THE JOURNAL OF PHYSICAL CHEMISTRY B

Article

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J. Phys. Chem. B, **2009**, 113 (12), 3704-3708• DOI: 10.1021/jp8068199 • Publication Date (Web): 15 December 2008

The Journal of Physical Chemistry B is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Shape and Director Field Deformation of Tactoids of Plate-Like Colloids in a Magnetic Field[†]

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Received: July 31, 2008; Revised Manuscript Received: October 24, 2008

We investigated by means of polarization microscopy the influence of a magnetic field on the shape and director field of nematic droplets in dispersions of plate-like colloidal particles. To interpret the experimental observations, we put forward a simple theory in which we presume strong anchoring and a sphero-cylindrical droplet shape. This model allows us to extract values for the interfacial tension and the splay elastic constant from the experimental data.

1. Introduction

The isotropic-to-nematic phase transition in dispersions of rod-like colloidal particles is accompanied by the formation of metastable nematic droplets or "tactoids" that eventually coalesce to become a nematic phase on macroscopic scales.[1] The shape and director field of a tactoid are determined by an interplay between its bulk elastic and interfacial free energy.[2,3] Depending on the size relative to a persistence length, $\xi \equiv K/w$, defined as the ratio between an average Frank elastic constant, K, and the anchoring strength, w, large droplets are nearly spherical and small droplets tend to be elongated and spindle-like because the surface anchoring for rods appears to be preferentially tangential. For both spherical and spindle shapes, the director field is bipolar for a sufficiently anisotropic surface tension and homogeneous if this is not the case.

The isotropic-to-nematic transition in dispersions of plate-like particles, the first unambiguous observation of which dates back to just ten years ago,[4] is also accompanied by tactoid formation. A simple scaling analysis of the elastic and interfacial free energy teaches us that the director pattern must be homogeneous in small tactoids and radial in large tactoids, which we also observed recently.[5] The reason is that plate-like particles for entropic reasons prefer homeotropic anchoring, i.e., point their main surface normal along the normal to the surface. Indeed, we found that larger tactoids have a radial director-field pattern with a point defect or hedgehog at its center, and with the platelet's surfaces aligned parallel to the isotropic−nematic interface.

Traditionally, magnetic fields have played an important role in the investigation of liquid crystals and the probing of their bulk and surface properties.[6] An important example is the Frederiks transition, where a thin layer of a well-aligned nematic between parallel plates undergoes a sudden change in the director field at a critical magnetic field strength. This method allows, e.g., for the experimental determination of the Frank elastic constants of nematic compounds. It is now widely applied and started with the work of Frederiks on thermotropic liquid crystals of rod-like molecules in the 20s[7] and was first applied in the 80s by Meyer et al. to lyotropic liquid crystals.[8] Recently, Van der Beek et al. applied this method to lyotropic liquid crystals of plate-like particles.[9]

Bipolar tactoids in colloidal dispersions of rod-like colloidal particles have been shown to orient and stretch under the influence of a magnetic field but do not exhibit a Frederiks transition.[2] This observation can be understood by applying standard elasticity theory and by realizing that the drops are freely suspended in solution. The measurements can in fact be described quantitatively if ratios of the bend and splay elastic constants of $K_3/K_1 \sim 10-100$ are inserted and a surface tension γ of order 10^{-6} N/m is invoked. The remarkably large values of K_3/K_1 found were in ref 10 attributed to the neglect of the saddle-splay surface elastic constant K_{24}.

Here, we study with the aid of polarization microscopic techniques tactoids of sterically stabilized plate-like particles with a radial director field in a magnetic field. We observe that above a critical field strength these undergo a drastic reorganization of the director field, quite unlike the situation in tactoids of rod-like particles, and that this reorganization is accompanied by a deformation of their shape. We put forward a simple model for this transformation. Our model allows us to determine experimentally the splay elastic constant from the critical magnetic field strength at which the director field starts to change, and the interfacial tension from the degree of deformation of the tactoid at higher magnetic field strengths.

