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Tactoids of Plate-Like Particles: Size, Shape, and Director Field

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We studied, by means of polarized light microscopy, the shape and director field of nematic tactoids as a function of their size in dispersions of colloidal gibbsite platelets in polar and apolar solvents. Because of the homeotropic anchoring of the platelets to the interface, we found large tactoids to be spherical with a radial director field, whereas small tactoids turn out to have an oblate shape and a homogeneous director field, in accordance with theoretical predictions. The transition from a radial to a homogeneous director field seems to proceed via two different routes depending in our case on the solvent. In one route, the what presumably is a hedgehog point defect in the center of the tactoid transforms into a ring defect with a radius that presumably goes to infinity with decreasing drop size. In the other route, the hedgehog defect is displaced from the center to the edge of the tactoid, where it becomes virtual again going to infinity with decreasing drop size. Furthermore, quantitative analysis of the tactoid properties provides us with useful information on the ratio of the splay elastic constant and the anchoring strength and the ratio of the anchoring strength and the surface tension.

1. Introduction

If an isotropic suspension of highly anisometric colloidal particles is brought under conditions where it coexists with a nematic liquid-crystalline phase, then nematic droplets form. These droplets, or tactoids, have a nontrivial shape and intricate internal structure, that is, a spatial distribution of the local preferred orientation of the particles, the director. Both the director-field configuration and the shape of tactoids are governed by the competition between the surface tension, anchoring strength, and bulk elastic properties of the nematic. Which of these properties prevails varies with tactoid size. This implies that the size dependence of the tactoid structure provides insight into these properties.

Tactoids formed in suspensions of rod-like colloidal particles have been studied for some time. The first observations by Zocher[1] on tactoids in vanadium pentoxide sols date back to the 1920s. After that, tactoids were studied in suspensions of tobacco mosaic virus[2] and aluminum hydroxide (boehmite)[3] and more recently fd virus,[4] vanadium pentoxide,[5,6] f-actin,[7] and carbon nanotubes.[8] In these studies, director-field configurations were probed by means of polarized light microscopy, which revealed elongated (spindle-shaped) droplets with a bipolar director field. The bipolar director field is characterized by two surface point defects called boojums. The origin of this director field can be contributed to the preferred parallel (planar) anchoring of the particles to the isotropic−nematic interface.[5,6,9−11]

As already advertised, tactoid shape and director field are determined by a balance of the surface anchoring and bulk elastic free energies. A simple scaling analysis proves useful here. While the anchoring free energy of a drop of radius R scales as the surface area, R^2, times the anchoring strength, w, the bulk elastic free energy scales as the relevant elastic constant, K, times the tactoid volume, R^3, times the square of one over the radius of curvature of the director field, $1/R^2$. This implies that for a more-or-less spherical drop there must be a crossover size $R \approx K/w$, above which the surface anchoring predominates.

For planar anchoring conditions, this leads to the aforementioned bipolar director-field configuration. For tactoids smaller than this critical size, the elastic free energy dominates, imposing a uniform director field on the drop.[8,10−12] Perpendicular (or homeotropic) anchoring to the isotropic−nematic interface gives rise to spherical tactoids with a radial director field emanating from a hedgehog point defect located in their center.[12−15] This point defect could in fact also be a small ring-shaped disclination line.[16,17] Obviously, the scaling argument holds irrespective of the anchoring conditions, so a crossover to a uniform director field has to be expected in the case of homeotropic anchoring as well if the tactoids are sufficiently small, that is, if $R \approx K/w$.

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Although the transition of a deformed to a uniform director field with decreasing tactoid size was predicted a long time ago and was also confirmed by means of computer simulations,[18,19] until very recently, there had not been any convincing experimental evidence of it. The main reason presumably is that the length scale K/w (known as the "extrapolation" length[20]) can be very small, in particular, in thermotropic liquid crystals where the transition is expected to take place in the submicrometer range.[21] Apart from the fact that it is difficult to prepare in a controllable way such small droplets, it is also problematic to analyze them properly with polarized light microscopy.

Still, about 1 year ago, Gupta and coworkers succeeded in preparing submicrometer-sized liquid-crystalline droplets confined in polymeric shells, allowing them to study their structure to sizes down to 0.7 μm.[22] Remarkably, they found that upon decreasing the shell size, the liquid crystal structure progresses from a bipolar director field (associated with a planar anchoring) via a preradial to a radial director field (typical of homeotropic anchoring). So, these authors did not observe a crossover to a uniform director field and argued that previously ignored saddle-splay and splay-bend elastic energies are responsible for this and that no transition to a uniform ordering for sufficiently small drops is to be expected if the saddle-splay constant is sufficiently large compared with the splay constant. Actually, according to their own analysis, the order of the transition should in that case be reversed with sufficiently large drops becoming uniform. This was not observed, however, so the issue remains somewhat contentious also because it requires negative free energies of elastic deformation.[22]

More recently, Haseloh and collaborators studied the internal structure of liquid-crystal-based colloidal particles in the micrometer range, where the anchoring could be controlled by different types of dispersion polymerization.[23] They did find a transition from a radial to an axial director field upon decreasing the droplet size to $\sim$1 μm. Unfortunately, they could not unequivocally confirm the existence of the uniform director field because of difficulties associated with the characterization of tactoids < 1 μm. Indeed, because of Brownian motion, these particles move around uncontrollably, leaving only a characteristic blinking if observed under the polarized light microscope. This blinking would indeed be indicative of a uniform director field.

In the various colloidal rod systems studied over the years, the transition to a uniform director field was never observed either, presumably because, apparently, the ratio K/w corresponds to tactoid sizes less than 10 times the rod length.[10] Still, very recently Puech and coworkers were able to observe highly elongated tactoids with a uniform director field in aqueous dispersions of carbon nanotubes.[8] For this particular system, the extrapolation length was deduced to be in excess of 35 μm, so this system would, in principle, be a good candidate to observe the crossover. Unfortunately, droplet sizes observed remained below this critical value.[8]

In suspensions of colloidal platelets, a value for the extrapolation length K/w of 70 μm has been reported, determined from the director-field configuration of a nematic phase near the interface between coexisting isotropic−nematic phases and a vertical solid wall.[24] This means that such a system is an excellent candidate to study the transition from a uniform to a nonuniform director field because this transition should occur for tactoid sizes well within the experimentally accessible range, provided that large enough drops are present in the dispersion. In this Article, we are indeed able to confirm this expectation and report on the size dependence of the shape and director field of tactoids observed in suspensions of colloidal gibbsite platelets.

