Rev. Cub. Fis. **29**, 1E59 (2012) CONTRIBUTIONS

THE FREDERIKS TRANSITION IN AN AQUEOUS CLAY DISPERSION

LA TRANSICIÓN DE FREDERIKS EN UNA DISPERSIÓN ACUOSA DE ARCILLA

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We show that under certain circumstances, aqueous dispersions of Na-fluorohectorite synthetic clay display transient spatially periodic structures when subjected to magnetic fields. These nematic structures result from the deformation of a uniform director pattern, a phenomenon which is known as the Frederiks transition. We study the samples between crossed polarizers, and present birefringence images of the particle reorganization as a function of time. Repeated measurements at different magnetic field strengths show that the threshold value for the inhomogeneous Frederiks transition with this setup is just below 0.5 *T*, and that the spatial wavelength of the structures decreases when the magnetic field is increased, as is expected.

Se muestra que, bajo ciertas circunstancias, las dispersiones acuosas de arcilla sintética de Na-fluorohectorita exhiben estructuras espacialmente periódicas transitorias, cuando se someten a campos magnéticos. Tales estructuras nemáticas resultan de la deformación de un patrón uniforme director, un fenómeno que se conoce como la transición de Frederiks. Se estudian las muestras entre polarizadores cruzados, y las imágenes de birrefringencia de la reorganización de partículas en función del tiempo. Las mediciones repetidas con diferente intensidad de campo magnético, muestran que el valor umbral de la transición de Frederiks inhomogénea con esta configuración está justo por debajo de 0.5 *T*, y que la longitud de onda espacial de las estructuras disminuye cuando el campo magnético se incrementa, como es de esperar.

PACS: Structure of nematic liquid crystals, 61.30.-v; phase separation and segregation in colloids, 64.75.Xc; birefringence in bulk materials and thin films, 78.20.Fm

The Frederiks transition [1] is a phenomenon occurring in liquid crystals when a field is used to realign the nematic director away from its (field-free) equilibrium position. The path between the initial and final states often involve transient, spatially periodic structures, where adjacent domains rotate in opposite directions [2-3]. Due to its usefulness for determining material properties of liquid crystals (e.g. the elastic constant of the mode involved in the distortion), several theoretical and experimental studies have been performed on the Frederiks transition, both with rod-like and disk-like molecules (see e.g. [4-6]).

Liquid crystalline order in aqueous clay dispersions has attracted attention in recent years, see e.g. [7-10]. Here we report an observation of the Frederiks transition in dispersions containing the synthetic smectite clay Na-fluorohectorite. When mixed in water and left to phase separate over time, this system develops several coexisting phases in a single sample tube [7]. From bottom to top, these are: an isotropic gel region, a nematic gel region, a nematic sol region, and an isotropic sol. Due to the comparatively high viscosity and shear thinning behavior of the nematic gel, its dynamic response to magnetic fields is strongly damped [11]. However, the liquid-like nematic sol has been shown to respond relatively fast to magnetic fields [7], allowing particle reorientation with fields on the order of 0.1 *T*.

The samples used for the present experiments were dispersions of 3 % *w*/*w* of Na-fluorohectorite in 10^{-3} *M* NaCl suspensions, contained in 2 *mm* diameter glass capillaries. We let the samples settle for 4-5 months, during which the largest particle aggregates sediment out, and the four different regions appear in the samples. Before applying any magnetic fields, the clay particles in the nematic sol orient antinematically, i.e. with their particle normals spread out in the plane perpendicular to the capillary axis [7]. This is due to the circular geometry of the capillary, and the fact that the disk-like particles anchor homeotropically to interfaces [7].

In order to induce the Frederiks transition, a magnetic field of about 1 Tesla was first applied to the nematic sol phase perpendicular to the capillary axis. Due to the negative diamagnetic susceptibility anisotropy of the particles, they respond to magnetic fields by orienting their plate normals perpendicular to the magnetic field lines. Combined with the influence of the particles that are homeotropically anchored to the capillary walls, the field acts to change the nematic configuration from antinematic to uniaxial nematic, with the particle normals oriented on average along a common direction in the horizontal plane, perpendicular to the magnetic field lines.

