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Liquid-crystal phase transitions in suspensions of plate-like particles

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We study the liquid-crystalline phase behaviour of suspensions of hard colloidal platelets, in particular, the relationship between their size polydispersity and the stability of a nematic, columnar and smectic phase. A first-order nematic-to-columnar transition is observed for suspensions up to 25% polydispersity in platelet diameter (σ_D). However, at densities slightly above nematic-columnar coexistence, the columnar order appears to vanish in the case of $\sigma_D = 25\%$, while columnar stability persists for $\sigma_D = 17\%$. The observed tolerance of polydispersity in the columnar phase, being a two-dimensional crystal, seems remarkable in light of current predictions for the terminal polydispersity for hard-sphere crystallization and hard-rod smectic ordering.

Keywords: suspension; colloid; non-spherical particles;
phase behaviour; nematic; columnar

1. Introduction

A marked feature of suspensions of non-spherical particles is their ability to form liquid crystals. In liquid crystals, the constituent particles exhibit long-range orientational order, either without long-range positional order (such as in a nematic phase), or with one-dimensional positional order (a smectic phase) or two-dimensional positional order (a columnar phase), as sketched in figure 1. For suspensions of rod-like particles, the liquid-crystal phase behaviour has been studied extensively for many decades, in experiments (Bernal & Fankuchen 1941; Dogic & Fraden 1997; Dong *et al.* 1996; Folda *et al.* 1988; Hurd *et al.* 1985; Kreibig & Wetter 1980; Maeda & Hachisu 1983; Pelletier *et al.* 1999; van Bruggen *et al.* 1999; Zocher 1925), theory (Onsager 1949; Vroege & Lekkerkerker 1992) and, more recently, also by simulations (Bolhuis & Frenkel 1997; Frenkel & Mulder 1985; Frenkel *et al.* 1988). The variety of experimental systems exhibiting a nematic and/or a smectic liquid-crystal phase includes suspensions of inorganic rods (vanadium pentoxide (V_2O_5) (Pelletier *et al.* 1999; Zocher 1925), akaganeite (β -FeOOH) (Maeda & Hachisu 1983), and sterically stabilized boehmite (AlOOH) (van Bruggen *et al.* 1999)), organic rods (microcrystalline cellulose (Dong *et al.* 1996), poly(tetrafluoroethylene) (Folda *et al.* 1988)), and biological rods (Tobacco Mosaic virus (Bernal & Fankuchen 1941; Hurd *et al.* 1985; Kreibig & Wetter 1980) and fd-virus (Dogic & Fraden 1997)). Often, these suspensions contain approximately hard (i.e. short-range repulsive) rods, which implies that the ordering of particles cannot be explained by attractive forces. In the 1940s, Onsager showed that for such systems the driving force for the formation of a nematic

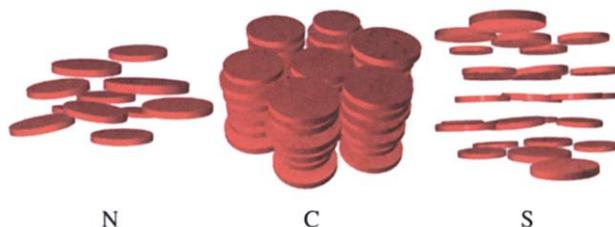


Figure 1. Structure of the three main classes of liquid crystals: the nematic phase (N), the columnar phase (C), and the smectic phase (S), schematically depicted here for the case of plate-like particles. While each of these phases exhibits long-range orientational order, they differ by the positional correlations between the particles. In the nematic phase, long-range positional order is absent. The columnar phase has a two-dimensional lattice of columns, which are made up of liquid-like stacks of particles. The smectic phase is characterized by a one-dimensional periodic array of layers of particles.