We study both sterically stabilized gibbsite in an apolar solvent (bromotoluene), and charged gibbsite particles in a polar solvent (water). These two systems, although based on the same colloidal particles, give rise to different elastic and surface properties of the respective nematic phases. The first question we attempt to answer is whether it is possible to observe tactoids with a uniform director field and, if so, what the shape of these droplets is. Platelike particles for entropy reasons prefer homeotropic anchoring, and, in that case, a flat (oblate or lens-shaped) droplet shape appears to be optimal shape for tactoids smaller than $R \approx K/w$. This is in line with what could be expected from the familiar Wulff construction if the anchoring strength is sufficiently large relative to the surface tension.[25−28]

Second, an interesting question we address is how precisely the transition from a radial to a uniform director field proceeds with tactoid size. On theoretical and experimental grounds,[12,23,29−31] one could imagine two plausible scenarios, illustrated in Figure 1: (1) The hedgehog point defect in the tactoid's center transforms into a ring defect, with a radius that increases to infinity with decreasing droplet size. This route involves both the splay and the bend elastic deformations of the director field. (2) The hedgehog point defect displaces itself from the center of the tactoid to its edge, where it becomes virtual and moves further away with decreasing droplet size. This route would involve a splay elastic deformation and suboptimal anchoring of the director field to the interface.

Of course, these scenarios represent a highly idealized and maybe somewhat naive picture of what is actually going on, and combinations of these two routes are conceivable as well. Which route turns out to be most favorable presumably depends on the values of splay and bend elastic constants relative to the anchoring strength. We may therefore expect a different kind of behavior in the sterically stabilized and charged gibbsite systems based on what we know to be the case for systems of rod-like particles, where these parameters are known to be sensitive to how particles are stabilized against demixing.[32,33] Also, we found in previous experiments that nematic dispersions of sterically stabilized gibbsite exhibit a considerably stronger anchoring of the director field to the isotropic−nematic interface than those of charged gibbsite do.[15,34]

The remainder of this Article is organized as follows. Section 2 deals with the experimental details and analysis of microscopy

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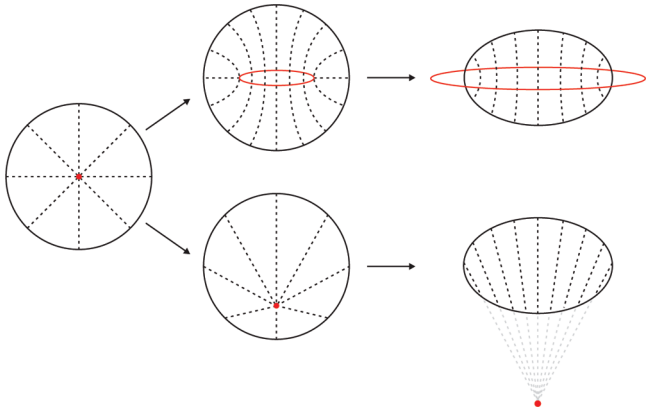

Figure 1. Sketch of possible transition pathways from a radial to a uniform director field upon decreasing tactoid size.

images. Then, in Section 3, we present the various observed tactoidal shapes and director fields as a function of tactoid size, in both aqueous gibbsite suspensions and sterically stabilized gibbsite dispersed in bromotoluene. In Section 4, we perform a quantitative analysis of the structural properties of the tactoids and extract from our results values for the ratio of the anchoring strength and surface tension and that of the splay elastic constant and the anchoring strength. Section 5 contains the discussion of our findings, and we finish in Section 6 with a concluding summary.

2. Experimental Methods

2.1. Particle Synthesis and Characterization. Colloidal gibbsite ($Al(OH)_3$) platelets were synthesized via the procedure developed in our laboratory, which consist of hydrothermal treatment of aluminum alkoxides (aluminum-*sec*-butoxide and aluminum-iso-propoxide) in acidic environment, followed by dialysis and centrifugation.[35] Two systems were synthesized to study tactoid properties in polar and apolar solvent. Both systems were characterized with transmission electron microscopy (TEM, Tecnai 10, Philips), which resulted in a particle diameter of 207 nm (±35%) for the platelets to be studied in polar solvent and 220 nm (±22%) for the gibbsite in apolar solvent. The stability of the aqueous gibbsite was enhanced by the addition of 0.5 m/m% aluminum chlorohydrate (Locron P, Hoechst),[36] after which the system was centrifuged and redispersed in a 10^{-2} M NaCl solution. To enable dispersion in apolar solvent, we coated the platelets with modified polyisobutylene (Shell, SAP 230).[37] The obtained sterically stabilized platelets were subsequently dispersed in 2-bromotoluene.

2.2. Sample Preparation. The suspensions were concentrated by centrifugation and redispersed to a concentration where phase separation occurs and the isotropic and nematic phases coexist, which we found to be at 24 v/v% for the charged gibbsite and 21 v/v% for the sterically stabilized gibbsite. A second sample of the charged stabilized gibbsite was prepared at a higher concentration (30 v/v%), where the isotropic, nematic, and columnar phases coexist. The tactoids in these two samples showed no significant differences. Samples of the homogenized suspensions were prepared in flat glass capillaries (VitroCom) with internal dimensions of $0.2 \times 4 \times 40\ mm^3$. The capillaries were flame-sealed and glued to prevent evaporation of the solvent and were subsequently kept in vertical position.

2.3. Polarized Light Microscopy. The tactoid shape and director fields were examined with a Nikon LV100Pol polarized light microscope, equipped with a 2× Nikon CFI Plan UW objective and a 10× Nikon CFI Plan Fluor ELWD objective. The microscope was in a tilted position with the focal plane along gravity to allow investigation of the samples in vertical position. Images were captured with a MicroPublisher 5 megapixel ccd camera (MP5, QImaging).

A full-wave retardation plate (λ = 530 nm) was used to determine the director orientation. Gibbsite has a positive intrinsic birefringence, which means that the largest refractive index is parallel to the main axis of the platelets. However, in the nematic phase, there is an additional contribution from the form birefringence, which is due to the elongated particle shape and is negative because both solvent refractive indices are smaller than the refractive index of gibbsite (n = 1.57). The resulting birefringence is positive when the refractive difference with the solvent is relatively small and negative when this difference is large. Effectively, this means a positive birefringence for the gibbsite system in bromotoluene (n = 1.55) and a negative birefringence for the system in water (n = 1.33).[38]

2.4. Image Analysis. Analysis of the microscopy images of the charged gibbsite was performed with a computer program created in IDL 7.1.[39] The program was developed to sample tactoids automatically and extract the relevant properties (size, shape, director field, color) with a combination of an edge detection[40,41] and an ellipse detection[42] algorithm. Tactoids that were obviously deformed by hydrodynamic interaction with other tactoids or coalescence events are either not detected or were removed manually. The micrographs of the sterically stabilized system were measured manually with the microscopy analysis software iTEM.[43]

3. Results

Soon after homogenization of both types of gibbsite suspension, many tactoids appeared in the isotropic phase, which, dependent on the sample, either rose ("creamed") or sedimented and coalesced to form the nematic phase. In the sterically stabilized gibbsite system, the isotropic phase is, as usual, the phase with the lowest density, in contrast with the aqueous gibbsite system, where the nematic phase has the lowest density. This density inversion is caused by a fractionation effect due to a bimodal distribution of the platelet aspect ratios in this particular gibbsite system, which we discussed in a previous publication.[44] Because this fractionation results in a monomodal distribution in the nematic phase, we do not expect this to influence significantly the results.

