The isotropic-nematic interface of colloidal goethite in an external magnetic field

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Polarization microscopy was used to study the behavior around the isotropic-nematic interface of colloidal goethite dispersions in a magnetic field. It has been found before that the nematic phase is favored in an external field. In the case of goethite this was also observed; nematic droplets formed inside the isotropic phase and coalesced with the nematic phase. However, the behavior was found to be much richer because of the particle rotation around a certain critical field strength. The simultaneous occurrence of (parallel)nematic-(perpendicular)nematic phase separation under the influence of a magnetic field also plays a role here. © 2010 American Institute of Physics. [doi:10.1063/1.3498738]

I. INTRODUCTION

Anisometric mineral particles can form all kinds of liquid crystalline phases depending on their concentration in suspension. Since these particles also have a high susceptibility to external fields, they can easily be manipulated.1,2

The isotropic (I) to nematic (N) phase transition was already described by Onsager3 in 1949, who developed an entropy-based theory. It has long been predicted that an external field, which aligns the particles, will facilitate a phase transition from the isotropic to the nematic phase4 and phase diagrams based on the Onsager theory were given by Khokhlov and Semenov.5 A number of density functional approaches have been used to describe this phase behavior of anisometric particles in an external field.6–8 Experimental evidence was found in fd virus suspensions9 and later also in gibbsite dispersions.10 For the virus particles, very large fields of about 20 T were used to observe this transition, while for the inorganic gibbsite, much lower fields of a few tesla were sufficient to observe an increase in the amount of nematic phase.

Boardlike colloidal goethite (α-FeOOH) particles are very sensitive to external fields. About 100 years ago, Majoran et al. examined the magnetic-field-induced birefringence of the “fer de Bravais,” a mixture of various iron oxide and hydroxide particles in suspension, one of which was goethite. They observed a nonmonotonical dependence of the birefringence on the field intensity.11,12 A positive birefringence was measured in small fields, then it reached a maximum after which it decreased again to reach even negative values. This effect was attributed to the fact that the dispersion consisted of a mixture of iron oxide and hydroxide particles, giving different contributions to the birefringence. Recently, Lemaire et al. studied the properties of pure goethite in dispersion. They found that similar birefringence effects were also observed for this dispersion.13 It was concluded that the particles possess not only a permanent magnetic moment along their long axis but also an enhanced susceptibility along their shortest axes. This induces an alignment along the field in low fields (up to about 250 mT) and an alignment perpendicular to higher fields.

These two different types of reaction to a magnetic field have been theoretically described by Khokhlov and Semenov.5 In a field the I phase aligns and is then called paranematic (pN). For the case of parallel alignment (dipolar), it was found that the pN+ and N+ phases have a uniaxial symmetry. The first-order pN+−N+ coexistence region terminates in a critical point above which the system changes from one state to the other continuously. In the situation that the particles align perpendicular to the field (be it dipolar or quadrupolar), the behavior is somewhat different. In the perpendicularly oriented N phase, the rods pack more favorably if they attain an additional direction of alignment within the plane. Therefore, the N phase actually becomes biaxial. The first-order pN+−N+ transition terminates in a tricritical point. Beyond this point, there is a second-order transition between the two phases. In both scenarios, in a magnetic field the N phase is favored over the I phase.

An idealized theoretical model for the behavior of goethite, based on the combination of these two situations, was developed by Wensink and Vroege.14 Goethite particles were represented by monodisperse, charged spherocylinders; the calculated phase diagram can be seen in Fig. 1. It gives a good qualitative picture of their behavior. The dashed line in the paranematic region represents the situation where the distribution of particle orientations is spreading out and the order parameter is zero. The upper dotted line shows the second-order phase transitions from the uniaxial pN+ phase...
magnetic properties of the system.\textsuperscript{14}

other scenarios are possible depending on the density gradient a color spectrum is visible within the aligned phases.


to the $N_b^-$ phase. The dotted line between the $N^+$ and $N_b^-$ phases indicates a sudden reorientation. The phase diagram shows indeed the reorientation from parallel to perpendicular to the field as well as the transition from the uniaxial to biaxial nematic phase. Furthermore, the nematic phase is favored over the paranematic phase in a magnetic field. A tricritical point exists where the $pN^--N_b^-$ transition becomes second-order. Other scenarios are possible depending on the magnetic properties of the system.\textsuperscript{14}