phase lies in a gain of entropy. This is due to the balance between orientational entropy (favouring the isotropic phase) and excluded volume entropy (favouring the nematic phase), which may give rise to a stable nematic phase at higher particle concentrations. Although the Onsager theory applies not only to rod-like particles but also to plate-like particles, observations of the I–N transition in platelet suspensions are particularly rare in the literature. In fact, the I–N transition in suspensions of plate-like clay particles—which was reported initially by Langmuir (1938) and inspired Onsager to extend his theory to platelets—is almost always obscured by the interference of gelation (Gabriel *et al.* 1996; Mourchid *et al.* 1995). In the 1980s, synthetic clays such as Laponite and Saponite were introduced in this field, in an attempt to circumvent the poorly understood behaviour of natural clays. However, the main result from persevering investigations on the phase behaviour (Gabriel *et al.* 1996; Mourchid *et al.* 1995) and mesoscopic structure (Morvan *et al.* 1994) of these suspensions is that gelation is again ubiquitous, and the principal mechanism underlying the obscured I–N transition remains an unresolved issue.

Recently, preparation methods have been developed for two new types of platelet suspensions, which may serve as model systems of approximately hard colloidal platelets. The first system comprises low-aspect-ratio $\text{Ni}(\text{OH})_2$ hexagons of low polydispersity, which are stabilized by a combined short-range electrostatic and steric stabilization. The aspect ratio, which is defined as the particles' diameter D divided by their thickness L , is given by $D/L \simeq 5$ in this case. The other platelet suspension consists of sterically stabilized gibbsite ($\text{Al}(\text{OH})_3$) hexagons with a higher aspect ratio ($D/L \simeq 12$) and a slightly higher polydispersity. The liquid-crystal phase behaviour of these two suspensions is structurally different. While the low-aspect-ratio platelets exhibit a transition from an (apparently) isotropic to a columnar phase (Brown *et al.* 1998, 1999), the high-aspect ratio platelets display the Onsager transition from an isotropic to a nematic phase (van der Kooij & Lekkerkerker 1998). The absence of a nematic phase in the first system is consistent with computer simulations for platelets with $D/L = 5$ (Veerman & Frenkel 1992). Moreover, in the case of higher-aspect-ratio platelets, computer simulations find not only the observed I–N transition, but also a nematic–columnar transition for densities roughly twice those at the I–N transition. A major difference, however, between the platelets studied in simulation and those of the experimental gibbsite suspension, is the polydispersity of the latter. The

polydispersity in diameter, defined by the standard deviation in diameter divided by the mean, is typically 25%. How does such a polydispersity affect the high-density liquid-crystal phase behaviour of platelets?

In the case of spheres, the effect of polydispersity has attracted considerable attention. The central question concerns the value and even the very existence of a so-called terminal polydispersity σ_t , above which no crystallization may occur. Experiments indicate the existence of a terminal polydispersity below 10% in the sphere diameter (Henderson *et al.* 1996; Pusey 1987). As for rods, computer simulation predicts a stable smectic phase up to a polydispersity in rod length of 18%, while for higher polydispersities the smectic phase is preempted by a columnar phase (Bates & Frenkel 1998). Accordingly, in experiments, almost-monodisperse rod-like virus particles show a smectic phase (Dogic & Fraden 1997), while polydisperse solutions of DNA rods show a columnar phase instead (Livolant *et al.* 1989).

In the present study we explore the liquid-crystal phase behaviour of sterically stabilized gibbsite platelet suspensions, up to concentrations beyond the I–N transition. We consider two systems which differ by the degree of polydispersity in diameter of the constituent platelets (17% and 25%, respectively). The aim of the experiments is to answer the following questions. Do these suspensions of plates, given their polydispersity, show a nematic–columnar phase transition, as predicted for monodisperse plates? Or do they, in order to circumvent the effect of polydispersity in diameter, form a smectic phase instead? What is the role and extent of particle-size partitioning between coexisting phases?