In the initial stages, the phase separation is quite a chaotic process, and most tactoids seem to have nonequilibrium shapes due to coalescence events and the presence of flow fields in the dispersion. Therefore, we probed the properties of the tactoids only after the macroscopic isotropic−nematic interface has been formed and the tactoids remaining in the isotropic phase are far enough apart that their shape is not distorted by hydrodynamic interactions between them, which is typically after a few days to weeks. Figure 2 presents a typical polarized light image showing tactoids of various sizes and different director fields (a) just below the isotropic−nematic interface in the aqueous gibbsite system and (b) just above the isotropic−nematic interface in the sterically stabilized system.

3.1. Charge-Stabilized Gibbsite. Starting with the aqueous gibbsite suspensions, we observe that the largest tactoids are

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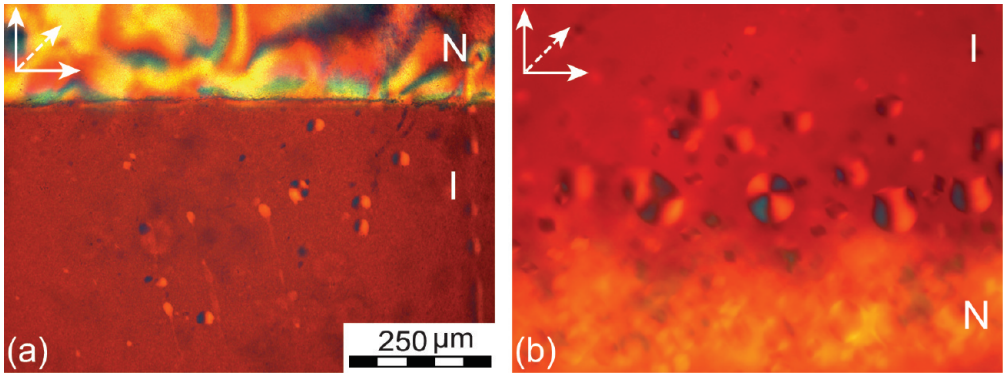

Figure 2. Nematic tactoids in the isotropic phase; just below (a) the IN-interface in an aqueous gibbsite system and just above (b) the IN-interface in a sterically stabilized gibbsite suspension. Polarizers are indicated with arrows, and the retardation plate is indicated with a dashed arrow.

spherical with a dark cross (also called a Maltese cross[45]) parallel to the polarizers, which rotates with the polarizers, indicating alignment of the particles parallel to these as well as the presence of rotational symmetry (Figure 3a,b). With the retardation plate inserted (Figure 3c), two opposite quarters appear as blue, whereas the other quarters are orange. The blue color corresponds to an addition of the optical path difference (largest refractive index parallel to the retardation plate), whereas orange corresponds to a subtraction (largest refractive index perpendicular to the retardation plate).

Because in aqueous gibbsite suspensions the birefringence is negative, this implies that the platelets are aligned with their director perpendicular to the interface and, in other words, exhibit homeotropic anchoring. Combining all of this information, we deduce that large tactoids in the aqueous gibbsite system have a radial director field with a hedgehog point defect near their center, see Figure 3d. For the tactoid shown in the micrographs presented in that Figure, the point defect is located somewhat off-center and as we observed this tactoid to move upward with time; this means that it is offset in the direction of the rear with respect to the translation direction. As we shall see, we also observe a similar phenomenon for tactoids with different director field structures. We attribute this to the influence of the flow fields caused by the sedimenting and creaming of the droplets in, respectively, the charge- and sterically stabilized systems. We return to this below.

Tactoids of smaller size in aqueous suspensions of colloidal gibbsite can have various appearances. Two representatives of droplets somewhat smaller than the ones that have a radial director fields are shown in Figure 3e−l. Focusing on the first one, which is only occasionally observed and shown in Figure 3e−h, one might surmise that this tactoid must have a hole through the center or even exhibit a toroidal shape, but this would seem energetically very unfavorable. A more plausible explanation of the extinction pattern is that in Figure 3e,g the director lines in the central part point into the image, in which orientation the nematic phase is not birefringent. This would correspond to an axial director field with a ring disclination, as drawn in Figure 3h, which in Figure 3e,g we observe in top view. In Figure 3f, the axial part is parallel to the polarizer and therefore also not birefringent. Below, we will observe this kind of director-field configuration in side view for the sterically stabilized gibbsite system, where it is more common.

More frequently observed is the distorted oblate-shaped tactoid displayed in Figure 3i−l. These tactoids have an asymmetric radial director field emanating from a point (or a small ring) defect at the edge of the tactoid. Because the dark bands in Figure 3j are slightly curved, there might be some bend deformation present as well, consistent with the director field drawn in Figure 3l. The tactoids in this system are creaming, and the defect is always located at their lower edge, in other words, at the rear end with respect to the translation direction. Occasionally, we find that if such a tactoid collides with another one, it rotates, and the top view can be observed, revealing a circular radial pattern. In that orientation, it becomes indistinguishable from a spherical tactoid with a radial director field. The anchoring with the interface in this peculiar configuration is clearly suboptimal, to be discussed further in the next section.

The smallest tactoids in the aqueous gibbsite system, as depicted in Figure 3, clearly have a different appearance. They have an ellipsoidal shape with rounded edges and are either entirely birefringent or nonbirefringent, depending on the orientation of the polarizers. This can only mean that the director field is uniform. Moreover, the aspect ratio of the droplets is independent of their size, which is another indication that these tactoids must have a uniform director field.[10] From the image taken with the retardation plate (Figure 3o), we conclude that the director must be oriented perpendicular to the major droplet axis, which is to be expected because in that configuration a larger fraction of the platelets has the preferred homeotropic alignment with the interface. This then also implies that for symmetry reasons these tactoids must have an oblate shape. The fact that we never observe a circular shape, which is the appearance of an oblate viewed from the top, is explained by the fact that the tactoid is not birefringent in top view. As we will see in the next section, the aspect ratio of this oblate-shaped tactoid contains interesting information because it solely depends on the ratio of the anchoring energy and the interfacial tension between the isotropic and nematic phases.

