Experimental Realization of Biaxial Liquid Crystal Phases in Colloidal Dispersions of Boardlike Particles

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Biaxial nematic and biaxial smectic phases were found in a colloidal model system of goethite (α-FeOOH) particles with a simple boardlike shape and short-range repulsive interaction. The macroscopic domains were oriented by a magnetic field and their structure was revealed by small angle x-ray scattering. In accordance with theoretical predictions, biaxiality appears in a system with particles that have a shape almost exactly in between rodlike and platelike. Our results suggest that biaxial phases can be readily obtained by a proper choice of the particle shape.

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The biaxial nematic (N_b) phase is a modification of the usual (uniaxial) nematic phase (N_u). In the N_u phase a spontaneous orientation of the main particle axis occurs: either the long particle axis in rodlike systems or the short particle axis in platelike systems. Biaxiality occurs if particles also orient along a second axis perpendicular to their main orientation as shown in Figs. 1(b) and 1(c). A large amount of theoretical work and many computer simulations have been spent on the N_b phase [1–8]. Freiser predicted the N_b phase for the first time in 1970 [1], and a few years later theoretical phase diagrams were published [2,3]. Similar phase diagrams were also found with simulations [4,5]. It was shown that a biaxial phase is expected to be found for molecules with a shape in between rodlike and platelike, so when $L/W \simeq W/T$ (with L, W, and T the length, width, and thickness). Taylor and Herzfeld also included other (liquid) crystalline phases to get a full phase diagram [6] and found that the formation of a biaxial layerlike smectic phase strongly competes with the N_b phase. This effect might be reduced by incorporating length polydispersity, which destabilizes the smectic phase [7].

For almost 40 years, there has been a search for biaxiality in liquid crystalline phases. The very few examples found so far have been under considerable debate and involve complicated interactions and complex (molecular) shapes [9–16]. For the classical lyotropic micellar system of Yu and Saupe [9], in which the first experimental evidence for an N_b phase was found, different suggestions have been raised about the nature of this biaxial phase. At first it was thought that it was a mixture of rodlike and platelike micelles, as predicted by Alben [17], but it was revealed that the micelles actually have a biaxial shape themselves [10], although it should be realized that micelles are living systems where particle shape and phase symmetry mutually influence each other. It took until 2004 before seemingly conclusive evidence was found for the presence of an N_b phase in thermotropic liquid crystals [11,12]. Yet, there still is a heated discussion on this subject [13–16]. Recently, the existence of N_b phases in bent-core molecular systems was questioned again [18,19]. In particular it is suggested that the ''biaxial nematic'' x-ray patterns are actually caused by smectic C type fluctuations in the nematic phase. In colloidal systems only a biaxial nematic gel state was reported for vanadium pentoxide [20].

A biaxial smectic A ($\mathrm{Sm}A_b$) phase was found for the first time in a side-chain polymer system that was aligned by a magnetic field [21]. Without alignment in an external field the phase was also found, for example, using bent-core molecules in an anisotropic medium [22] and in a binary mixture of a boardlike metallomesogen with trinitrofluorenone [23].

All these examples of biaxial phases are difficult to compare with theory because of the different types of interactions and an ill-defined or complex shape. Mineral liquid crystalline particles are potentially interesting in this respect because they can be synthesized in different shapes and have short-range repulsive interactions. Although most attention has been paid to rodlike or platelike particles, boardlike particles can also be obtained. This is important because theory and simulations suggest that a biaxial nematic phase can be formed if particles have dimensions $L/W \simeq W/T$ [2,3,5]. A good candidate is goethite which is a versatile mineral liquid crystal, already known to readily

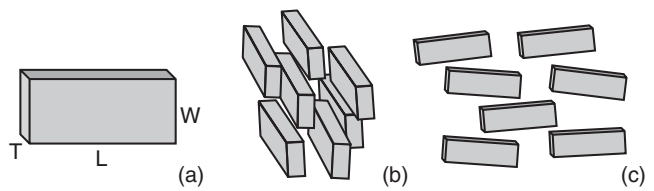

FIG. 1. (a) Shape of a goethite particle, (b) N_b phase oriented with the largest dimension (L) of the particles into the paper, (c) N_b phase oriented with the smallest dimension (T) of the particles into the paper.

form nematic, columnar, and smectic phases [24,25]. By tuning the experimental conditions during synthesis we were able to make systems with a range of particle dimensions [26]. Here, we focus on a system with $L/W = 3.1$ and $W/T = 3.0$.