2. Experimental section

A suspension of sterically stabilized gibbsite ($\text{Al}(\text{OH})_3$) colloids is prepared by hydrothermal treatment of an acidic aluminium alkoxide solution, followed by a grafting procedure using a modified polyisobutylene ($M_n \approx 1000 \text{ g mol}^{-1}$) steric stabilizer to provide the particles with approximately hard-core interactions when dispersed in apolar solvents, like toluene in this case. A more-detailed description of the synthesis of this suspension can be found in van der Kooij & Lekkerkerker (1998), Philipse *et al.* (1994), Wierenga *et al.* (1998) and van der Kooij *et al.* (2000).

To obtain a suspension of platelets with a lower polydispersity, part of the parent suspension is submitted to fractionation at the I–N transition. We use a scheme which resembles the method of depletion-enhanced crystallization fractionation of emulsion droplets, as described by Bibette (1991). Samples are left to I–N phase separate, using $\pm 2 \text{ g l}^{-1}$ of added non-adsorbing polymer to enhance fractionation, yielding *ca.* 80% nematic phase in coexistence with 20% isotropic phase. The isotropic upper phase is subsequently removed. By dilution of the remaining nematic phase (using polymer solution) back to the I–N region and repeating this scheme twice, the suspension thus obtained is lower in polydispersity than the original system. Note that the depletion attraction (Asakura & Oosawa 1954) induced by the non-adsorbing polymer is essential in this scheme, as fractionation (and hence the possibility of reducing the system's polydispersity) is rather limited for the I–N transition in the absence of polymer (Bates & Frenkel 1999; van der Kooij & Lekkerkerker 1998). The non-adsorbing polymer is subsequently removed by redispersing in polymer-free solvent after sedimentation. The number-average diameter $\langle D \rangle$ of the grafted platelets is based on the diameter of the core, determined from TEM micrographs,

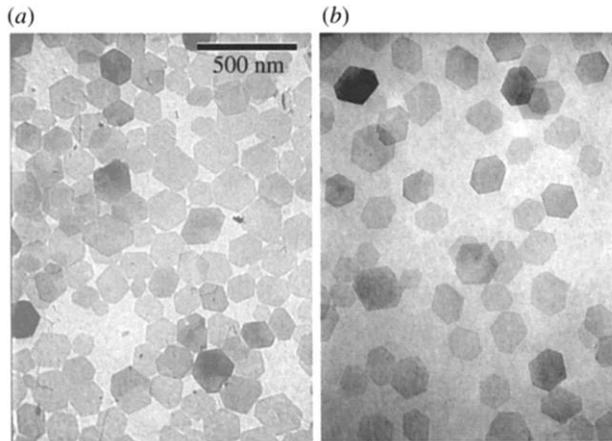


Figure 2. Transmission electron microscopy (TEM) images of (a) the parent suspension ($\sigma_D = 25\%$) and (b) the fractionated suspension ($\sigma_D = 17\%$).