3.2. Sterically Stabilized Gibbsite. We now turn to the various tactoid shapes and director fields that we find in suspensions of sterically stabilized gibbsite, a system with similar behavior to that of the charged-stabilized gibbsite but also with marked differences. We start again with the largest tactoids, a typical example of which is shown in Figure 4a−c. The Maltese cross can be observed again, and like in the previous case of aqueous gibbsite, the tactoids are spherical with a radial director field and a hedgehog defect in the center (Figure 4d). Note that the retardation colors are reversed (Figure 4c) as a result of the positive birefringence of colloidal gibbsite in bromotoluene.[38]

Figure 4e−h shows a typical tactoid of intermediate size in the sterically stabilized gibbsite system. The tactoid still has a spherical shape, but the Maltese cross, typical for the radial director field of the large tactoids, has now opened (Figure 4f). Together

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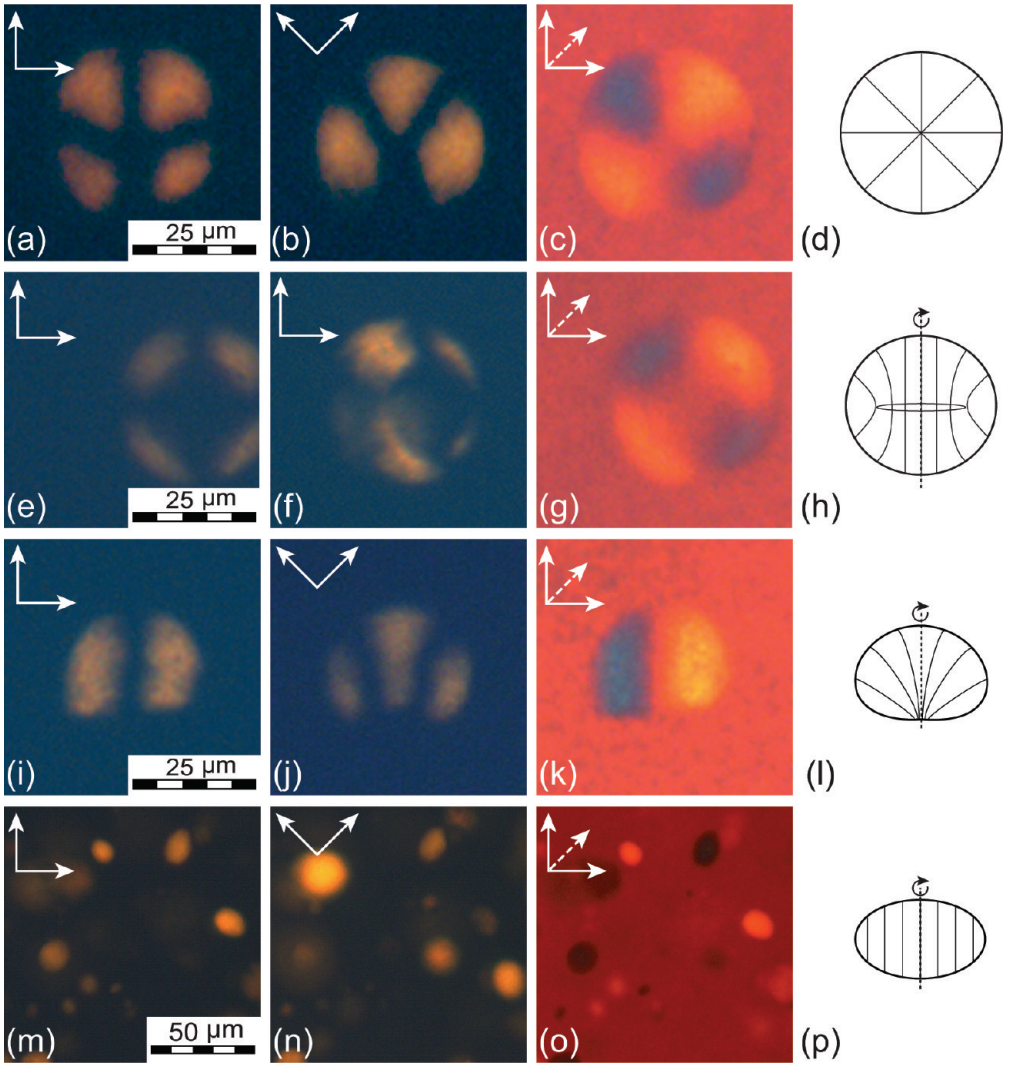

Figure 3. Nematic tactoids in aqueous gibbsite system imaged with polarized light microscopy with a sketch of the director field configuration in the final row. Polarizers are indicated with solid arrows, and the retardation plate is indicated with a dashed arrow. Large tactoids (a−d) are spherical with 3D splay director field and a point defect in the center. Tactoids of intermediate size are either spherical with an axial director field and ring disclination (e−h) or oblate-shaped with an asymmetric radial director field (i−l). The smallest tactoids (m−p) have an oblate shape and uniform director field.

with the image of the polarizers in horizontal−vertical orientation and with retardation filter (Figure 4e,g), we conclude that the intermediate tactoid has an axial director field with a ring disclination positioned off-center, near the upper part of the tactoid. In the sterically stabilized system, the tactoids slowly sediment toward the macroscopic isotropic−nematic interface, which means that this ring disclination is located away from the translation direction, similar to what we observed in the aqueous gibbsite system.

Small tactoids in this system, shown in Figure 4i−l, appear rather different from the small tactoids that we found in aqueous gibbsite. They seem more lens-shaped and clearly have a nonuniform director field. When the polarizers are parallel to the droplet axes, a nonbirefringent cross is observed parallel to the polarizers. Rotation of the polarizers of 45° makes the droplet (almost) completely birefringent, and this birefringence is much more intense. Furthermore, the image taken with a retardation plate (Figure 4k) reveals that the director is again perpendicular to the tactoid interface, implying homeotropic anchoring.

From these observations, we deduce an axial director field, as drawn in Figure 4l. The director pattern is not exactly symmetric with respect to the equator; the lower part is somewhat larger. We will return to this in the discussion. We have not observed a tactoid with a uniform director field in this system but this might be simply because we have not been able to analyze tactoids $< 10\ \mu$m because of the poor contrast as a consequence of the small birefringence in this system.