Furthermore, goethite particles [Fig. 1(a)] have a permanent magnetic moment along their long axis (L), presumably due to uncompensated spins within their antiferromagnetic crystal structure. In contrast, their magnetic easy axis is along the shortest particle dimension (T). Therefore, the particles have the opposing tendencies to align with their long axis parallel to the field at a low magnetic field strength and to orient perpendicular to a higher magnetic field (>250 mT). In lyotropic systems a good anchoring is usually difficult to realize, making it hard to obtain large domains of a certain orientation. In this case the magnetic properties can be used to overcome this problem, since already a very small magnetic field can be sufficient to align the domains along the field direction.

The combination of small angle x-ray scattering (SAXS) and the magnetic properties of the system provided indeed evidence for an N_b and also SmA_b phase. This is the first example of biaxial phases formed by particles with $L/W \simeq W/T$ which confirms theory and simulations.

The particles studied here have average dimensions of $L \times W \times T = 254 \times 83 \times 28$ nm, with a polydispersity of 20%–25% in all directions. For experimental details, see Ref. [27]. To study the phase behavior of these particles, glass capillaries (Vitrocom RT3524, with internal dimensions of $0.2 \times 4.0 \times 100$ mm^3) were used containing a concentrated goethite dispersion. At the time of the measurements (several years after preparation, see Ref. [27]), Capillaries 1 and 2 had an overall volume fraction of 13.5% and 25.6%, respectively, and a schematic picture is given in Fig. 2. Because of sedimentation a concentration profile developed and several liquid crystalline phases could be observed in one capillary. SAXS was used together with a small external magnetic field to determine the phases present in the system [27,28]. For thermotropic systems the main technique to prove biaxiality is NMR, but this technique cannot be used here because

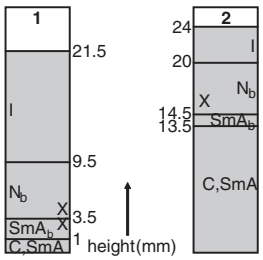

FIG. 2. Schematic picture of the measured capillaries, indicating the isotropic (I), biaxial nematic (N_b), biaxial smectic (SmA_b), and combination of columnar and smectic (C, SmA) phase. The x's correspond to the measurement positions discussed in this article.

at fields above 250 mT the induced magnetic moment becomes larger than the permanent magnetic moment and the system changes dramatically.

Capillary 1 was first measured in a very small magnetic field of 3 mT, which is the residual magnetic field with the magnetic poles at maximum distance, with the field aligned along the x-ray beam, so perpendicular to the paper. The SAXS pattern of the nematic phase is shown in Fig. 3(a). Two orthogonal peaks at larger angles were observed corresponding to the width and thickness correlations; for the peak profiles in the horizontal (solid line) and vertical (dashed line) direction, see Fig. 3(d). The fact that the peaks are perpendicular to each other indicates that the particles are orientationally ordered in three directions, as in Fig. 1(b). This phase is clearly an N_b phase: in case of an N_u phase one or two uniform scattering rings would be obtained. It is also evident that an external field of as low as 3 mT is sufficient to orient the particles along the field because no peak was observed at a small angle corresponding to the length correlations.

Increasing the field to 40 mT [Figs. 3(b) and 3(e)] the pattern remained similar to the one at 3 mT, but the peaks had a higher intensity, indicating that the particles were better aligned at this field strength. After changing the field direction perpendicular to the x-ray beam [Figs. 3(c) and 3(f)], peaks at small angles emerged in the field direction corresponding to correlations between the long axes of the particles. These peaks are liquidlike which confirms the nematic nature of the phase [27]. In the vertical direction the width correlations can be seen. There also appeared weak scattering corresponding to the thickness, which presumably originated from a differently oriented domain caused by the reorientation process. The N_b phase changed orientation with the change of the magnetic field direction and was then predominantly like the situation depicted in Fig. 1(c).

