Magnetic-Field-Induced Nematic-Columnar Phase Transition in Aqueous Suspensions of Goethite (α-FeOOH) Nanorods

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(Received 23 July 2004; published 20 December 2004)

Colloidal aqueous suspensions of goethite lath-shaped nanorods form nematic and isotropic phases. We show that they also display a 2D rectangular ($c2mm$) columnar phase at volume fractions ϕ larger than 15%. Interestingly, the nematic-columnar first-order transition can also be triggered by applying to the nematic phase a magnetic field of intensity decreasing with ϕ (1 T at 8.5%; 0.5 T at 12%). Single domains of the columnar phase were thus produced and their structure investigated by synchrotron x-ray scattering. This magnetic-field-induced transition is fully reversible and reproducible.

DOI: 10.1103/PhysRevLett.93.267801 PACS numbers: 64.70.Md, 61.10.–i, 61.30.Gd, 82.70.Kj

Colloidal suspensions provide very popular model systems to investigate the statistical physics of phase transitions due to their slow dynamics and the large size of the particles, which allows their direct observation [1,2]. Anisotropic nanoparticles (rods, disks, etc.) are interesting in this respect because they readily form liquid-crystalline phases, leading to richer phase diagrams [3,4]. Among the various kinds of particles available for such studies, mineral ones have the advantage of sometimes displaying physical properties rather uncommon for organic colloids [5,6]. For instance, we recently reported the outstanding magnetic properties of nematic aqueous suspensions of goethite (α-FeOOH) nanorods [7]. These suspensions align in very low magnetic fields. Moreover, the nanorods align parallel to the field at low intensity ($B \leq 0.35$ T), but they reorient perpendicularly to the field at high intensity ($B \geq 0.35$ T). This unusual behavior could be explained by the fact that the nanorods bear a small longitudinal remanent magnetic moment and also have a negative anisotropy of magnetic susceptibility. Such a combination of dipolar and quadrupolar orders induces original symmetries somewhat hybrid between those of nematics and ferrofluids. In this work, we report the existence in goethite suspensions of a 2D columnar mesophase and its quite unexpected stabilization by a magnetic field with respect to the nematic phase.

Suspensions of goethite nanorods were synthesized according to already described procedures [7,8]. A molar NaOH solution was slowly added to a 0.1 M $Fe(NO_3)_3$ solution at room temperature under stirring until $p\mathrm{H} \sim 11$ is reached. An ochre ferrihydrite precipitate instantly forms, and the suspension is left undisturbed for 10 d while goethite nanorods grow. The precipitate is rinsed twice with distilled water to decrease the ionic strength and redispersed in a 3 M HNO_3 solution. Finally, distilled water is added to reach $p\mathrm{H} \sim 3$. Goethite nanorods bear surface −OH groups that can be ionized so that the point of zero charge lies around $p\mathrm{H} \sim 9$. At pH 3, the nanorods are positively charged with an electric surface charge density of about $0.2\ \mathrm{C\,m^{-2}}$ and electrostatic repulsions ensure the colloidal stability of the suspensions over years [9]. The ionic strength is 0.05 M, arising mostly from $NO_3{}^-$ counterions. The dimensions of goethite particles of the synthesis batch used in our studies were previously determined by combining x-ray scattering and electron microscopy techniques [7]. Goethite nanorods are polydisperse lath-shaped particles of average length $L = 150$ nm, width $w = 25$ nm, and thickness $t = 10$ nm. In first approximation, the polydispersity distributions of these three dimensions can be described by a (truncated) Gaussian of width $\Delta L/L = \Delta w/w = \Delta t/t = 0.4$. The nanorod magnetic properties were previously investigated with a SQUID apparatus [7]. The particles bear a longitudinal remanent magnetic moment of about $1000\mu_B$ ($= 9.27 \times 10^{-21}\,\mathrm{A\,m^2}$), and they have a magnetic-susceptibility anisotropy $\Delta\chi = -3 \times 10^{-4}$.

Samples were held in flame-sealed flat glass optical capillaries (VitroCom Inc., Mountain Lakes, NJ) 20 to 100 μm thick for microscopic observations. Sample textures were examined in polarized light with an Olympus BX51 microscope and recorded with a digital camera. A small device equipped with permanent magnets allowed us to apply a variable magnetic field, from 0 to about 1 T, in a direction perpendicular to the light beam. This device is fitted onto the microscope sample stage and can rotate with respect to the polarizer and analyzer directions.