If we consider all of the observed tactoid shapes and director fields, then we envisage two pathways for the transition from a radial to a uniform director field:

1 Via the opening of the point defect into a ring disclination. Upon decreasing tactoid size, this ring defect increases in diameter. As it becomes larger, the tactoid shape adapts by flattening the droplet so that the anchoring conditions are met. This ultimately leads to the observed lens-shaped tactoids with axial director field, where the ring defect runs along the equator. Finally, we expect the ring defect to become virtual, leading to a uniform tactoid where the radius of the virtual defect is large compared with the size of the drop.
2 Via the displacement of the central point defect. With decreasing tactoid size, the point defect moves toward the edge of the tactoid. This may induce a flattening in

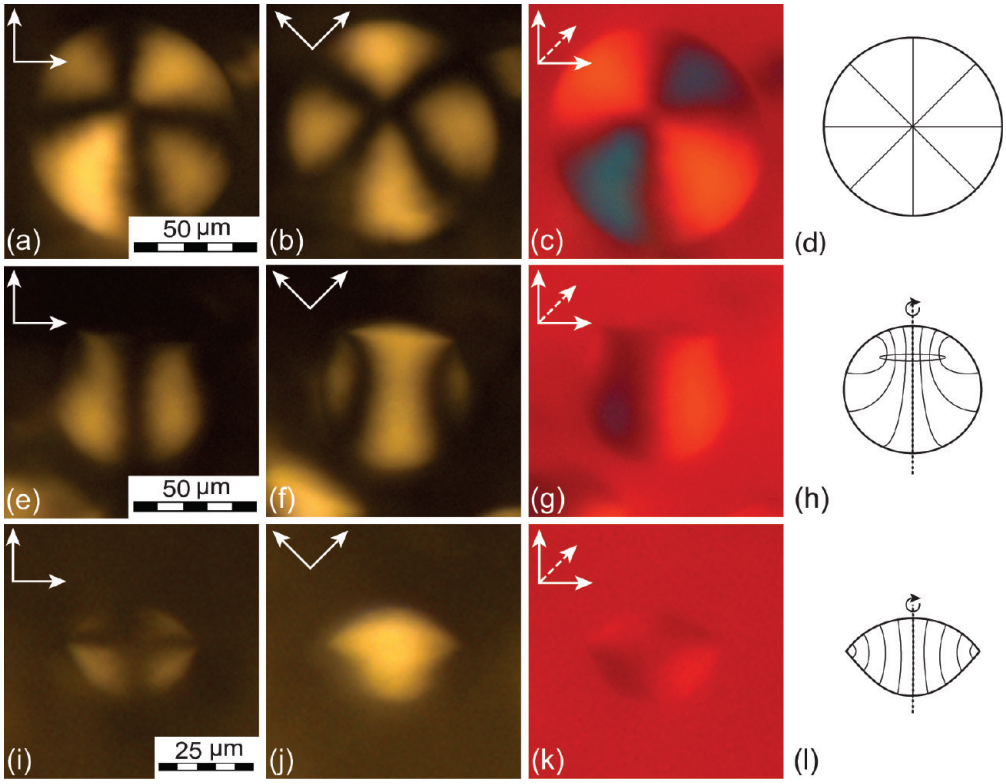

Figure 4. Nematic tactoids in a suspension of sterically stabilized gibbsite imaged with polarized light microscopy, with a sketch of the director field configuration in the final row. Polarizers are indicated with solid arrows, and the retardation plate is indicated with a dashed arrow. Large tactoids (a−d) are spherical with a 3D splay director field and a point defect in the center. Tactoids of intermediate size (e−h) are spherical with an axial director field and an out-of-center ring defect. The smallest tactoids (i−l) are lens-shaped with an axial director field.

the droplet shape due to suboptimal anchoring and to the introduction of a bend deformation of the director field to counteract this further. For yet smaller tactoid sizes, the defect becomes virtual, yet the characteristic radial director field approximately survives in the drop. In the limit where the virtual defect is infinitely far removed from the drop, the director field becomes truly uniform.

The first transition pathway was mainly observed in the sterically stabilized system, although a ring disclination was also observed occasionally in aqueous gibbsite suspensions. The second pathway was mainly observed in aqueous gibbsite suspensions; although the defects in the sterically stabilized gibbsite were sometimes also out of the tactoid center but never at the tactoid edge. We will come back to these asymmetric defects in the discussion below.

4. Analysis

Now that we have identified the various director fields and tactoid shapes present in suspensions of colloidal gibbsite, we proceed to analyze these tactoids quantitatively to obtain useful material properties from the observations. To begin with, and as previously alluded to, the crossover tactoid size from a uniform to a radial director field is set by the so-called extrapolation length $\xi \equiv K_1/w$, that is, the ratio of the splay elastic constant, K_1, and the anchoring strength, w. So, by finding the crossover size, we can establish a value of this length scale.

Before doing that, it is useful to recall how this follows from a simple free-energy analysis, presuming for simplicity that the drops are spherical, even though that this is not quite the case. If the interfacial energy σ has the familiar Rapini−Papoular form, then $\sigma = \gamma + w \sin^2\phi$, where γ is the bare surface tension and ϕ is the angle between the surface normal and the director field at the surface.[1,46] A straightforward calculation now shows that the anchoring energy associated with a uniform director field then equals $(8/3)\pi w R^2$, where R is the tactoid radius, whereas the elastic deformation energy of the radial director field is $8\pi K_1 R$.[47] The free energy associated with the surface tension is the same for both configurations, so the radial director field is adopted if the anchoring energy of the uniform director field exceeds the elastic energy of the radial field, which happens if $R > 3\xi$. So, using this inequality, we can deduce the value of ξ if we know R.

Of course, from the experiments, we know that the tactoids with a uniform director field are not quite spherical but oblate. A slightly better estimate may be obtained by invoking the Wulff construction that gives the optimal shape for a homogeneous configuration.[25,48,49] Indeed, we do find a lower free energy than that for the sphere and, as a consequence, a slightly higher bound than $R > 3\xi$ for the radial field to take over from the uniform one.[34] However, the difference is so small that our estimate presuming a spherical shape remains excellent for the smallish aspect ratios found here.

To find the crossover radius from the experiments, we present a histogram of all of the observed tactoid shapes and director fields as a function of size in Figure 5 for both systems of charge- and

[1] The interfacial free energy of coexisting isotropic and nematic phases in dispersions of rod-like particles seems to follow the Rapini−Papoular form, as was recently determined by an inverse Wulff construction for tactoids of carbon nanotubes.[8]

(46) Rapini, A.; Papoular, M. J. *J. Phys., Colloq.* **1969**, *30*, 54−56.
(47) Dubois-Violette, E.; Parodi, O. *J. Phys., Colloq.* **1969**, *4*, 57–64.
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(49) Virga, E. G. *Arch. Ration. Mech. Anal.* **1989**, *107*, 371–390.

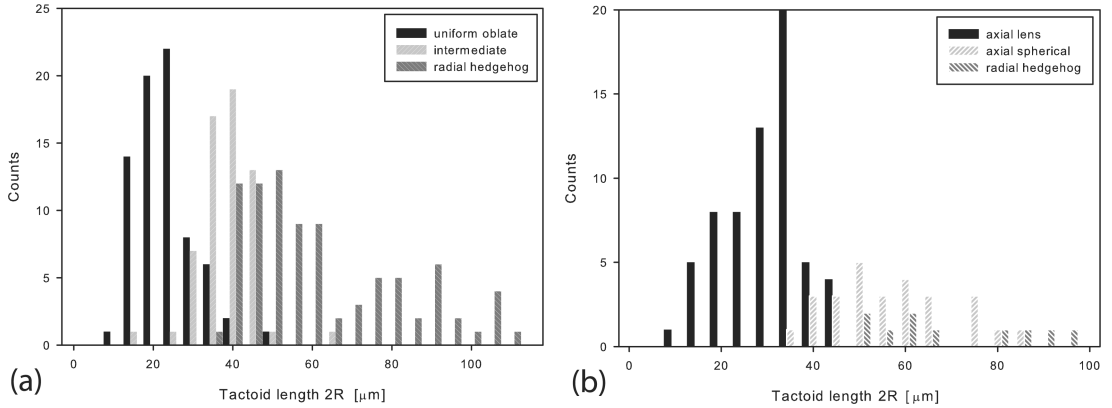

Figure 5. Histograms of the observed tactoid shapes and director fields as a function of size in (a) an aqueous suspension of charged gibbsite and (b) a suspension of sterically stabilized gibbsite in bromotoluene.