2. Materials and Methods

Colloidal gibbsite platelets were synthesized following the procedure developed in our laboratory.[11] The hexagonal platelets, with a diameter of 220 nm and thickness of 8 nm, were sterically stabilized with a modified polyisobutylene (Shell, SAP 230) and dispersed in bromotoluene.[4] The dispersion was concentrated so as to be in the biphasic (isotropic−nematic coexistence) regime (21 v/v %). The sample was homogenized and left to phase separate, which evolved via the formation, sedimentation and subsequent coalescence of tactoids. Samples

[†] Part of the "PGG (Pierre-Gilles de Gennes) Memorial Issue".
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10.1021/jp8068199 CCC: $40.75
Published on Web 12/15/2008

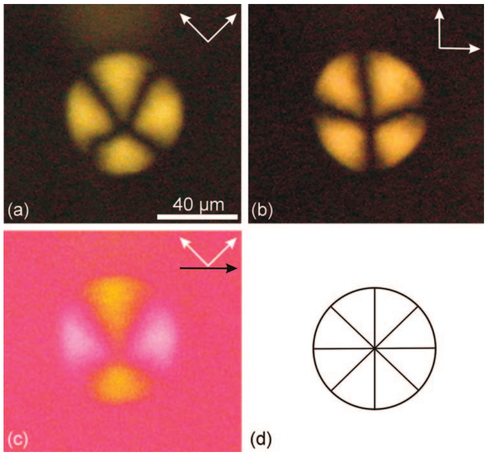

Figure 1. Tactoid of sterically stabilized platelike gibbsite particles with a radial director field and a point defect (hedgehog) in its center. (a) Polarization microscopy image, with the white arrows indicating the polarizers. (b) The same tactoid with the polarizers rotated for 45°. The black cross, where the particles are oriented along the polarizers, rotates with the polarizers, indicating a rotationally symmetric director field. (c) The same as (a), now with retardation plate, the black arrow indicating the direction of the slow axis. In the blue parts the director is parallel and in the yellow parts perpendicular to the slow axis of the retardation plate. (d) Deduced director field of the tactoid.

were studied in flat optical capillaries (VitroCom), with internal dimensions of 200 μm × 4 mm × 4 cm, and flame-sealed to avoid evaporation of the solvent.

The magnetic field was generated with a Bruker BE25v electromagnet, equipped with large flat pole shoes producing a very homogeneous magnetic field in the sample volume. Field strengths ranged from $B = 0-2$ T and were monitored with a LakeShore 421 Gaussmeter. The samples were investigated with a polarization microscope setup, assembled from the head of a Zeiss Axiolab microscope, equipped with crossed polarizers, a 20× Nikon CFI Plan Fluor ELWD objective, and a Nikon Coolpix 995 CCD camera. The microscope is tilted 90°, so its focal plane is along gravity.

Previous studies on sterically stabilized gibbsite suspensions[9,12] established that the magnetic susceptibility $\Delta\chi$ is -10^{-22} J/T^2, which means that the particles align with the director perpendicular to the magnetic field. These studies also demonstrated that the largest index of refraction in the nematic phase, Δn_{sat}, is along the director.

3. Results

Figure 1 shows a typical large tactoid of the sterically stabilized colloidal gibbsite platelets with homeotropic anchoring. From the fact that there is rotational symmetry (Figure 1a,b) and the observed interference colors (Figure 1c), the director field shown in Figure 1d can be deduced. (Note: the director is perpendicular to the long side of the platelets.) The tactoid has a radial director field with a point defect of topological charge +1 (a so-called hedgehog defect) in its center.

When a tactoid with such a director field is placed in a magnetic field, starting at a certain critical field strength, the dark cross inside the tactoid (where the platelets are oriented along the polarizers) transforms into a dark line along the magnetic field, as depicted in Figure 2. Platelets in this dark region are oriented with their director perpendicular to the focal plane and therefore do not exhibit birefringence. This implies that the point defect in the center of the tactoid is stretched to a line defect along the direction of the magnetic field, from

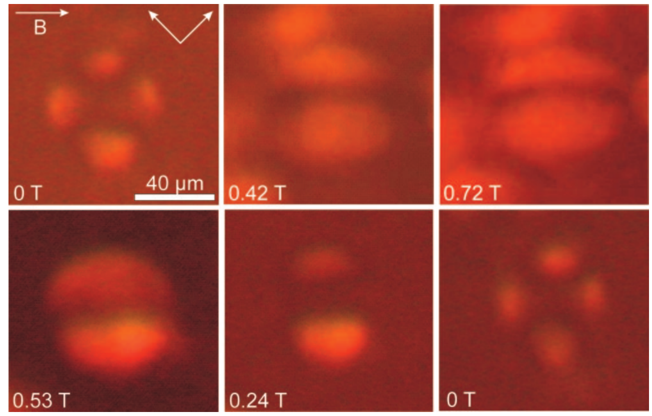

Figure 2. Deformation of a tactoid of sterically stabilized gibbsite platelets in a magnetic field of increasing strength (upper figures). The point defect is stretched to a line defect, and the tactoid becomes elongated in the magnetic field direction. When the field is decreased (lower figures) the tactoid relaxes back to its original configuration.