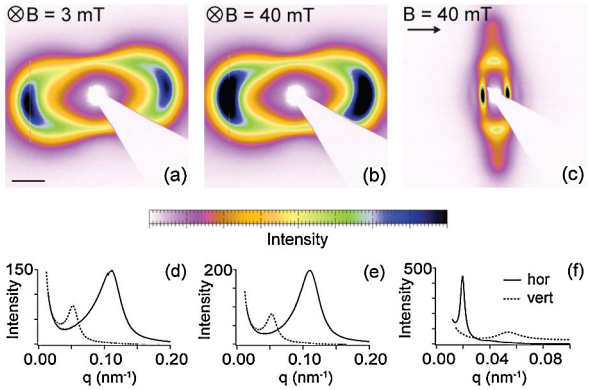

FIG. 3 (color online). SAXS patterns of the N_b phase in capillary 1 in a small magnetic field of (a) 3 mT and (b) 40 mT parallel (⊗) to the x-ray beam, and (c) of 40 mT perpendicular (→) to the x-ray beam, with the intensity profiles of a (d), b (e), and c (f) in the horizontal (solid line) and vertical (dashed line) direction. The scale bar is 0.05 nm^{-1}.

Using the patterns measured with the different orientations of the magnetic field, distances (d) were calculated from the scattering vector (q) of the three orthogonal peaks by applying $d \approx 2\pi/q$. Ensemble-averaged distances d_L, d_W, and d_T were found of 320, 120, and 58 nm, which are slightly larger than the particle dimensions L, W, and T of 254, 83, and 28 nm. Because the particles are charged, there is an electric double layer around them, at least of the order of the Debye length (10 nm at most in this case, see Ref. [27]). Adding 20 nm (10 nm at each side) to the particle dimensions brings them already close to the distances measured. Furthermore, polydispersity causes fractionation in the system and therefore mainly the longer particles are expected to be in the lower part of the capillary (where these measurements were done, see Fig. 2) [29]. The d_L/d_W and d_W/d_T ratios calculated from the measurements are 2.7 and 2.1. They are different from the actual particle ratios $L/W = 3.1$ and $W/T = 3.0$, but adding again 20 nm to the particle dimensions gives $L_{\text{eff}}/W_{\text{eff}} = 2.7$ and $W_{\text{eff}}/T_{\text{eff}} = 2.1$, which now correspond well to the peak ratios measured. Together with the SAXS patterns these values give convincing evidence that an N_b phase was indeed found.

1.5 mm lower in the same capillary a smectic A phase was found, in which particles are ordered in layers. In a field of 3 mT (parallel to the x-ray beam, that is perpendicular to the paper) this phase was not aligned along the field [Fig. 4(a)], as can be seen from the small angle peaks originating from the length correlations. These very sharp and intense peaks, oversaturated in this picture, are characteristic for the periodicity of the smectic phase. Perpendicular to them, liquidlike peaks were observed at larger angles corresponding to distances comparable to the width of the particles, whereas no peaks were observed at even larger angles, so the smallest dimension of the particles was oriented perpendicular to the paper. This means that again the three different dimensions of the particles were oriented orthogonally to each other and an SmA_b phase was observed [Fig. 4(d)].

By increasing the field to 40 mT, peaks appeared at larger angles, while the peaks at small angles vanished [Fig. 4(b)]. The SAXS pattern was then similar to the aligned N_b phase [Fig. 3(a) and 3(b)]; the smectic phase was also aligned along the field and the widths and thicknesses of the particles were perpendicular to the field and perpendicular to each other. This shows that also the smectic phase is clearly biaxial. After rotation of the field direction, from parallel to perpendicular to the x-ray beam, sharp peaks (oversaturated in this picture) appeared at small angles from the length correlations [Fig. 4(c)]. Second order peaks were observed [Fig. 4(c), zoom], indicating a well aligned smectic phase. From these different SAXS patterns the distances corresponding to the three different peak angles were calculated and found to be $d_L = 327$, $d_W = 120$, and $d_T = 56$ nm, comparable to the distances found in the N_b phase. The d_L/d_W and d_W/d_T ratios measured are again 2.7 and 2.1.

To be sure that the biaxial phases are not field induced, capillary 2 (Fig. 2) was used. This capillary had not been in a magnetic field before and was first measured without any field [Fig. 5(a)]. For the nematic phase a similar SAXS pattern was observed as for the SmA_b phase in capillary 1 in 3 mT [Fig. 4(a)], but with broader peaks at small angles. It seems that there is an anchoring effect of the capillary walls, the particles preferring to be aligned along the wall. This measurement at zero field proves that the N_b is not induced by the magnetic field. Furthermore, the domain of the N_b phase is larger than the x-ray beam, which is about 0.5–1 mm in diameter at the sample position.