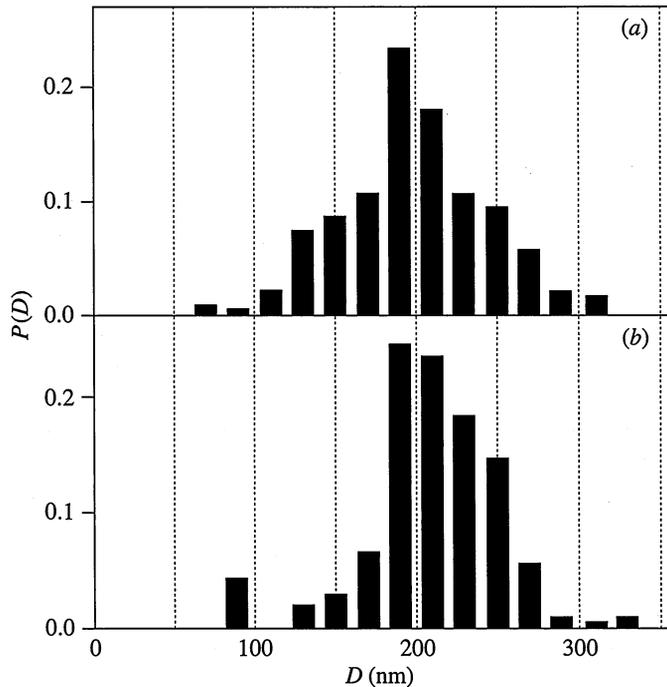


Figure 3. Diameter distributions $P(D)$ of the (a) parent and (b) fractionated platelet suspension, as determined from TEM. Distributions are normalized such that $\sum P(D_i) = 1$. Values for the diameter include the estimated thickness of the grafted polymer layer.

plus twice the estimated thickness (4 nm) of the grafted polymer layer (Smits *et al.* 1989). We define the diameter of the hexagons by the diameter of a circle of equal area, with a relative standard deviation $\sigma_D = \sqrt{\langle D^2 \rangle - \langle D \rangle^2} / \langle D \rangle$. Diameter distributions, as determined from TEM pictures of the parent and fractionated suspensions (figure 2), are presented in figure 3. Quite clearly, figure 3 shows that the

Table 1. Fractionation in the N-C coexistence region

(The diameter distributions of the parent (I) and the pre-fractionated system (II), before and after N-C phase separation. Values are determined from TEM micrographs by measuring *ca.* 200 particles in each case.)

system	after phase separation					
	before phase separation		N phase		C phase	
	$\langle D \rangle$ (nm)	σ_D (%)	$\langle D \rangle$ (nm)	σ_D (%)	$\langle D \rangle$ (nm)	σ_D (%)
I	198	25	196	26	200	18
II	212	17	209	18	220	14

fractionation procedure, based on the removal of the coexistent isotropic phase, has largely cut off the small-diameter part of the particle-size distribution. The resulting polydispersity σ_D of the fractionated system is 17%, compared with 25% of the parent suspension (table 1).

The number-average thickness $\langle L \rangle$ of the plates (including the grafted polymer layer) is *ca.* 14 nm, with a standard deviation which is experimentally not readily accessible, but which is probably lower than that in diameter (van der Kooij & Lekkerkerker 2000). The aspect ratio $\langle D \rangle / \langle L \rangle$ of the grafted particles is, thus, approximately equal to 13.

The particle volume fraction ϕ (which includes the solvent immobilized in the grafted polymer layer) is calculated as the mass concentration (determined by drying a known amount of dispersion to constant weight at 75 °C) divided by the effective mass density of the grafted particles. Following van Bruggen *et al.* (1999), the latter is derived from the TEM particle dimensions, the estimated thickness of the stabilizing layer (Smits *et al.* 1989), the polymer mass fraction from elemental analysis, and the mass density of gibbsite (Gitzen 1970). This yields a mass density of *ca.* 1.3 g cm⁻³, with an estimated error of 10% due to the uncertainty in polymer-layer thickness.

Small angle X-ray scattering (SAXS) experiments are performed on the DUBBLE beam line at the ESRF, Grenoble, France. A 512 × 512 pixel detector is placed 8.5 m from the sample, which gives, using a wavelength $\lambda = 0.138$ nm, an accessible q range of *ca.* 0.02–0.7 nm⁻¹ (the scattering vector $q = (4\pi/\lambda) \sin(\frac{1}{2}\theta)$, with θ the scattering angle). After correction for transmission and background radiation, the two-dimensional scattering patterns are radially averaged, while masking the beam-stop. Suspensions are placed in round \emptyset 2 mm cells and left for two weeks to reach equilibrium. For the tilting experiments, flat 0.2 mm cells are used, in order to obtain an approximately single-crystalline state.