The exact shape of a goethite particle was not taken into account in the theory. The fact that the particles are actually boardlike (with three different dimensions) makes the biaxiality of the $N_b^-$ phases stronger. Induced biaxiality is always observed in fields higher than about 250 mT since the particles have the highest susceptibility along their shortest axis, so they align with their shortest particle axis along the field. Particles with specific particle dimensions even show spontaneous biaxiality.\textsuperscript{15,16}

It was found before that $N-N$ phase separation occurs when a magnetic field is applied around the critical field where particles rotate from parallel to perpendicular to the field.\textsuperscript{17} The two nematic phases have different orientations, parallel and perpendicular to the field. The lower, perpendicular one was found to be biaxial. This phase might be denser because the particles can pack closer in the biaxial nematic phase. In this article mainly the behavior of goethite around the $I-N$ interface in a magnetic field will be discussed, based on results from polarization microscopy. The behavior of $I-N$ phase separated plateletlike particles in a magnetic field, including gravity, has been theoretically described by Reich and Schmidt,\textsuperscript{18} who calculated the birefringence colors observed by polarization microscopy. Because of the density gradient a color spectrum is visible within the aligned phases.

II. EXPERIMENTAL

A. Synthesis

The particles used are the same as the g29 system discussed in Ref. 17. It was obtained by hydrolysis of iron nitrate at high $pH$ according to Lemaire et al.\textsuperscript{19} 800 ml of a 0.1M Fe(NO$_3$)$_3$ solution (Acros, $pH$) was mixed with 1M NaOH (Merck, p.a.), while stirring, until $pH$ 11 was reached. As the NaOH was added to the Fe(NO$_3$)$_3$ solution, a dark-brown precipitate formed. The mixture was then centrifuged for 30 min (Beckman Coulter Avanti J-20XP, rotor JLA-8,1000, 6000g), the supernatant was removed, and the particles were redispersed in 800 ml millipore (mp) water. 1M NaOH was added to bring the solution at $pH$ 12 and the suspension was put into the oven, for a day, at 70 °C. The solution was taken out of the oven and the supernatant was removed. The particles were redispersed in 750 ml mp water and centrifuged at 6000 g for 30 min. The centrifuging procedure was followed twice. After the last centrifugation step, the particles were redispersed in 250 ml of 3M HNO$_3$ (Merck, 65%) to electrostatically charge the particles by proton adsorption. The solution was centrifuged again at 6000 g for 30 min and redispersed in 750 ml mp water. The procedure was performed three times. Following the third centrifugation step, the particles were redispersed in 250 ml mp water of $pH$ 3 (prepared with HNO$_3$). Size polydispersities were determined by transmission electron microscopy using a Technai 10 and 12 (FEI company) electron microscope and iTEM imaging software.

B. Polarization microscopy

Capillaries of $0.05 \times 1.0 \times 100$ mm (VitroCom) were filled with goethite dispersions and flame sealed at both ends. They were kept in a vertical position to establish a sedimentation equilibrium profile. $I-N$ phase separation was observed within a day after preparation.

Phase separated samples were studied in a magnetic field using polarized light microscopy. A Bruker BE25v electromagnet with large flat poles was used to produce a homogeneous magnetic field (which was measured with a LakeShore 455 DSP Gauss meter with a HMMT-6J04VR Hall probe). On one side of the magnet there was a light source and a polarizer and on the other side a microscope (head of a Zeiss Axiolab microscope) with an analyzer and a 10× objective (Edmund Optics HR), connected to a CCD camera (QImaging MicroPublisher 5.0 RTV). The microscope was tilted 90° to be able to study the sample in a vertical position and observe gravity effects. The microscopy pictures shown are composed of several microscopy pictures joint together. The magnetic field is always in the horizontal direction, as depicted in Fig. 2.

III. RESULTS AND DISCUSSION

A. Parallel alignment in small fields

The particles used have dimensions of $242 \times 49 \times 17$ nm with a polydispersity of 30%. The critical field, where particles rotate from parallel to perpendicular to the field, was found to be 285 mT for this system.\textsuperscript{17} This was measured in an isotropic sample with a volume fraction of 5%. $I-N$ phase separated samples were studied at different magnetic field strengths, focusing on the behavior around the $I-N$ interface. The first measurements were performed at fields below the critical field strength. The behavior in a field of 100 mT can be seen in Fig. 2. Both the isotropic and
The nematic phase were aligned parallel to the field. The interface was first visible as a red line but it slowly became vague turning into a wider band. The nematic phase was homogeneous in this field, but in the paranematic phase interference colors could be observed (superimposed on the color of goethite itself). The different color bands are caused by a gradient in the birefringence as is presented in the Michel–Levy birefringence chart shown in Fig. 3, although with colors modified by the absorption of goethite itself. The occurrence of such a color spectrum has also been calculated before.18

