsite plates. From polarized light microscopy and optical Bragg reflection measurements we deduce that these droplets consist of stacks of platelets in a hexagonal arrangement, forming a disk-shaped droplet. We discuss the relation of this droplet structure to the nucleation pathway of the columnar phase and to the anisotropic nematic–columnar interfacial tension.

The columnar liquid crystal phase, a two-dimensional hexagonal lattice of columns constituted of liquid-like stacks of particles,¹ was first predicted to occur in suspensions of hard plate-like particles by computer simulations by Veerman and Frenkel.² In the last decade, this phase was indeed observed both in systems of hard colloidal platelets³ and charged platelets.^{4,5} Several studies have been devoted to the detailed analysis of its structural properties^{6–8} and use as a template for the generation of advanced materials such as ordered silica structures.⁹ However, the formation of this highly ordered phase is still largely unexplored.

Here, we investigate the nucleation and formation of the columnar phase in aqueous suspensions of gibbsite platelets (see Fig. 1). The studied system has a bimodal distribution of the platelet aspect ratio (diameter/thickness), which leads to rich phase behavior. Upon increasing the particle volume fraction, the system goes from a regular isotropic–nematic phase coexistence to a phase coexistence with inverted density, *i.e.* with the nematic phase on top of the isotropic phase. At still higher particle concentration, the system exhibits a three phase coexistence with the nematic phase on top, a columnar phase at the bottom and an isotropic phase between these

two. A further increase of the volume fraction leads to a nematic–columnar coexistence. Both the density inversion and the three phase equilibrium can be attributed to fractionation with respect to the particle aspect ratio, as we have shown in ref. 10.

In this article we study, with polarized light microscopy, the columnar phase formation in samples with isotropic–nematic–columnar phase coexistence (30 v/v%) as well as samples with nematic–columnar phase coexistence (36 v/v%). Details on the particle synthesis and analysis methods can be found in the ESI.†

We first consider the macroscopic phase separation kinetics of a gibbsite suspension with a volume fraction of 30 v/v%. After homogenization the suspension first phase separates into a nematic upper phase and an isotropic lower phase, as shown by the photograph in Fig. 2(a) taken after two days. Subsequently, in the nematic upper phase droplets nucleate and grow, and when large enough they sediment under gravity and accumulate at the bottom of the sample, resulting in a three phase coexistence with a nematic upper phase, an isotropic middle phase and a columnar bottom phase (Fig. 2(a), 1 month). Phase separation continues for over a month, with droplets travelling between the nematic phase and the columnar phase.

These differences in time-scales for the formation of the nematic and columnar phase indicate that the homogenized suspension is unstable towards separation in to the isotropic and nematic phase, while metastable with respect to the nematic–columnar phase transition, leading to the relatively slow, homogeneous nucleation of the columnar phase in the form of small nuclei. There is a remarkable similarity to the phase separation process in the three phase region in colloid polymer mixtures observed by Renth *et al.*¹¹ They first observed colloidal gas–colloidal liquid phase separation, followed by nucleation of colloidal crystals in the colloidal liquid.

To study the columnar phase formation in more detail, the sample was examined with polarized light microscopy. We first focus on the isotropic middle phase. There, two types of droplets can be observed

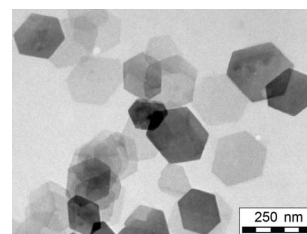


Fig. 1 Gibbsite platelets observed with transmission electron microscopy.

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† Electronic Supplementary Information (ESI) available: (1) details on synthesis and analysis methods. (2) Columnar droplets in the nematic phase that exactly follow the nematic director field. (3) Movie of the rising and sedimenting liquid crystal droplets in the isotropic phase. See DOI: 10.1039/c2sm25208b