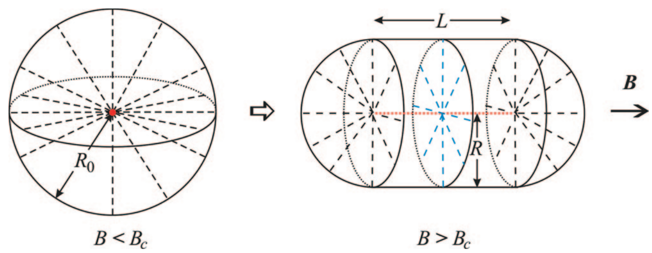

Figure 3. Left: for a magnetic field B smaller than a critical field B_c, the droplet is spherical with radius R_0: the director field (dashed lines) is radial in 3D (pure splay) with a point defect (central dot). Right: for a magnetic field larger than B_c, the tactoid adopts an elongated shape that we model by a cylinder of length L and radius R with hemispherical end caps. In the cylinder, the field is radial in 2D with a defect line on the axis and in the caps the field is radial in 3D, originating from the ends of the defect line.

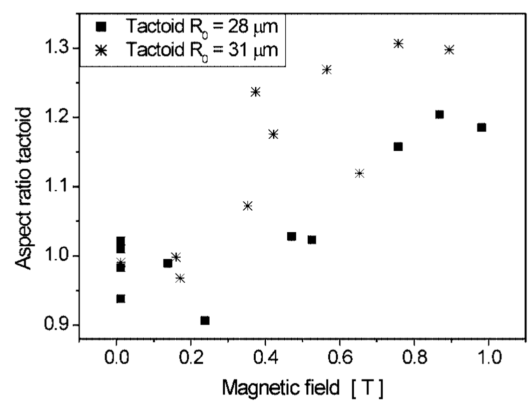

Figure 4. Aspect ratio of two different sized tactoids of sterically stabilized platelike gibbsite particles as a function of magnetic field strength.

which the director lines go to the surface, as illustrated in Figure 3. When the magnetic field is increased even more, the tactoid is elongated with its long axis in the direction of the magnetic field. When the magnetic field is decreased, the tactoid relaxes back to its original configuration within a few minutes, so the process is reversible. Figure 4 shows the degree of deformation as a function of magnetic field strength of two different tactoids in terms of the ratio of the length L' and the diameter D.

4. Theoretical Model

We now describe a simple model that can explain the director field transition and the accompanying elongation of a tactoid for a sufficiently strong magnetic field. We presuppose a particular shape and internal structure of the elongated droplet that permits a straightforward calculation of the magnitude of the deformation of the director field and the computation of the overall surface area. The approach we follow is first to write down an appropriate free energy given the model description and to subsequently minimize this free energy with respect to a variational parameter that describes the elongated shape of the tactoid. The application of this model to the experimental data then enables us to extract values for the splay elastic constant and the surface tension.

In the spherical nematic droplet, the platelets are presumed to exhibit perfect parallel alignment to the surface throughout the entire tactoid, so we assume strong-anchoring conditions to hold. This expresses itself in a radial director field characterized by a hedgehog point defect at the center of the drop. For a sufficiently strong magnetic field, its influence on the orientation of the particles becomes significant. This field biases a certain orientation of the platelets, determined by the sign of the diamagnetic susceptibility anisotropy χ_a. For negative χ_a, as is the case for our colloidal gibbsite platelets,[9,13] the particles tend to align their director perpendicular to the magnetic field. In the spherical droplet with radially symmetric director field, the orientation of the particles does minimize the surface energy but not their magnetic energy. Therefore, by way of compromise a nonspherical shape, elongated in the direction of the magnetic field, allows more particles to align with the magnetic field and yet remain their homeotropic alignment to the surface.