Small angle x-ray scattering (SAXS) experiments were performed at the ID02 station of the European Synchrotron Radiation Facility synchrotron in Grenoble, France, using an already described configuration [10]. The incident beam had a wavelength $\lambda = 0.0995$ nm, and the sample-to-detector distance was 10 m. The beam size at the sample level was $0.1 \times 0.1\ \mathrm{mm}^2$. The q range was $0.02 \leq q \leq 0.6\ \mathrm{nm}^{-1}$, where $q = \frac{4\pi}{\lambda}\sin\theta$ and 2θ is the scattering angle. The scattered x rays were detected with a specially developed CCD camera. The samples were also held in flat glass capillaries for SAXS experiments in spite of the strong glass absorption because this allowed us to use 100 μm thick samples, which is suitable at this wavelength. The flat faces of the capillaries were set perpendicular to the x-ray beam. A variable magnetic field **B** could be applied either parallel to the x rays or perpendicular (in the horizontal plane) by using two stacks of NdFeB permanent magnets. The field intensity could be varied up to 1.7 T.

At volume fractions (ϕ) smaller than 5.5%, suspensions of goethite nanorods form an isotropic (I) phase, whereas they display a nematic (N) phase at volume fractions larger than 8.5% [7]. An I/N coexistence domain is found in between 5.5% and 8.5% where the suspensions spontaneously demix, in agreement with the first-order character of the I/N transition [11,12]. This simple observation proves that goethite suspensions reach thermodynamic equilibrium.

In this work, we have first examined the phase behavior of more concentrated goethite suspensions. At $\phi > 15\%$, the SAXS patterns start displaying sharp diffraction lines superimposed onto the diffuse peak arising from the liquid-like order of the nematic phase [Fig. 1(a)]. This is due to the appearance of a new colloidal phase that has long-range positional order of the nanorods. The diffuse peak of the nematic phase completely disappears at $\phi = 20\%$, which represents the upper bound of this coexistence region. Beyond this value, the columnar phase is almost pure. The two-dimensional SAXS patterns of the new phase show inhomogeneous diffraction rings typical of a "powder" distribution of domains with slight alignment. Only four diffraction rings were observed, and the production of a single domain would be very helpful at this stage to index the scattering pattern and to identify the phase.

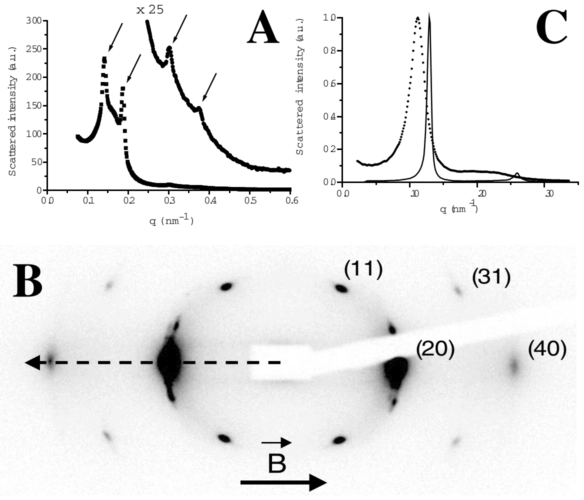

FIG. 1. (a) x-ray scattered intensity (in arbitrary units) versus scattering vector modulus q of a goethite suspension sample of 15.3% volume fraction. The arrows point to the sharp reflections of the columnar phase. (b) SAXS pattern of a single domain of the $c2mm$ columnar phase grown by applying a $B = 1.35$ T magnetic field on a nematic sample of 8.5% volume fraction. The reflections are indexed with a rectangular centered lattice, as described in the text. The (02) reflection could be observed on overexposed patterns. Additional small reflections, very close to the (20) one, arise from other small domains in the beam. (c) Comparison of the linewidths of the nematic diffuse ring (solid circles) and the (20) reflection (solid line) obtained from a linear scan of (b) along the dotted arrow.

We then applied to the samples a variable magnetic field in the horizontal direction perpendicular to the x-ray beam. Surprisingly enough, the SAXS pattern of a nematic sample of 8.5% volume fraction developed strong sharp reflections in a few minutes when submitted to field intensities of about 1 T. Moreover, a large single domain grew within the volume illuminated by the x rays [Fig. 1(b)]. The SAXS pattern of this single domain can now easily be indexed. All (hk) reflections obey the condition $h + k = 2n$ of a centered lattice, and this lattice has rectangular symmetry [13]. The unit-cell parameters are $a = 96$ nm and $b = 75$ nm, and there are two particles per unit cell. Moreover, no additional reflection was found in the direction perpendicular to the (hk) plane. Therefore, there are no long-range positional correlations along the third direction and the phase is ordered in two dimensions only. In other words, this phase is a columnar mesophase of rectangular symmetry and its (2D) space group is $c2mm$.