Bright interference colors indicate a small birefringence, a decreasing intensity of the color bands indicates an increasing birefringence. The birefringence ($\Delta n$) in a uniaxial (para)nematic phase increases with the volume fraction ($\phi$) and the nematic order parameter ($S^2$) according to

$$\Delta n = \Delta n_{\text{sat}} \phi S^2,$$

(1)

where $\Delta n_{\text{sat}}$ is the specific birefringence (the hypothetical birefringence limit when $\phi$ and $S^2$ would be 1). For the biaxial nematic phase the relation becomes more complicated but it will not be discussed here. Since goethite has a large density (4.26 g/ml) and the particles are relatively large, there is a large concentration gradient in the sample, which causes the gradient in the birefringence.

In the nematic phase interference colors were not observed. Here, the order parameter is much larger than in the paranematic phase [typically 0.95 compared to 0.05 (Refs. 19 and 20)]. Therefore, the interference colors will be much lighter in color (see the higher orders in Fig. 3) and cannot be seen in the strongly absorbing goethite.

After switching off the field, the initial situation came back within seconds, except for the exact domain structure within the nematic phase. The pictures in Fig. 2(c) were taken 2 min after switching off the field. Right below the $I-N$ interface, interference colors were visible just after switching off the field, which indicates that there is still a gradual transition from the isotropic to the nematic phase. Within hours after switching off the field, the interference colors disappeared and a sharp $I-N$ interface was reformed.

At fields above 180 mT $N-N$ phase separation takes place.17 The upper nematic phase has an orientation parallel...
to the field and the lower nematic phase is biaxial with an orientation perpendicular to the field. At these field strengths the behavior starts to be more complicated. In Fig. 4 the behavior in a field of 200 mT can be seen. Interference colors were again observed in the paranematic phase. In the field, these bands gradually moved downward over time. This implies that the order just below the original $I-N$ interface was decreasing. The field was switched off after 7 days and it can be seen in Fig. 4(c) that the $I-N$ interface changed its position; it reformed lower than it initially was. This confirms the lower order deduced from the observation of interference bands while it was still in the field. Besides the behavior around the $I-N$ interface, it can be seen that now also that $N-N$ phase separation has taken place. The newly formed, biaxial nematic phase is apparently denser than the original nematic phase, since it forms at the bottom part of the capillary. Because of the formation of this denser phase, the total volume of nematic phase has decreased and the level of the $I-N$ interface lowered. Nevertheless, the decrease in the height of the $I-N$ interface seems to be too large to be accounted for just by the denser lower nematic phase which is still very small. This would suggest that the parallel nematic phase might also be denser than the nonaligned nematic phase.

**B. Reorientation in intermediate fields**

An interesting change in the paranematic phase was observed in a field of 250 mT (see Fig. 5 and supplementary material for a movie\(^\text{21}\)). First, small droplets formed in the paranematic phase and larger droplets in the nematic phase (8 min) and the interface between the paranematic and nematic phase was not clear for a while (1 h). Then, a new interface was formed, at a slightly higher position, while droplets were still sedimenting from the paranematic to the nematic phase (3.5 h). The movement of these droplets induced a wiggly black band which could be clearly observed after 10 h. Above and below this band, interference colors were observed. The black color indicates a region of zero birefringence and thus a spread of particle orientations. Below this black band the particles were probably oriented perpendicular to the field, and above the black band the orientation is expected to be parallel to the field. From this upper region nematic droplets sedimented to the nematic phase with the same orientation. After 3.5 days the interface between the parallel nematic phase and perpendicular paranematic phase was well developed. Within the paranematic phase, the interference bands were also better developed and the black band can be clearly seen.

The orientation of the particles within the paranematic phase was further studied with different orientations of the polarizers both in crossed and parallel configurations. Since the particles are dichroic, the absorption of light will depend on the orientation of the particles compared to the orientation of the polarizers. If the particles are oriented parallel to the orientation of the polarizers, they will absorb more light than if they are oriented perpendicular to the polarizers. A different system (216×35×16 nm with a polydispersity of 50\%) was used for these studies but it shows similar behavior. Pictures of the $pN-N$ interface after 11 days in a field of 270 mT are shown in Fig. 6. With crossed polarizers (a), birefringence color bands were clearly observed in the paranematic phase. There was again a, in this case very small, black band, as was also observed in the former experiment. The hypothesis of the different orientations above and below this band was tested by rotating the polarizers. With horizontal polarizers (b) it can be seen that the nematic phase, just below the $pN-N$ interface, is very dark. Here, the particles have an orientation parallel to the field and parallel to the polarizers. The upper part of the $pN$ phase was also

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**FIG. 4.** Polarization microscopy picture of an $I-N$ phase separated sample ($\phi=9\%)$, (a) before applying the field, (b) in a 200 mT field for 7 days, and (c) just after switching off the field.