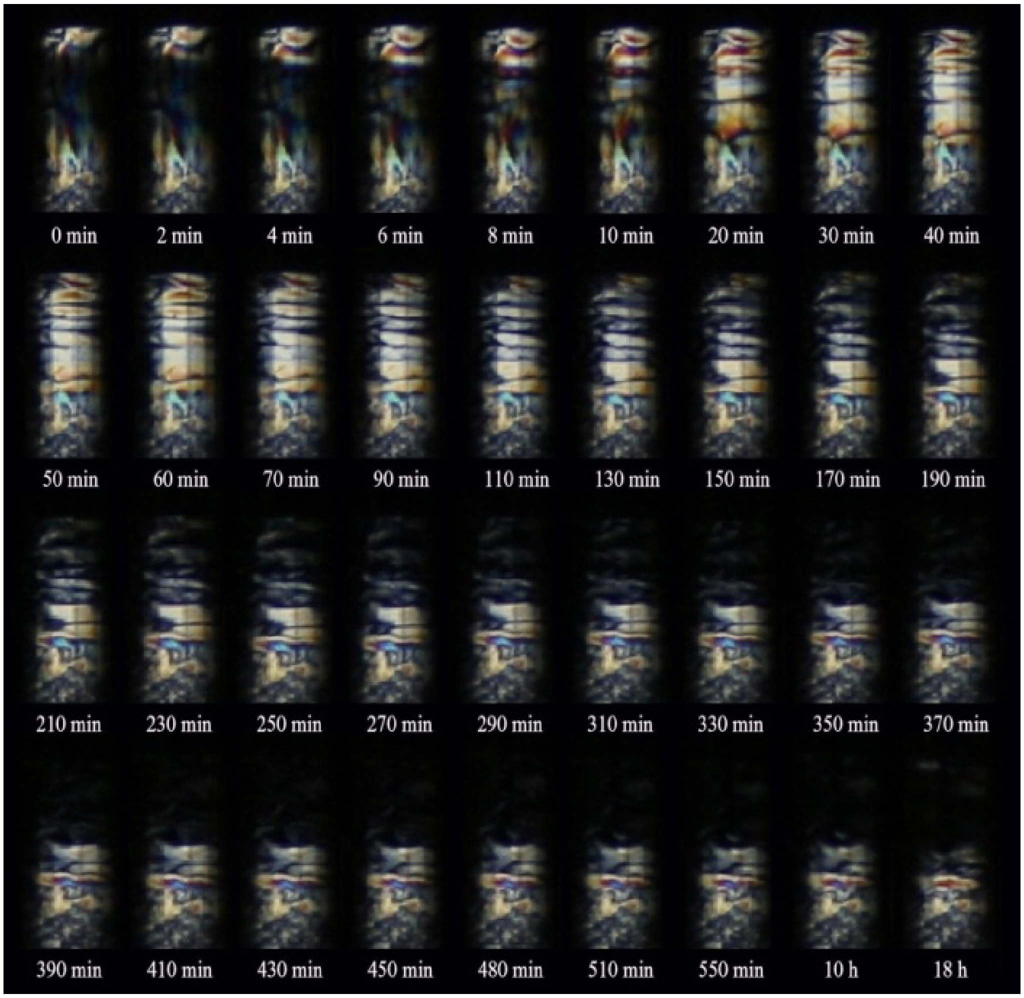

Figure 1: Photo series of the reorientation process of a nematic phase in a 1 T magnetic field. The particles are initially aligned with the director horizontally in the paper plane, and a reorientation is triggered by applying the magnetic field in the same direction. The first sign of stripes appears after a couple of minutes, being most visible in the upper part. After about 8 hours, the majority of the particles are reoriented to a stable configuration where their plate normals point along the line of sight (out of the paper) or vertically, and therefore do not contribute to the birefringence. The vertical black stripes in the pictures are reflections from the magnet

Once this particle configuration was obtained, the capillary was rotated 90 degrees around its axis, thus initially causing the clay plate normals to be aligned in the magnetic field direction. This unstable configuration promoted realignment of the nematic phase. During the subsequent realignment process, visual images were recorded through crossed polarizers, allowing a visualization of the anisotropy in the particle alignment. The polarizers were oriented such that their fast axes were respectively vertical (parallel to the capillary axis), and horizontal (parallel to the magnetic field). A time series of the recorded images with a magnetic field strength of 1 T can be seen in Figure 1. As the magnetic field reorients the particles, transient periodic stripes gradually appear and disappear during the hours-long process of reorientation. The stripes correspond to regions where the particles are oriented with the average plate normal at an angle to the transmission axes of the polarizers.