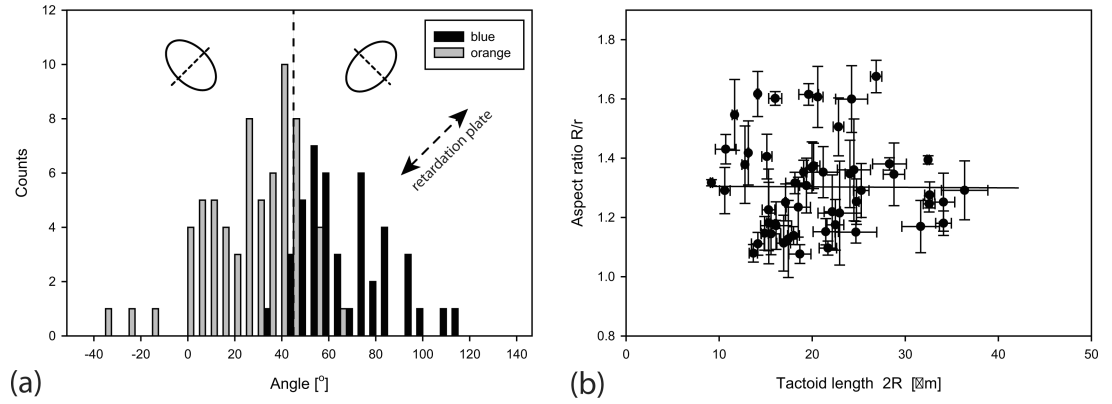

Figure 6. (a) Interference color of uniform tactoids in the aqueous gibbsite system as a function of the angle of the tactoid symmetry axis with respect to the retardation plate. See also the main text. (b) Aspect ratio R/r as a function of length of small uniform tactoids in the aqueous gibbsite system. The line represents a least-squares fit of a horizontal line at $R/r = 1.3 \pm 0.07$.

sterically stabilized gibbsite. Interestingly, in the charged gibbsite system, the size ranges of the uniform and radial tactoids both overlap with the size range of the intermediate tactoids, but they hardly overlap each other. This allows for a fairly accurate determination of the crossover tactoid size. What we have to keep in mind, though, is that the intermediate tactoid with the defect at the edge has a radial appearance in top view, so that occasionally an intermediate tactoid might have been identified as a radial tactoid.

We therefore determined the crossover tactoid size from radial to uniform from the largest uniform tactoid, which has a size $2R = 36$ μm, resulting in a value for the ratio $K_1/w = 6$ μm. Although for the sterically stabilized gibbsite system, we cannot accurately determine K_1/w because we have not been able to observe tactoids with a uniform director field, the lack of this observation provides us with an upper bound for K_1/w, being $K_1/w < 2$ μm. These rather different values seem to point to quite different surface and elastic properties of nematic phases of the two types of system. Note that in both systems we do see for a range of sizes coexistence of the different tactoid shapes and director field structures, which means that in this crossover regime the free energy difference between the different structures must be small, as is to be expected.

The shape of the uniform tactoids in the aqueous gibbsite system provides us with additional information. First, we measured the color of these tactoids as a function of the angle of their symmetry axis with respect to the retardation plate. Recall that if the nematic director is parallel to the retardation plate, then the tactoid will appear blue, whereas in the perpendicular orientation it will appear orange. The histogram in Figure 6a clearly shows that the droplets with their symmetry axis parallel (−45 to 45°) to the retardation plate mostly appear orange, whereas the tactoids in perpendicular orientation (45−135°) are blue. This means that the nematic phase indeed has its director parallel to symmetry axis of the droplet, as is to be expected for the case of homeotropic anchoring.

As we already mentioned, the aspect ratio of the uniform tactoids contains information on the anchoring strength. From the Wulff construction,[25,48] it follows that the ratio, R/r, of the long and short axes of the oblate shapes is determined only by the ratio of the anchoring strength and the surface tension w/γ[26,27,49]

$$R/r = \begin{cases} (w/\gamma)+1 & \text{if} \quad 0 < w/\gamma < 1 \\ 2\sqrt{w/\gamma} & \text{if} \quad w/\gamma > 1 \end{cases} \qquad (1)$$

These two equations reflect the transition from an oblate droplet for values of $0 < w/\gamma < 1$ to a lens shape with a sharp rim for $w/\gamma > 1$.

In Figure 6b, the aspect ratio of the tactoids is plotted as a function of tactoid size, showing a cloud of data points without correlation. So, the aspect ratio is independent of the tactoid size, as should be the case for tactoids with a uniform director field. The horizontal line is obtained from a least-squares fit resulting in an average value for $R/r = 1.3$ (± 0.07). From this we find that $w/\gamma = 0.3$. The huge spread in the aspect ratio is indicative of an (ultra)low interfacial tension but is here also partially caused by

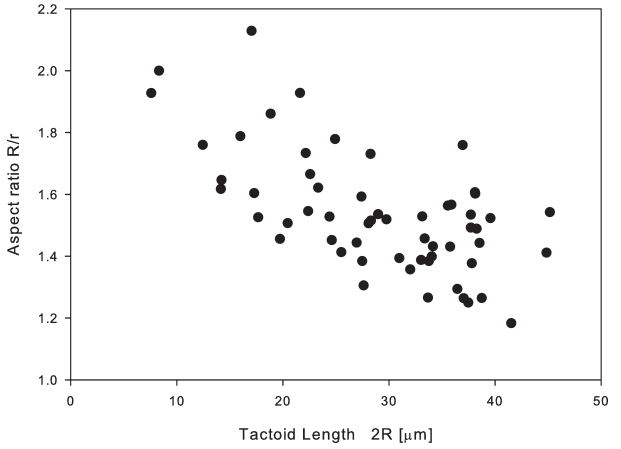

Figure 7. Aspect ratio R/r of the small, lens-shaped tactoids in suspensions of sterically stabilized colloidal gibbsite.

the fact that with polarization microscopy, which is based on transmission, we measure a 2D projection of a 3D object in different orientations. Therefore, the average aspect ratio found by the fit is probably too low, although we are aided by the fact that the tactoids are practically invisible (not birefringent) if viewed from the top and, on the other hand, have the largest contrast when viewed from the side. Hence, a better estimate for the aspect ratio would be 1.6, which provides us with a value of $w/\gamma = 0.6$. This is in line with what could be expected given the oblate shape of these tactoids.