At 40 mT, the N_b phase aligns along the field as was observed before [Fig. 5(b)]. After the field was reduced to 3 mT for 1 h, it was observed that the N_b phase slowly relaxed into the direction of its original orientation [Fig. 5(c)].

Interestingly, no N_u phase was found in both capillaries; instead a direct transition from the isotropic (I) to the N_b phase was observed. The particles have dimensions close to $L/W = W/T$, but already if they are slightly different

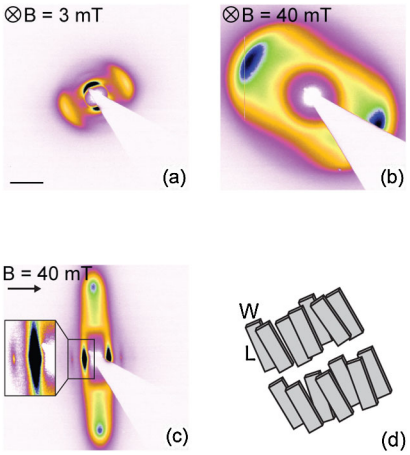

FIG. 4 (color online). SAXS patterns of the SmA_b phase in capillary 1 in a small magnetic field of (a) 3 mT and (b) 40 mT parallel (⊗) to the x-ray beam, and (c) of 40 mT perpendicular (⟶) to the x-ray beam (including zoom). The scale bar is 0.05 nm^{-1}. (d) Shows the structure of the biaxial smectic phase, corresponding to (a).

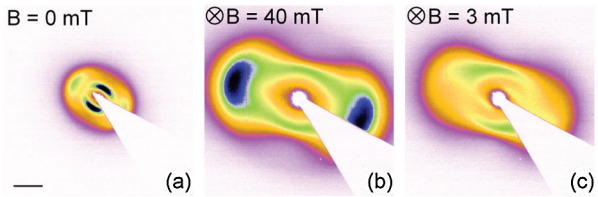

FIG. 5 (color online). SAXS patterns of (a) the N_b phase in capillary 2 in 0 mT, (b) in 40 mT (parallel ⊗ to the x-ray beam), and (c) the relaxation of the N_b phase shown at 3 mT. The scale bar is 0.05 nm^{-1}.

an intermediate N_u is expected [2–5]. It might be that polydispersity has a stabilizing effect for the N_b phase compared to the N_u phase, which has been shown to be the case for the N_u phase compared to the I phase [30–32]. Another aspect can be a possible electrostatic heterogeneity of the particles.

Finally, it is worth noting that the observed biaxiality cannot be induced by artifacts such as anchoring at the capillary walls. The results shown in Figs. 3(a), 3(b), 4(b), and 5(b), are obtained from domains with the long particle axis normal to the capillary walls. In that case there can be no (biaxial) anchoring effect of the capillary walls. Moreover, the biaxiality is not induced by the magnetic field since the biaxial structure remains after removal of the field.

In summary, while the thermotropic biaxial phases are still highly debated, we clearly show the existence of a biaxial nematic and biaxial smectic phase in colloidal dispersions of simple boardlike goethite particles with $L/W \simeq W/T$. In other goethite dispersions, with particle ratios L/W larger than W/T by at least a factor of 1.5, a biaxial phase was never observed [24–26,29]. The magnetic properties of the particles have been used to align the domains in different directions during SAXS measurements, which allowed us to construct a complete picture of the biaxial phases. The macroscopically large domains are also observed without alignment by a magnetic field. Surprisingly, the N_b phase is stable over a large concentration range and no N_u phase was found. These results suggest that the biaxial nematic and biaxial smectic phases can be readily obtained by a proper choice of the particle dimensions, which for the first time confirms earlier theoretical work. Compared to the work of Yu and Saupe [9], our particles have a fixed and well-defined shape. Our system can be a model for smaller nanoparticles that could be useful for applications.