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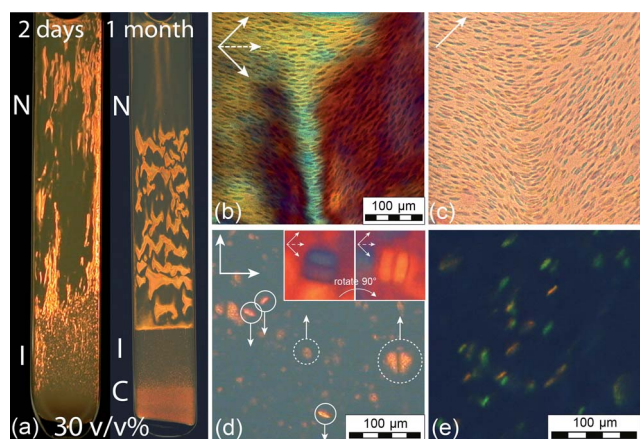


Fig. 2 Gibbsite suspension at 30 v/v% (a) suspension between crossed polarizers, two days and one month after homogenization; (b) micrographs of columnar droplets forming in the nematic phase between crossed polarizers and a retardation plate; (c) idem, with only the polarizer; (d) the isotropic middle phase contains rising nematic tactoids and sedimenting columnar droplets, here 2 weeks after homogenization. Insets: two aligned columnar droplets observed using a full wave retardation plate (see the main text for an explanation of the colors); (e) columnar droplets show iridescence in reflected light. The polarizer and analyzer are indicated with arrows and the slow axis of the retardation plate with a dashed arrow.

moving in opposite directions, as presented in Fig. 2(d) and the movie that is available in the ESI.† The rising droplets originate from the columnar phase and move through the isotropic phase to the nematic phase with which they coalesce. They have a spherical or ellipsoidal shape and can be identified as the well-known nematic droplets, or tactoids, that we studied previously.^{12,13} Furthermore, we observe sedimenting droplets that originate in the nematic phase and settle through the isotropic phase towards the columnar phase. They appear as elongated droplets with a typical thickness ranging from 1.5 to 10 μm and a length ranging from 6 to 25 μm , and are strongly birefringent, indicating a high degree of orientational ordering. Moreover, in reflected light the droplets exhibit bright iridescence with colors ranging from green to orange (see Fig. 2(e)), which implies that there is periodic ordering of the platelets. Indeed, the observed Bragg colors correspond to a hexagonal columnar phase with a lattice spacing of about 250 nm, somewhat larger than the average platelet diameter. The iridescence color is angle-dependent but homogeneous within a droplet, indicating that they consist of a single domain columnar phase.

The orientation of the platelets within these columnar droplets can be determined using a full wave retardation plate (a filter with a known optical path difference, $\lambda = 530 \text{ nm}$). The insets of Fig. 2(d) show that if the retardation plate is parallel to the long axis of the droplet it appears blue, while in the perpendicular case the droplet appears orange. This implies that the particles are oriented with their director parallel to the short axis of the droplet,¹⁴ which raises the question of what the exact shape of these droplets is. Until now they appeared elongated, that is with the symmetry axis along the long axis. If this is indeed the case, it would mean that the symmetry axis (director) of the columnar phase does not coincide with the symmetry axis of the droplet. We will return to this point later.

The high particle concentration and strong birefringence of the upper nematic phase complicate the observation of the columnar

droplets in the nematic phase, where they originate. However, by using a very thin capillary (50 μm path length), we can nevertheless observe the columnar droplets, especially if using only the polarizer. Fig. 2(b and c) show a region in the nematic phase containing many elongated droplets that are not yet large enough to sediment to the bottom of the sample. Interestingly, the droplets are rather uniform in size and are evenly distributed, which points again to the homogeneous nucleation of the columnar phase.¹¹ Another remarkable observation is that the director field of the nematic background that can be derived from the retardation colors in Fig. 2(b) corresponds exactly to the orientation of the columnar droplets in that region (Fig. 2(c)). We will come back to this observation in the discussion.

If the particle concentration is increased to 36 v/v%, the suspension is significantly more viscous and displays shear induced birefringent (nematic) patterns due to the filling of the capillary, which persists over a few days. Phase separation starts at the top of the suspension, indicated by the nematic texture becoming granular, while the lower part of the sample first remains unchanged (see Fig. 3(a), 2 days). The fact that the phase separation starts at the top of the suspension is possibly caused by a small density gradient in the sample due to the centrifugation step after the filling of the capillary. In the course of a week columnar regions sediment towards the bottom of the capillary while nematic domains move upwards, resulting in a nematic–columnar phase coexistence with the columnar phase at the bottom and the nematic phase on top (Fig. 3(a), 1 month).