In systems of platelets with negative diamagnetic susceptibility anisotropy, the non-uniform Frederiks transition is different from that observed in systems with positive diamagnetic susceptibility, in that the first case possesses degeneracy in tilt-angles directions perpendicular to the director axis. For a round flat particle with negative anisotropy of the magnetic susceptibility, a static magnetic field cannot by itself determine which orientation the final director will obtain. In other experiments on systems of disks with this behavior [5-6], the degeneracy is removed by rotating the magnetic field or the sample in the plane normal to the final director orientation.

As these are preliminary measurements, we have not yet modified our setup in this way, and thus we are not yet able to fully characterize the nature of the transition, partly because from birefringence images using only linear polarizers one cannot unambiguously determine the orientation of the particle normals. This could have been achieved using a more complex polarizer setup, e.g. Mueller matrix ellipsometry [12]. However, based on previous experiments using small angle x-ray scattering to determine particle orientation, we expect that the particles in the top part of the nematic sol region reorients to a mainly horizontal alignment (particle normal parallel to the capillary axis), due to the anchoring to the isotropic-nematic interface. After several rotations, all particles will eventually reach this orientation, as it is the only configuration where the particle normal stays perpendicular to the magnetic field. Additionally, several factors of the clay water system, such as gelation and long range colloidal interactions, makes the nematic phase in a clay suspension different from ordinary liquid crystals. From the images of the evolution of the periodic patterns (Figure 1) it can be seen that the stripe formation commences at the top of the nematic sol, close to the isotropic-nematic interface. This could be due to a viscosity gradient in the nematic sol along the capillary axis, i.e. lower viscosity near the isotropic-nematic interface and highest near the transition to the nematic gel.

Figure 2 shows repeated measurements with identical samples, using magnetic fields from 0.5 to 1 Tesla. The threshold value for the inhomogeneous Frederiks transition with this setup is found to be just below 0.5 Tesla. Because of irregularities in the nematic domains, and the limited extent of the nematic sol region, it is with the present samples not possible to obtain precise values for the wavelength for a specific magnetic field strength. However, it seems clear that there is a decrease in wavelength when the magnetic field is increased, and close to 0.5 Tesla, the wavelength looks to diverge, as expected.

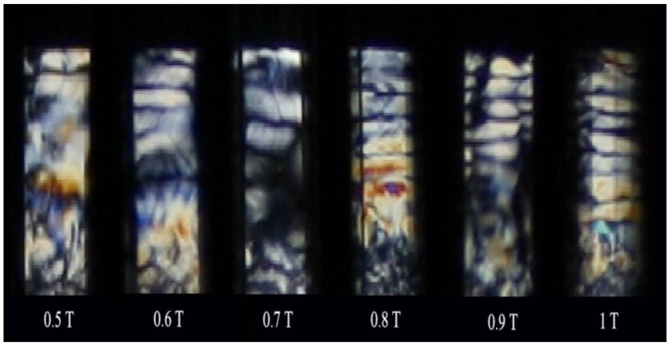

Figure 2: Stripe patterns for magnetic fields from 0.5 to 1 Tesla in the same sample. The pictures were taken at the point in time when the stripes were most clearly defined.

For all the measurements the wavelength shows a tendency to increase as we move down in the sample, which could be due to a viscosity gradient in the nematic gel as the concentration of particles in the nematic sol increases downwards. Furthermore, the duration of the instability decreases with increasing field strengths: the whole process lasts for over 3 hours with magnetic fields close to the threshold, and under 2 hours for fields of 1 Tesla. For low field strengths, the first sign of stripe formation appears after 10 minutes, while for the highest strengths it can take less than five minutes. The periodic structures are clearly transient phenomena, and are seen to decay soon after the magnet is removed. The lifetime is around 2 hours after which there is no longer any pattern with systematic structure.

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