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[1] M. J. Freiser, Phys. Rev. Lett. **24**, 1041 (1970).
[2] R. Alben, Phys. Rev. Lett. **30**, 778 (1973).
[3] J. P. Straley, Phys. Rev. A **10**, 1881 (1974).
[4] F. Biscarini, C. Chiccoli, P. Pasini, F. Semeria, and C. Zannoni, Phys. Rev. Lett. **75**, 1803 (1995).
[5] P. J. Camp and M. P. Allen, J. Chem. Phys. **106**, 6681 (1997).
[6] M. P. Taylor and J. Herzfeld, Phys. Rev. A **44**, 3742 (1991).
[7] A. G. Vanakaras, M. A. Bates, and D. J. Photinos, Phys. Chem. Chem. Phys. **5**, 3700 (2003).
[8] R. Berardi, L. Muccioli, S. Orlandi, M. Ricci, and C. Zannoni, J. Phys. Condens. Matter **20**, 463101 (2008).
[9] L. J. Yu and A. Saupe, Phys. Rev. Lett. **45**, 1000 (1980).
[10] Y. Galerne, A. M. Figueiredo Neto, and L. Liebert, J. Chem. Phys. **87**, 1851 (1987).
[11] L. A. Madsen, T. J. Dingemans, M. Nakata, and E. T. Samulski, Phys. Rev. Lett. **92**, 145505 (2004).
[12] B. R. Acharya, A. Primak, and S. Kumar, Phys. Rev. Lett. **92**, 145506 (2004).
[13] G. R. Luckhurst, Thin Solid Films **393**, 40 (2001).
[14] G. R. Luckhurst, Nature (London) **430**, 413 (2004).
[15] Y. Galerne, Phys. Rev. Lett. **96**, 219803 (2006).
[16] L. A. Madsen, T. J. Dingemans, M. Nakata, and E. T. Samulski, Phys. Rev. Lett. **96**, 219804 (2006).
[17] R. Alben, J. Chem. Phys. **59**, 4299 (1973).
[18] K. Van Le, M. Mathews, M. Chambers, J. Harden, Q. Li, H. Takezoe, and A. Jakli, Phys. Rev. E **79**, 030701(R) (2009).
[19] N. Vaupotic, J. Szydlowska, M. Salamonczyk, A. Kovarova, J. Svoboda, M. Osipov, D. Pociecha, and E. Gorecka, Phys. Rev. E **80**, 030701 (2009).
[20] O. Pelletier, C. Bourgaux, O. Diat, P. Davidson, and J. Livage, Eur. Phys. J. B **12**, 541 (1999).
[21] H. F. Leube and H. Finkelmann, Makromol. Chem. **192**, 1317 (1991).
[22] R. Pratibha, N. V. Madhusudana, and B. K. Sadashiva, Science **288**, 2184 (2000).
[23] T. Hegmann, J. Kain, S. Diele, G. Pelzl, and C. Tschierske, Angew. Chem. **113**, 911 (2001).
[24] B. J. Lemaire, P. Davidson, J. Ferré, J. P. Jamet, P. Panine, I. Dozov, and J. P. Jolivet, Phys. Rev. Lett. **88**, 125507 (2002).
[25] G. J. Vroege, D. M. E. Thies-Weesie, A. V. Petukhov, B. J. Lemaire, and P. Davidson, Adv. Mater. **18**, 2565 (2006).
[26] D. M. E. Thies-Weesie, J. P. de Hoog, M. H. Hernandez Mendiola, A. V. Petukhov, and G. J. Vroege, Chem. Mater. **19**, 5538 (2007).
[27] See EPAPS Document No. E-PRLTAO-103-160952 for more details. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[28] A. V. Petukhov, J. H. H. Thijssen, D. C. 't Hart, A. Imhof, A. van Blaaderen, I. P. Dolbnya, A. Snigirev, A. Moussaid, and I. Snigireva, J. Appl. Crystallogr. **39**, 137 (2006).
[29] E. van den Pol, D. M. E. Thies-Weesie, A. V. Petukhov, G. J. Vroege, and K. Kvashnina, J. Chem. Phys. **129**, 164715 (2008).
[30] H. N. W. Lekkerkerker, P. Coulon, R. Van Der Haegen, and R. Deblieck, J. Chem. Phys. **80**, 3427 (1984).
[31] A. Speranza and P. Sollich, J. Chem. Phys. **117**, 5421 (2002).
[32] H. H. Wensink and G. J. Vroege, J. Chem. Phys. **119**, 6868 (2003).