Now that we have a value for the ratio w/γ, we are also able to determine the interfacial tension between coexisting isotropic and nematic phases in aqueous gibbsite suspensions, γ, because in previous work we determined the anchoring strength $w = 4 \times 10^{-8}$ N/m from the deformation of our tactoids in a magnetic field.[34] This produces a surface tension of $\gamma = 7 \times 10^{-8}$ N/m, which indeed is quite low.

For the sterically stabilized gibbsite, the aspect ratios of the lens-shaped tactoids that we measured as a function of size is depicted in Figure 7. In contrast to the aqueous gibbsite, where the aspect ratio of uniform tactoids was a constant of size, there is a clear trend of a decreasing aspect ratio with increasing tactoid size. This is to be expected, of course, because in this case the drops are not quite uniform but have an axial director field, and because the largest drops that have a radial director field are spherical.

Although there is no prediction available giving the relationship between the aspect ratio and the tactoid size in the case of an axial director field, we can still obtain a lower bound for w/γ from the largest aspect ratio observed. The aspect ratio of uniform tactoids in this system (which, again, we have not found in our experimental setup) should be larger than the largest aspect ratio found for tactoids with an axial director field. This means that the aspect ratio of uniform tactoids should be > 2.2, which via eq 1 provides us with a lower bound for $w/\gamma > 1$, in agreement with the value $w/\gamma = 2$ that we found in previous work from the deformation behavior of such tactoids in an external magnetic field.[34] Again, we see that the properties of dispersions of gibbsite are fairly sensitive to the mode of colloidal stabilization, even if they seem to behave as hard particles.

5. Discussion

An observation in our view worthy of some discussion concerns the shapes and director fields of the intermediate tactoids, and, in particular, their asymmetric nature. We know from the literature

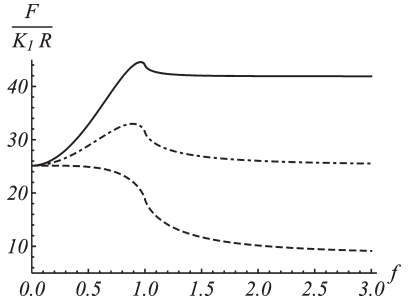

Figure 8. Free-energy, F, of a spherical drop with a point defect with radial director field as a function of the location of the defect. F has been made dimensionless by dividing it by K_1R, where K_1 is the splay elastic constant and R is the tactoid radius. The defect is located a distance fR from the drop center, such that for $f = 0$ it is in the center, for $f = 1$ it is on the boundary, and for $f \rightarrow \infty$ it lies at infinity, giving a uniform director field in the drop. Shown are the free energies for $Rw/K_1 = 1$ (dashed), 3 (dotted-dashed) and 5 (solid). For $Rw/K_1 = 3$, the configurations with central defect and the uniform director field have the same free energy.

that transitions of the director structure can involve exotic structures such as those observed by Volovik and Lavrentovich, who established that the transition from a radial to a bipolar director field upon changing the boundary conditions also involves asymmetric hedgehog defects and disclination rings.[50] We focus, in particular, on the oblate tactoid with a point (or small ring) defect off center, that is, at or near the symmetry axis of the drop but away from its center of mass.

Let us first, for simplicity, presume that this drop is more-or-less spherical and consider the second route from a radial director field to a uniform field we put forward in the introduction. The change of the free energy of a radial nematic drop that occurs if we displace the point defect from the center of the drop to the boundary and ultimately place it infinitely far away from the drop is straightforward to calculate within the usual macroscopic description if we presume that the (virtual) director field remains radial in the process. Not surprisingly, we find that the elastic free energy of the drop is lowered by displacing the defect away from the center until it has half of its original value if at the boundary of the drop. However, displacing the core of the defect goes at the expense of the introduction of an anchoring free energy, which is zero if it resides in the center of the drop. If the defect moves outside the droplet, then the anchoring cost increases further, albeit the elastic energy decreases further until it vanishes completely at infinity. In that case, the director field inside the drop has effectively become uniform.

Our calculations show that no configuration in which the hedgehog defect is not in the center or at infinity can be a free-energy minimum; see also Figure 8. So, to go from the radial field to the uniform field, a free-energy maximum has to be overcome associated with a configuration where the defect is close to the surface of the tactoid. The argument remains valid for nonspherical drops as well because the more realistic lens shape associated with the uniform field has a lower free energy than a sphere considered before, making a defect even more unfavorable. This is confirmed by a calculation, in which we fixed a defect on the surface of the drop and optimized the shape of the drop, presuming the deviation from the spherical shape remains small. We find that the configuration with a surface defect never has the lowest free energy of the three for a given tactoid size and anchoring strength, w/γ. So, we conclude that the boundary

(50) Volovik, G. E.; Lavrentovich, O. D. *J. Exp. Theor. Phys.* **1983**, *58*, 1159–1166.

hedgehog must be an unstable configuration, at least for pure splay fields. We speculate that its occurrence must be caused by the effects of the flow field around the creaming tactoid, as discussed in Section 3.1.

In fact, it is well known that flow fields can considerably distort the director field in tactoids.[51] The fact that the defect is consistently located at the rear of the tactoid is a strong indication that this effect plays an important role here, too. Also, the shape of the intermediate tactoid in Figure 3i−l strongly resembles the shape of a sedimenting drop of an isotropic fluid in another isotropic fluid, where an initially oblate-shaped droplet develops to an asymmetric oblate, very similar to what we observe at Bond numbers (*Bo*, defined as the ratio of gravitational and surface forces) of 10−20 and a viscosity ratio of ∼1.[52] If we estimate the Bond number for tactoids with this director field in our system, then we obtain values in that range.[2]

The other intermediate director field structure, the one with a ring disclination, is also interesting from theoretical point of view. Such a ring disclination is in fact unstable unless it is very small,[53,54] the reason being that it is under tension. In our case, it might be stabilized because of the confinement by the droplet and the interaction of the director field with the surface. In fact, this director-field configuration has been observed before as an intermediate in the transition from a radial to uniform director structure in thermotropic liquid crystals of E7 confined to spherical cavities of decreasing size.[31]

We end this section with a comparison of our findings with results we obtained previously from the deformation of tactoids in a magnetic field,[15,34] summarized in Table 1. We conclude that the values for K_1/w we obtained via the two methods are in good agreement for both sterically stabilized and charged gibbsite. The value for $w/\gamma = 0.6$ that we find for aqueous gibbsite from the aspect ratio of the uniform tactoids is larger than the estimate close to zero obtained from the deformation behavior by magnetic field. The latter was based on the observation that the tactoids remained spherical even at high magnetic field strengths. However, if we closely examine the calculated phase diagram in that paper for $w/\gamma = 0.5$, close to what we find here, a tactoid elongation of 3 to 5% is expected, which we could have easily missed in our previous experiments.[34] So, the apparent discrepancy does not seem to be a real one. Note that the lower bound we find for w/γ for sterically stabilized gibbsite is in very good agreement with our results obtained from the tactoid deformation in a magnetic field.[34]

If we compare the two gibbsite systems, then it is clear that the surface anchoring of the director field in our aqueous gibbsite dispersions is considerably weaker than that of the sterically stabilized gibbsite dispersions. Because the elastic splay constant K_1 seems to have a comparable value in both systems,[34] K_1/w must also be significantly smaller in sterically stabilized than in the charge-stabilized gibbsite. The values for the bare interfacial tension that we deduce from our measurements are also larger in the sterically stabilized than in the charge-stabilized system.