The columnar ordering induced by the magnetic field is fully reversible (possibly with some field hysteresis) as the sharp spots disappear and the nematic diffuse spots reappear when the field is suppressed. The diffuse and sharp spots coexist in a field-intensity range that depends on volume fraction. At intensities beyond this range, the columnar phase seems pure. Furthermore, the field-induced transition was reproduced many times, with different samples, not only at the synchrotron facility but also in the laboratory where SAXS patterns of lesser quality were also recorded with a rotating-anode setup. In many cases, single domains were produced, which confirms that the columnar phase grows in large domains when stabilized by the magnetic field.

Figure 1(c) shows radial scans of the scattered intensities through the nematic diffuse peak and through the (20) columnar reflection. Although the nematic peak is unusually narrow, the (20) reflection is obviously much sharper. Its width corresponds to a domain size of at least 1 μm, over which the positional order is perfect.

The field-induced nematic-columnar transition is readily observed by polarized-light microscopy with nematic samples of volume fraction $\phi = 8.5\%$. At $B = 0.4$ T, the texture of the nematic phase is uniform because it is aligned. Distinct anisotropic domains, roughly 100 μm large, develop in a few hours within the nematic texture

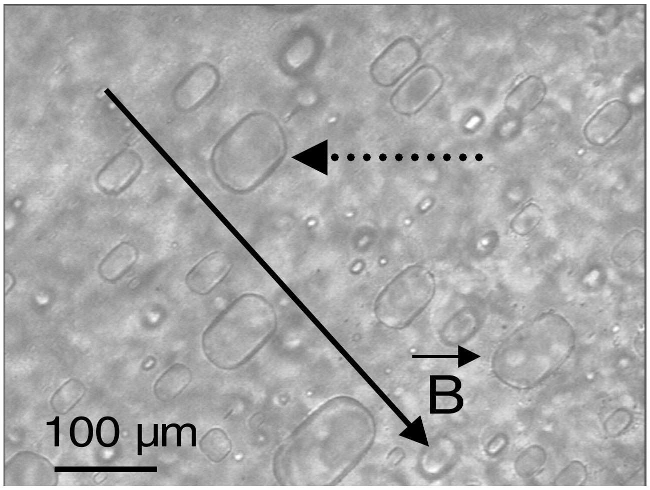

FIG. 2. Texture photograph, in polarized light, of an initially nematic sample ($\phi = 8.5\%$) submitted to a $B \sim 1$ T field (solid arrow), showing domains (the dotted arrow points to one) of the columnar phase.

when the field is increased (Fig. 2). They show a uniform texture because they are also aligned. The domains have sharp boundaries, are aligned parallel to each other, and also completely disappear when the field is suppressed. SAXS experiments *in situ* show that they are domains of the columnar phase. Since both phases are fully aligned in the field, the columnar domains differ only from the nematic phase by a slight difference of birefringence.

The sharp diffraction lines observed at $\phi = 15.3\%$ [Fig. 1(a)] can also be indexed in the same space group with slightly different lattice parameters ($a = 65.9$ nm, $b = 59.4$ nm). Therefore, the SAXS patterns shown in Figs. 1(a) and 1(b) probably belong to the same phase. The critical field intensity needed to achieve the nematic-columnar transition is a decreasing function of ϕ. The sharp diffraction spots appear at about 1 T for $\phi = 8.5\%$, at 0.9 T for $\phi = 10\%$, and at about 0.5 T for $\phi = 12\%$. Besides, $\phi = 15\%$ represents the lower limit of the nematic-columnar biphasic region in zero field. These observations mean that, in a (ϕ, B) phase diagram, the nematic-columnar transition line is quite tilted towards lower volume fractions, a rather original effect in the field of liquid crystals. Applying a field intensity of up to 1.7 T on an isotropic sample of 5.5% volume fraction (lower limit of I/N coexistence) did not, however, result in the appearance of sharp reflections in the SAXS patterns. We also examined the evolution with ϕ of the unit-cell parameters of the columnar phase for concentrated samples ($\phi \geq 15\%$) in zero field and for more dilute nematic samples ($8.5\% < \phi < 15\%$) submitted to a large enough field to reach the columnar transition. As expected, both lattice parameters regularly decrease as ϕ increases (data not shown); they have no discontinuity at $\phi = 15\%$, which strongly suggests that the columnar patterns recorded in the (8.5%–25%) ϕ range do correspond to a unique columnar phase.