In order to study the sample in more detail with polarized light microscopy, we use again a very thin capillary. Fig. 3(b) shows the region around the nematic–columnar interface using both the polarizer and the analyzer, and we can already discern some columnar droplets in the columnar phase. If the analyzer is removed (Fig. 3(c)) the columnar droplets are much clearer.

The first remarkable observation is that the columnar phase is not a continuous phase, but rather a close-packed collection of columnar droplets. These droplets also display iridescent colors, again ranging from green to orange (not shown). Furthermore, in addition to the elongated droplets that we saw above, we now also observe droplets

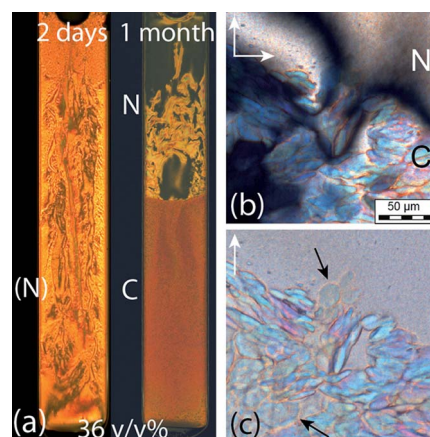


Fig. 3 Gibbsite suspension at 36 v/v%. (a) Suspension between crossed polarizers, two days and one month after homogenization; (b) Bragg reflections displayed by the columnar phase; (c) a polarized light micrograph of the region near the nematic–columnar interface 4 days after homogenization; (d) the same sample, now with the analyzer removed, the black arrows point at droplets with 120° angles. The white arrows indicate the orientation of the polarizers.

with two long axes, suggesting that the droplets have a flat shape. The latter observation is not as surprising at it may seem at first sight. From the experiment with the retardation plate in Fig. 2(d) we learnt that in the elongated droplets the gibbsite platelets are oriented with their director parallel to the short droplet axis. If we assume that the flat droplet is a similar droplet only viewed from another orientation, this means that the platelets again have their director parallel to the short droplet axis, resulting in the columnar director pointing into the optical focal plane. In this configuration the nematic phase does not display birefringence independent of the orientation of the polarizers, so that the droplet will be invisible if located between crossed polarizers. Similarly, for Bragg reflections to occur light needs to enter perpendicularly to the column direction, *i.e.* the edge of a flat droplet. This again allows observation only from the edge side of the droplet, so that also in iridescence measurements the droplets will only appear elongated.

From these observations we can conclude that columnar droplets consist of a disk-like structure containing a single domain of hexagonally arranged columns of platelets, as schematically presented in Fig. 4. In this configuration, the droplet symmetry axis coincides with the columnar director. Note that the columnar droplets in the three-phase sample have the same characteristics as in the suspension with nematic–columnar coexistence.

It is interesting to compare the present results to observations on the nucleation of the smectic phase in suspensions of rod-like particles.¹⁵ Maeda and Maeda first observed laterally growing clusters. Then, as the number of clusters increased, multiple layering of the clusters occurred, resulting in a 1D ordered structure (smectic liquid crystal). Similar phenomena were observed by Dogic and Fraden in the isotropic–smectic phase transition in a colloidal rod–polymer mixture.^{16,17} Computer simulations also showed preferred lateral growth,^{18,19} which was attributed to a tendency of rods to align normal to an already formed smectic layer, thereby reducing growth in the longitudinal direction.¹⁸

Extending this idea to the case of platelets, one would expect the particles to align with the director perpendicular to the plane of a cluster. This implies a reduction of lateral growth and would result in clusters that are elongated in the column direction. However, we observe the opposite: the droplets have their largest dimension in the lateral direction. Clearly, there must be another mechanism at work here. Imagine that it is not the individual platelets that are the nucleating units of the columnar droplets, but rather short stacks of platelets. These stacks could then play a role similar to that of the rods in the simulations of Frenkel and Schilling,¹⁸ leading to preferred lateral growth. The presence of such stacks was established in other gibbsite suspensions from small angle X-ray scattering and cryogenic scanning electron microscopy experiments.²⁰ In a gibbsite system of similar size it was found that, at an ionic strength of 10^{-2} M, the high

concentration nematic phase (above 450 g L^{-1}) contained small stacks of particles. In the present suspensions the particle concentration is about 727 g L^{-1} and 884 g L^{-1} , so well above this concentration.