In our model we presume the droplet shape to by described by a cylinder of length L and radius R with two hemispherical end caps; see Figure 3. In addition, we suppose the director field in the end caps to be of the same type as in the spherical tactoid, i.e., radial in three dimensions, and in the cylindrical part to be radial in two dimensions with the cylinder axis as the axis of symmetry. This implies that the point defect in the spherical configuration is stretched to a line (or disclination) defect of topological charge +1. Associated with the formation of the line defect from the point defect is an increase of the elastic free energy of the director field. Furthermore, the surface area increases with the elongation, giving rise to an additional surface free energy cost. These two effects are compensated for by the free energy gain on account of an increase of the number of particles aligning with the magnetic field.

The free energy we set up comprises three contributions: magnetic, elastic, and surface energy. The magnetic energy F_{mag} obeys[6]

$$F_{mag} = -\frac{\rho\chi_a}{2}\int d\boldsymbol{r}\,(\mathbf{n}\cdot\mathbf{B})^2 = \Sigma R^3$$

with $\mathbf{n}$ the director field, $\mathbf{B}$ the uniform magnetic field with magnitude B, ρ the particle number density, and $\Sigma \equiv -{}^2/_9\pi\rho\chi_a B^2$. This contribution comes from the end caps, since the director field is perpendicular to the magnetic field in the cylinder.

The elastic energy F_{el} associated with the distortion of the director field has contributions from the hemispherical end caps and from the cylindrical mid section. The contribution of the cylindrical part can in turn be divided into a part from the bulk and a part from the core containing the defect line on the cylinder axis. This gives an elastic free energy proportional to $f_{core}La^2$, with f_{core} the energy density of the core of the defect and a the core diameter of the defect line. We absorb this contribution into the bulk free energy of the cylindrical portion of the drop by introducing an effective defect core diameter b that we expect to be of the order of the diameter of the platelets.

A radial director field in the cylinder portion and in the end caps implies that it is irrotational in the entire droplet. This makes the deformation of the field a pure splay one, giving an elastic deformation energy of the form[14] $F_{el} = (K_1/2)\int d\mathbf{r}\,(\nabla\cdot\mathbf{n})^2$, where K_1 is the splay elastic constant. We conclude that the elastic energy of our model tactoid must obey

$$F_{el} = K_1 L\pi \ln\left(\frac{R}{b}\right) + 8\pi K_1 R \tag{1}$$

The surface energy F_{surf} is proportional to the surface area of the elongated droplet, so

$$F_{surf} = \gamma(2\pi RL + 4\pi R^2)$$

with γ the surface tension.

From the total free energy $F \equiv F_{mag} + F_{el} + F_{surf}$ we subtract the reference free energy of a spherical droplet of the same volume. Invoking volume conservation enables us to express the shape in terms of a single parameter, i.e., the radius R of the cylinder, which allows for the minimization of F to be performed by differentiation with respect to R. The equation for the optimal shape we find reads

$$3\xi r^2 + \frac{4K_1'\pi}{3}\left(\left(-\frac{2}{r^3} - 1\right)\ln\left(\frac{r}{b_0}\right) + \frac{1}{r^3} - 1\right) + 8\pi K_1' + \frac{8\pi}{3}\left(r - \frac{1}{r^2}\right) = 0 \tag{2}$$

where $\xi \equiv \Sigma R_0/\gamma$, $K_1' \equiv K_1/\gamma R_0$, $r \equiv R/R_0$, and $b_0 \equiv b/R_0$, with R_0 the radius of the spherical tactoid. If the optimal value of R is larger than R_0, then by construction $R \equiv R_0$ because the model allows for negative values of the length of the cylindrical part of the drop.

The critical value of the magnetic field strength, B_c, where the director-field transition occurs can be obtained from eq 2 by insisting that $r = R/R_0 = 1$, giving

$$B_c^{\,2} = \frac{6K_1}{\rho\chi_a R_0^{\,2}}(\ln b_0 + 2) \tag{3}$$

This critical magnetic field is independent of the surface tension γ because at the onset of the transition the droplet is not deformed yet. This allows us to determine K_1 from eq 3, which can then be used to find γ by fitting eq 2 to the experimental data of the tactoid size for different magnetic fields.