**FIG. 5.** Polarization microscopy pictures of an $I-N$ phase separated sample ($\phi=9\%)$ in a 250 mT field. The white mark indicates one specific position in the capillary.

**FIG. 6.** Polarization microscopy pictures of an $I-N$ phase separated sample after 11 days in a 270 mT field with different orientations of the polarizers.
dark and there the particles are also parallel to the field (although with a lower order parameter). However, the lower part of the \( pN \) phase is clearly brighter, indicating that the particles have an orientation perpendicular to the field in this region. The same phenomenon can be observed with the polarizers in a vertical position (c). The dark regions in (b) now become bright and vice versa.

A more complete study of this rich behavior was performed at 270 mT (Fig. 7). In the paranematic phase similar behavior was observed as in the nematic phase. Droplets formed in a large part of the sample, where the droplets were smaller in the paranematic phase compared to in the nematic phase as can be seen from the picture taken after 40 min. The droplets formed in the paranematic phase were nematic and they sedimented to the nematic phase, thereby increasing the level of the \( pN-N \) interface, as could be seen after 2 h in the field. Just below this interface interference colors were observed indicating that the parallel alignment was still distorted by droplets and the \( pN-N \) interface was not clearly distinguishable yet. There seemed to be a flow from the nematic to the paranematic phase as well and after 5 days the level of the interface had lowered a bit. However, it was still clearly higher than the initial position, even though a denser biaxial nematic phase had formed at the bottom. The nematic phase is stabilized in the field, which confirms both theoretical predictions\(^4,5,14\) and earlier experiments.\(^9,10\) Compared to previous experiments the process can be followed more directly in our case. In the work of Tang and Fraden,\(^9\) droplets that formed a network were observed when a magnetic field was applied to an initially fully isotropic sample, but no formation of a macroscopic nematic phase was seen. Van der Beek \textit{et al.}\(^10\) observed a rise of the \( I-N \) interface only when letting homogenized samples phase separate in a magnetic field, but no formation of droplets in the isotropic phase was observed when simply increasing the field.

In the paranematic phase some interference colors were observed after 5 days in 270 mT and there was a large area more or less black. This implies that there was a small part with some (perpendicular) alignment, but in the largest part the orientational distribution function was spread out giving a zero order parameter. The field is clearly close to the critical field where the order parameter is expected to be zero in the paranematic phase.

Just after switching off the field, the \( I-N \) interface formed at the same position where it was in the field. After 1 h, it could already be seen that the interface position was clearly going down and it was then close to the situation before a field was applied. Therefore, it was expected that equilibrium was reached soon after that. However, the interface dropped even further and after 2 days it was clearly lower than it initially was. This was attributed to the denser perpendicular nematic phase which was still present at the bottom of the capillary. The dynamics in the isotropic phase is faster than in the nematic phase, so while equilibrium is reached around the \( I-N \) interface, the nematic phase is still changing. Particles have to diffuse within the nematic phase, especially from the denser biaxial nematic phase which formed in the field. This diffusion is a slow process. After 9 days, it could be seen that the interface was rising and the nematic phase was probably getting less dense again.

The slow diffusion can also be seen when repeating the experiment in a field of 270 mT, 9 days after the previous experiment. In Fig. 7 [270 mT (2)] the behavior after 2 h in a field can be seen. Compared to the situation in the earlier experiment after 2 h, it was observed that \( N-N \) phase separation was much more localized near the bottom of the capillary in the second experiment. It is clear that the composition of the nematic phase was still very different from the initial situation. The behavior around the \( I-N \) interface was similar in the first and second experiments indicating that the \( I-N \) region reached the equilibrium situation in zero field considerably faster than the lower region of the nematic phase.

\section*{C. Perpendicular alignment in large fields}

In a field of 300 mT, droplets were again forming in a large part of the sample (Fig. 8), except for the upper part of the isotropic phase which remained more or less dark. The droplets in the paranematic phase were still small after 10
min, but they grew over time as can be seen from the pictures taken after 1 h. After 1 day, a new interface has formed between the paranematic and nematic phase, which was a bit higher than the $I$-$N$ interface at zero field, even with the large dense nematic phase formed at the bottom of the capillary. From the paranematic phase still some droplets sedimented to the nematic phase.