An indication that there is indeed a strong relationship between the micro structure of the nematic phase and the droplet growth is provided by the observation that growing droplets seem to follow the director field structure of the nematic phase, which we show in Fig. 2(b and c). Another example of this phenomenon is given in the ESI,[†] where a defect of topological charge $+1/2$ in the nematic phase is followed exactly by the columnar droplets. On the other hand, stacks of platelets do not necessarily behave in the same way as solid rod-like particles.

We do not think that the hexagonal arrangement in the columnar droplets and phase is directly related to the individual hexagonal shape of the gibbsite particles, as the simulations of Veerman and Frenkel² and Marechal *et al.*²¹ demonstrate that cut spheres and oblate spherocylinders also exhibit hexagonal columnar phases.

The explanation above for the observed flat droplet shape is in essence a kinetic one. However, if we are dealing with an equilibrium droplet shape, the shape might be described in terms of an equilibrium Wulff construction.²² Although the droplet shape is not very uniform, some droplets appear more or less hexagonal, or have 120° angles (see for example droplets indicated with the arrows in Fig. 3(c)), which suggests that the droplet shape might, at least to a certain degree, be determined by the anisotropic interfacial tension.

According to Wulff, the length of a vector from the droplet center drawn normal to a crystal face will be proportional to its interfacial energy.²³ This implies that the interfacial tensions γ_{\parallel} and γ_{\perp} for the director oriented parallel and perpendicular to the interface normal are related as:

$$\frac{\gamma_{\parallel}}{h_{\parallel}} = \frac{\gamma_{\perp}}{h_{\perp}} \quad (1)$$

with h_{\parallel} and h_{\perp} the distances from the droplet center to the respective interface. From the observed droplet aspect ratio we then obtain a value in the range 3–5 for the ratio of $\gamma_{\parallel} : \gamma_{\perp}$ for the nematic–columnar interface. This implies that the columnar phase prefers homeotropic anchoring with respect to the nematic–columnar interface.

The gibbsite *nematic* phase also exhibits homeotropic anchoring with respect to the *isotropic–nematic* interface.^{12,24} For comparison, we can determine the ratio of $\gamma_{\parallel} : \gamma_{\perp}$ for the isotropic–nematic interface from the value for the dimensionless anchoring strength $\omega \equiv w/\gamma$ that we obtained previously.¹² We use the Rapini–Papoular type form for the anisotropic surface tension σ :

$$\sigma = \gamma + w \sin^2 \theta \quad (2)$$

with γ the bare surface tension, w the anchoring strength, and θ the angle between the surface and the director field at the surface.²⁵ This implies that the interfacial tension for the director perpendicular and parallel to the interface are related as:

$$\frac{\gamma_{\parallel}}{\gamma_{\perp}} = 1 + \frac{w}{\gamma} = 1 + \omega \quad (3)$$

Using $\omega = 0.6$ from ref. 12 we then obtain $\frac{\gamma_{\parallel}}{\gamma_{\perp}} = 1.6$, which is considerably smaller than the value we find here for the

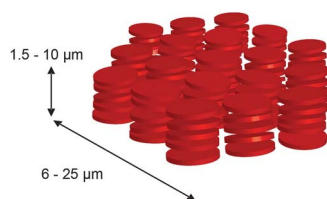


Fig. 4 Schematic illustration of the structure of the columnar droplets (not to scale).

nematic–columnar interface. This difference might be related to the higher particle concentration and order parameter in the columnar phase, leading to larger elastic constants and probably also stronger anchoring, but this point needs further investigation.

To conclude, ordered phases in suspensions of colloidal particles with different shapes are fascinating as they are direct physical manifestations of the great variety and subtlety of entropy driven structures. The observations presented here, together with earlier work on the formation of colloidal crystals and smectic liquid crystals, demonstrate that shape is also a decisive factor in the nucleation pathways of these structures. To obtain further insight into the formation, shape and structure of the remarkable columnar liquid crystal droplets described here and the possible relation to the nucleation of the columnar phase, is a challenge for both theory and simulation.

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