5. Analysis

The model described above enables us to extract material parameters of the liquid crystal from the deformation of the tactoid in the magnetic field. First of all, from the critical magnetic field, where the deformation starts, we obtain the splay elastic constant K_1. From Figure 4 we observe for the tactoid with $R_0 = 28$ μm a critical field strength $B_c = 0.3-0.4$ T and for the tactoid with $R_0 = 31$ μm a critical field strength $B_c = 0.2-0.3$ T.

Using eq 3, with $\Delta\chi$ is -10^{-22} J/T^2, $\rho = 4 \times 10^{-22}$ and $b_0 = 10^{-2}$ (where we assume that the size of the defect is of the order of the platelet diameter), we find $K_1 = (1.4-2.6) \times 10^{-13}$ N for the 28 μm tactoid and $(0.9-2) \times 10^{-13}$ N for the 31 μm tactoid. From the deformation of the shape above the critical

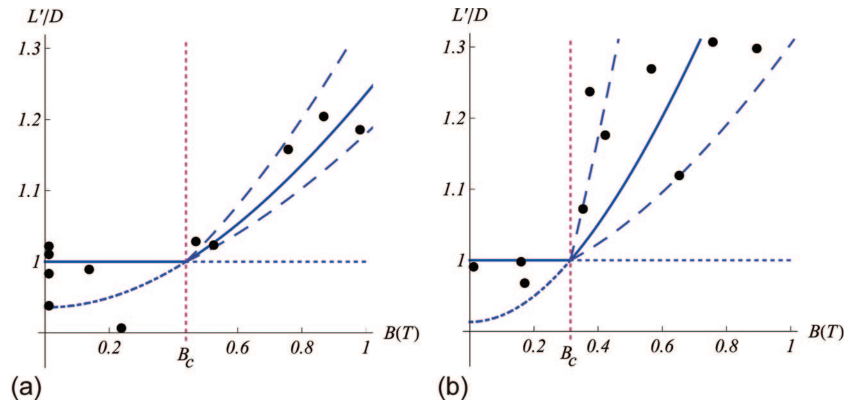

Figure 5. Aspect ratio in terms of L'/D of tactoids of sterically stabilized platelike gibbsite particles as a function of magnetic field strength. The points depict the experimental data and the solid lines the fit to our theoretical model. The dashed-dot line for $B < B_c$ and $L'/D < 1$ represent the nonphysical solution of equation 2. (a) Fit of the deformation data of the 28 μm tactoid, using $K_1 = 3 \times 10^{-13}$ N, $\gamma = 5 \times 10^{-7}$ N/m (solid line), and $\gamma = 3 \times 10^{-7}$ and 7×10^{-7} N/m (dashed lines). (b) Same results for the 31 μm tactoid with $K_1 = 2 \times 10^{-13}$ N and $\gamma = 2 \times 10^{-7}$ N/m (solid line) and 0.2×10^{-7} and 5×10^{-7} N/m (dashed lines). The steepest lines correspond to the smallest γ.

field strength the interfacial tension γ can be determined. Figure 5a depicts a fit of the deformation of the 28 μm tactoid with eq 2, using $\gamma = 5 \times 10^{-7}$ N/m. The dashed lines, representing theoretical results for $\gamma = 3 \times 10^{-7}$ and 7×10^{-7} N/m, show that the shape is strongly dependent on the interfacial tension where a lower interfacial tension results in a stronger deformation, and the value we find for γ therefore robust. A similar fit for the 31 μm tactoid, depicted in Figure 5b, gives an interfacial tension of 2×10^{-7} N/m, with the dashed lines representing 0.2×10^{-7} and 5×10^{-7} N/m.

6. Discussion

The value we find for the splay elastic constant $K_1 = (0.9-2.6) \times 10^{-13}$ N should be compared to the value for the bend elastic constant K_3 measured by Van der Beek, $K_3 = (7 \pm 1) \times 10^{-14}$ N.[9] We see that K_1 is 1.5−3 times larger than K_3, in agreement with theoretical predictions by Osipov and Hess[15] and recent computer simulations by O'Brien et al.[16]

As expected for these large particles, the interfacial tension is low,[6] though recent capillary rise experiments resulted in an even lower value for the interfacial tension of $\gamma = 3 \times 10^{-9}$ N/m.[12] To understand this rather significant difference, it should be noted that in our analysis of the elastic free energy we ignored the so-called saddle-splay deformation of the field,[14] which is nonzero for a three-dimensional radial director field. This means that the second term of eq 1, originating from the elastic deformation in the end caps, actually contains a renormalized elastic constant $K_1 - K_{24}$, with K_{24} the unknown saddle-splay deformation constant.