Table 1. Values for K_1/w, γ, and w/γ As Obtained from Analysis of Tactoid Shape and Director Field As a Function of Size and Compared to Previously Published Values Obtained from the Deformation of Tactoids in an Externally Applied Magnetic Field

		tactoid shape and director field	tactoid deformation in a magnetic field
K_1/w [10^{-6} m]	charged	6	5
	steric	2[a]	0.3
w/γ	charged	0.6	≪1
	steric	1.1[b]	2
γ [10^{-7} N/m]	charged		0.7[c]
	steric	−	1.3

[a] Upper bound. [b] Lower bound. [c] Value for γ of aqueous gibbsite was determined by combining results of the two methods.[15,34]

Theoretically, these differences in the behavior of our two types of system are hard to rationalize. The reason is that both should and seem to behave more or less as hard-platelet systems. Indeed, with an ionic strength of 10^{-2} M, the Debye screening length of the charge-stabilized gibbsite dispersion is ∼3 nm, whereas the thickness of the stabilizing polymer layer of the sterically gibbsite platelets is ∼4 nm.[55] A naive rescaling of the charged platelet dimensions that effectively includes the impact of the Debye length and the stabilizing brush height, respectively, would clearly not sufficiently explain the differences. Clearly, a deeper theoretical (or simulational) investigation of the influence of the electrostatic interaction on the liquid-crystalline properties of plate-like systems would be very helpful.

Interestingly, the interfacial tensions that we find for the coexisting isotropic and nematic phases in dispersions of charge- and sterically stabilized gibbsite are two orders of magnitude larger than the one previously found for a comparable system from capillary rise experiments.[24] The origin of this large difference is unclear, but it might partially be due to the different stages in which the respective experiments are carried out. Our tactoid experiments were carried out when the phase separation process is not quite finished, whereas the capillary rise experiments require a fully equilibrated sample where all tactoids have sedimented and the different domains in the nematic phase have annealed. Such an equilibrated sample might very well have a higher order parameter. Whereas elastic constants are generally accepted to be proportional to the square of the scalar order parameter of the nematic, the anchoring strength is linear in this order parameter.[20] This implies that a higher order parameter would lead to a larger value for the extrapolation length. Moreover, during the equilibration, a sedimentation equilibrium might have started to develop, which would change the concentrations in the coexisting phases and, as a consequence, also change the elastic and surface properties of the nematic.

Finally, the question arises why the transition from radial to uniform director field follows different pathways in the two systems studied here. We put forward that this might be due to differences on the one hand in the anchoring strength and on the other hand in the relative magnitudes of the splay and bend elastic constants. This is because for the intermediate tactoid with the defect on or near the tactoid edge, the anchoring conditions are only partially met, and hence it is understandably more present in the aqueous gibbsite system where anchoring is weak. Also, the intermediate structure with the ring disclination involves a stronger bend deformation than the asymmetric defect structure does and is more splay deformed. This suggests that for the sterically stabilized gibbsite, where this ring disclination is mostly observed,

(51) Fernandez-Nieves, A.; Link, D. R.; Marquez, M.; Weitz, D. A. *Phys. Rev. Lett.* **2007**, *98*, 087801.
(52) Stone, H. A. *Annu. Rev. Fluid Mech.* **1994**, *26*, 65–102.
[2] The Bond number is defined as $Bo \equiv \Delta\rho g R^2/\gamma$, where $\Delta\rho$ is the isotropic−nematic density difference, g is the gravitational acceleration, R is the droplet radius, and γ is the isotropic−nematic interfacial tension. For tactoids with the asymmetric hedgehog defect, we find that depending on the tactoid size, Bo varies from 5 to 15.
(53) Terentjev, E. M. *Phys. Rev. E* **1995**, *51*, 1330–1337.
(54) Kléman, M.; Lavrentovich, O. D. *Soft Matter Physics: An Introduction*; Springer: New York, 2003.
(55) van der Kooij, F. M.; Kassapidou, K.; Lekkerkerker, H. N. W. *Nature* **2000**, *406*, 868–871.

the bend elastic constant might be relatively smaller. Obviously, without any quantitative measurements of the various elastic constants, this remains pure speculation and further study is needed.

6. Conclusions

We have studied the shape and director field of nematic tactoids as a function of size in suspensions of charged gibbsite in water and sterically stabilized gibbsite in bromotoluene. The properties of the tactoids are determined by a competition of interfacial and elastic free energies, which because of homeotropic anchoring of the platelets leads to an oblate shape with a uniform director field for small tactoids, whereas large tactoids are spherical with a radial director field. In our studies, we observed various intermediate tactoid structures, from which we deduce two different pathways for the transition from a radial to a uniform director field.

The route found mostly in sterically stabilized gibbsite proceeds via the opening of the central point defect to a ring defect of increasing size with decreasing tactoid size, leading to a lens-shaped tactoid with axial director field where the ring defect runs along the equator and eventually to a uniform director field when the defect is much larger than the tactoid. In the other pathway, mainly observed in the aqueous gibbsite dispersion, the central point defect moves to the edge of the tactoid, accompanied by a flattening of the droplet shape, until for even smaller tactoid size the defect becomes virtual, resulting in an oblate tactoid with a (for all intents and purposes) uniform director field.

From a quantitative analysis of the shape and director field of our tactoids, we have been able to extract values for the ratio of the splay elastic constant and the anchoring strength as well as the ratio of the anchoring strength and the surface tension, showing that aqueous gibbsite exhibits weak and sterically stabilized gibbsite strong anchoring of the platelets to the isotropic−nematic interface, all in agreement with results obtained from our previous studies of the deformation of nematic tactoids in dispersions of gibbsite in an externally applied magnetic field.[34] The observed differences in transition pathways for charged and sterically stabilized gibbsite can be attributed to this difference in anchoring strength and possibly also partially to different magnitudes of the splay and bend elastic constants.

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