Let us now discuss the nanorods organization in the columnar phase. We know that goethite nanorods align perpendicularly to the field direction for $B > 350$ mT [7]. The SAXS pattern shown in Fig. 1(b) corresponds mostly to a single domain (8.5%, 1.35 T) in homeotropic orientation as the nanorods are perpendicular to the capillary flat faces, i.e., parallel to the x-ray beam. Since goethite nanorods are not cylindrical but lath shaped, the columnar phase has rectangular rather than hexagonal symmetry. The respective directions of the nanorod width and thickness with respect to the magnetic field remain to be determined. We note that the (20) and (40) reflections are much stronger, respectively, than the (02) and (04) reflections. The reflection intensities are governed by the particle form factor that we can approximate by that of a square parallelepiped. The nanorod width being larger than its thickness, the form factor decays faster in the direction parallel to the width, which suggests that the nanorods orient their thickness along the field direction (Fig. 3). (This conclusion was checked by wide-angle x-ray scattering through the orientation of the crystallographic reflections of goethite.) This orientation agrees with that previously observed in the nematic phase for $B > 0.35$ T: Since the nematic phase aligns perpendicularly to the field, it must be biaxial. The field-induced biaxiality of a single domain was demonstrated by birefringence measurements [7]. The sign of the birefringence in the plane perpendicular to the nanorod length already proved that the nanorods align their thickness along the field direction. Then, the field-induced nematic-columnar transition occurs without any change in particle orientation.

SAXS patterns of samples at $\phi = 8.5\%$ in a 1 T field were also recorded in other scattering geometries, allowing us to explore directions perpendicular to the (hk) plane (data not shown), and we found no sign of long-range positional correlations along the particle length. The appearance of a well-defined periodicity (i.e., a lamellar

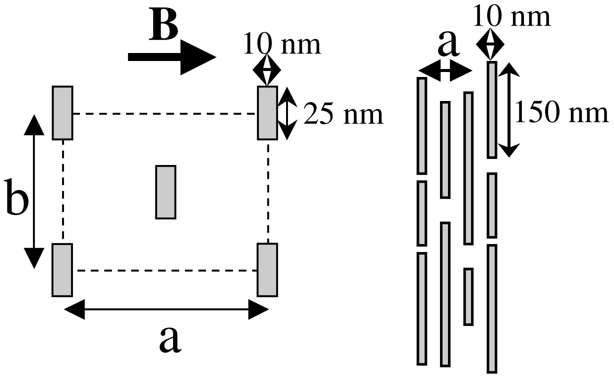

FIG. 3. Schematic of the structure of the $c2mm$ columnar phase: Left, in the (**a**, **b**) plane perpendicular to the nanorods main axes; right, in a plane containing the nanorods main axes.

phase) requires very small length polydispersities and was mostly observed in suspensions of viruses and of fairly monodisperse akageneite (β-FeOOH) nanorods [14,15]. Our goethite nanorods are so polydisperse that the SAXS patterns hardly display weak diffuse streaks corresponding to the particle length. Very interestingly, the large polydispersities in particle width and thickness do not prevent here the formation of the columnar phase. This reminds one of the appearance (in zero field) of a hexagonal columnar phase in concentrated suspensions of polydisperse gibbsite disks [16]. Much more monodisperse goethite nanorods should be produced to investigate these points in more detail.

To the best of our knowledge, the only cases of magnetic- or electric-field-induced phase transitions in liquid crystals deal with the isotropic/nematic transition [17]. There, the field breaks the isotropic symmetry of the disordered phase and directly affects the orientational degrees of freedom, which is rather intuitive. The case of goethite suspensions is different because the magnetic field favors the onset of long-range positional order and therefore affects the translational degrees of freedom, although probably in an indirect way.

Magnetic-field-induced structural transitions have already been reported in other fields of soft matter, such as magnetorheological fluids and confined (2D) suspensions of magnetic spheres [18,19]. In these systems, magnetic interactions can often be tuned from attractive to repulsive by varying the field direction. The magnetic-field-induced nematic-columnar transition in goethite suspensions does not seem to arise from the onset of attractive interactions because we do not observe any aggregation or flocculation. Moreover, the sharp reflections in the SAXS patterns correspond to distances far larger than the particles width and thickness, and the average areas per particle offered in the two phases are very similar. At this moment, we cannot think of a repulsive field-related interaction that could drive the positional ordering. Our best guess is that the field probably tends to freeze some orientational fluctuations, which then helps the establishment of the positional ordering through the usual excluded-volume interactions. Incorporating such an effect into classical statistical physics models of the nematic-columnar phase transition remains a tantalizing but challenging open theoretical question.

We are deeply indebted to J. Bibette, I. Dozov, P. Pincus, C. Santangelo, M. Henle, H. Lekkerkerker, and G. J. Vroege for very helpful discussions and to F. Camerel and J. C. P. Gabriel for help during the synchrotron experiments. We also gratefully acknowledge ESRF for the use of beamtimes SC725 and SC728.

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