Still, even invoking a renormalized splay elastic constant cannot quite account for the discrepancy because the corresponding third term of eq 2 is relatively small compared to the first and second term with $b_0 \sim 10^{-2}$. So the shape is determined primarily by a balance between the magnetic contribution and the term associated with the director field deformation in the cylinder.

A moot point, apart from the quite idealized shape description of the tactoids, is that we presume strong anchoring of the platelets, which may be too strong an assumption both in the cylinder and in the end caps. In the end caps, this assumption implies that there are relatively many particles that show (almost) perpendicular alignment with the magnetic field, which is expensive energetically. In the cylinder, complete anchoring is imposed by choosing a cylindrical tactoid shape, whereas a shape with nonzero curvature of the tactoid surface along the direction of the magnetic field, e.g., an ellipsoid, is probably a more realistic model of a tactoid.

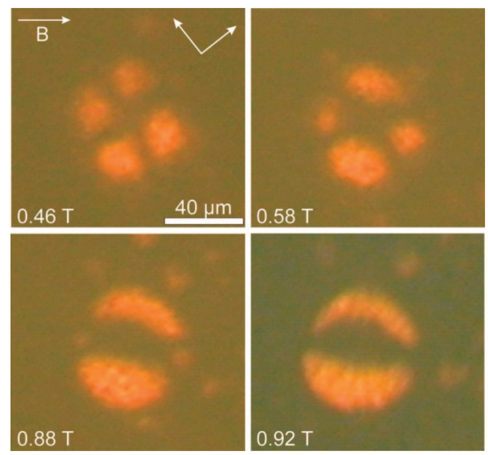

Figure 6. Deformation of a tactoid of charge stabilized gibbsite platelets in a magnetic field. At a field strength of 0.46 T the tactoid still has its original configuration. From 0.58 T on the director field deforms.

If we presume imperfect anchoring, the critical magnetic field strength becomes a function of the anchoring strength,[17,18] w. Also, this would lead to a reduction in the deformation of the droplets with increasing magnetic field strength, because the droplet can adjust its director field without actually deforming its shape. This implies that the observed deformation is smaller than one would expect based on perfect anchoring, and therefore that an estimate for this interfacial tension γ based on it must produce a value that is larger than the actual value.

We found some direct evidence for incomplete anchoring in the case of tactoids of *charge-stabilized* gibbsite platelets, which were prepared by the addition of aluminum chloro hydrate to the starting gibbsite suspension.[19,20] As shown in Figure 6, the director field changes as in the case of sterically stabilized platelets, i.e., the point defect is stretched to a line defect, but the tactoid still seems to preserve its spherical shape. The interfacial tension, which is presumably larger in this particular system, does not allow the tactoid to enlarge its surface by deviating from the spherical shape, but prefers non homeotropic anchoring of the platelets.

7. Conclusions

Tactoids of plate-like colloidal particles characterized by a radial director field and a hedgehog point defect in the center exhibit a very interesting deformation behavior when exposed to an externally applied magnetic field. This includes a symmetry change of the director field as well as a shape deformation.

By studying the deformation of tactoids of plate-like particles in a magnetic field, we have been able to determine both the splay elastic constant and the interfacial tension in a single experiment by applying a theory that balances surface, elastic, and magnetic forces.

Our approximate theoretical model explains why a minimal (critical) magnetic field strength is required to deform the tactoid. The splay elastic constant $K_1 = (0.9-2.6) \times 10^{-13}$ N obtained from this critical magnetic field strength is 1.5−3 times larger than the previously measured bend elastic constant K_3, and in reasonable agreement with theory and simulations.

The value of $\gamma = (2-5) \times 10^{-7}$ N/m we found for the interfacial tension is significantly larger than found previously for the same system from capillary rise experiments. We attribute this to effects of imperfect surface anchoring neglected in the theory.

Acknowledgment. We are grateful for the expert technical assistance of B.W.M. Kuipers in realizing the magnetic polarization microscopy setup. We thank D. van der Beek for providing the sterically stabilized gibbsite particles. A.A.V. thanks the Royal Netherlands Academy of Arts and Sciences for financial support. The work of R.H.J.O. and P.v.d.S. forms part of the research programme of the Dutch Polymer Institute (DPI, project # 648).

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