After 5 days, the interface had lowered its position and it became unstable. Droplets from the paranematic phase were falling through the interface and channels were being formed. At the left side of the capillary, a channel connecting the paranematic and the lower nematic phase can be seen. This lower nematic phase had the same orientation of the particles as the paranematic phase just above the $pN$-$N$ interface; they were both oriented perpendicular to the field. Apparently, these phases had a small density difference and were very similar; channels connecting the two phases were made through the upper nematic phase with a parallel orientation.

In a field of 400 mT, most particles had an orientation perpendicular to the field. As can be seen in Fig. 9 (2.5 h) some small droplets still formed in the paranematic phase. These droplets had a parallel alignment as could be concluded from the observation that they coalesced with the nematic droplets with a parallel alignment. After 7 h, hardly any droplets were observed in the paranematic phase anymore. The position of the $I$-$N$ interface does not seem to have changed, but it was not easy to determine since there was no sharp interface present.

After 6 days, the amount of paranematic phase seemed to have increased, based on the change of the position of the interference bands and of the areas of parallel nematic phase. Probably, the perpendicular, biaxial nematic phase increased in density. Within the parallel nematic phase there was apparently a density gradient, since the areas were stretched over a large part of the capillary.

The paranematic phase was aligned perpendicular to the field; no dark areas were observed which would indicate a spread in the orientations of the particles. This phase was clearly better aligned than at 300 mT, as can be seen from the interference colors that were now less intense.

Higher fields were not studied in detail here. At least more than 600 mT is needed to see no $N$-$N$ phase separation anymore. The paranematic phase becomes better aligned and the interface with the nematic phase fades. It was observed by Lemaitre et al.\textsuperscript{22} that the difference between the paranematic and nematic phase vanishes at a certain field strength, in their case they used 1 T.

### IV. CONCLUSIONS

The behavior of the region around the $I$-$N$ interface of colloidal goethite dispersions in a magnetic field was studied using polarization microscopy. In a small magnetic field (up to 180 mT), the paranematic and nematic phases both align parallel to the field. In time, the interface between the paranematic and nematic phase fades, but the difference is still clear from the interference colors observed in the paranematic phase. After the field is switched off, the $I$-$N$ interface is still in the same position.

In fields where $N$-$N$ phase separation occurs (above 180 mT), there are two effects affecting the position of the $I$-$N$ interface. First, at least the lower, biaxial nematic phase that forms has a higher density and perhaps the upper, parallel nematic phase as well. This reduces the total volume of the nematic phase and it lowers the position of the $I$-$N$ interface. Second, nematic droplets form in the paranematic phase which sediment to the nematic phase, thereby increasing the height of the $I$-$N$ interface. Which of the two factors wins over the other depends on the field strength. In smaller fields no droplets are formed in the paranematic phase yet and the interface drops. Increasing the field, droplets start to form and the interface rises.

At fields above around 300 mT, the $I$-$N$ interface starts to go down again, probably because of the large denser nematic phase. Furthermore, the interface starts to get unstable.
Within the paranematic phase now there are also regions with different orientations like in the nematic phase. The lower part of the paranematic phase has a perpendicular alignment similar to the lower nematic phase. In high fields these two phases connect and form channels through the parallel nematic phase. At fields above about 600 mT, there is no $N$-$N$ phase separation anymore and the interface between the paranematic and nematic phase starts to fade.

The dynamics in the isotropic phase was observed to be much faster than in the nematic phase. The $I$-$N$ interface restores within a day, but the composition of the nematic phase was found to be still much different from the initial situation 9 days after switching off the field.

The behavior of $I$-$N$ phase separated goethite dispersions turns out to be very rich, showing, for example, phase transitions, coalescence, and reorientation phenomena. The observed behavior largely confirms the theoretical phase diagram (Fig. 1). However, $N$-$N$ phase separation was not predicted for the theoretical monodisperse model system. In low and high fields, birefringence colors were observed similar to calculations, although these colors were more difficult to observe because goethite particles strongly absorb light. In principle, for monodisperse systems, these modified birefringence colors could be used to determine density and order parameter profiles [e.g., using Eq. (1) for low fields], but this is exceedingly difficult for a polydisperse system. In intermediate fields, the situation for goethite is more complicated because of the reorientation of the particles.

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