3. Results and discussion

The first phase transition that is encountered upon increasing the volume fraction of the platelet suspensions is the I-N transition, just below $\phi = 0.2$ (see figure 4). In the I-N biphasic gap, an isotropic upper phase coexists with a birefringent nematic bottom phase, and they are macroscopically separated within 12 h after homogenizing the sample. There is a marked discrepancy between the two systems of different diameter polydispersity (σ_D) in terms of the width of their biphasic region, $\Delta\phi_{IN}$.

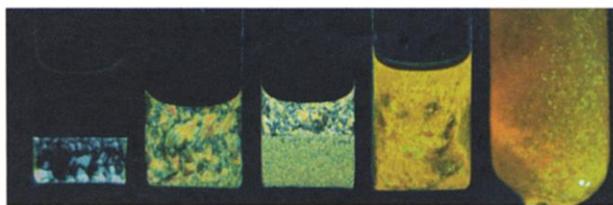


Figure 4. Tubes containing suspensions at varying concentrations, photographed between crossed polarizers. The suspensions depicted here comprise platelets with 17% polydispersity in diameter. From left to right, ϕ ranges from 0.19 (I + N), 0.28 (N), 0.41 (N + C), to 0.47 (C). The tube to the right depicts the monophasic columnar sample at $\phi = 0.45$ as observed without polarizers but illuminated by white light. The colour of the Bragg reflections varies from yellow to green, as the angle between the incident light and viewing direction is in the range $50\text{--}70^\circ$.

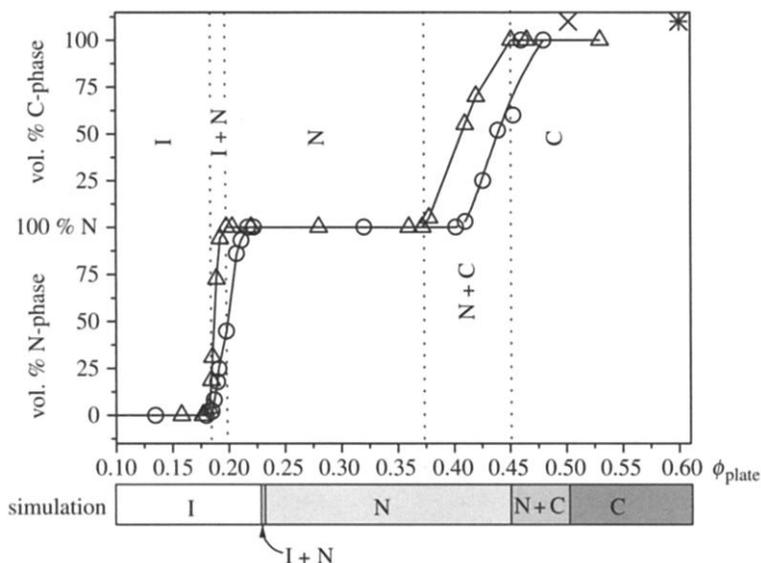


Figure 5. Phase diagram of the suspensions, depicting the relative volume of the nematic and columnar phase after phase separation as a function of the platelet volume fraction ϕ . Results apply to $\sigma_D = 17\%$ (open triangles) and $\sigma_D = 25\%$ (open circles), respectively. The crosses and asterisks belong to the latter system but at densities beyond columnar stability, corresponding to curves c and d, respectively, in figure 6. The dotted lines indicate the boundaries of the coexistence regions of the suspension with $\sigma_D = 17\%$. Results from computer simulation (Veerman & Frenkel 1992) of monodisperse hard discs, extrapolated to the current aspect ratio $\langle D \rangle / \langle L \rangle$ of approximately 13, are included for comparison.

If we define $\Delta\phi_{IN}$ by the volume fraction difference between the upper and lower boundaries of the biphasic gap, divided by their mean, we find that this width is twice as broad in the case of the suspension with $\sigma_D = 25\%$ as that with $\sigma_D = 17\%$ (figure 4). A comparably strong broadening of the biphasic gap was observed earlier in computer simulations, where $\Delta\phi_{IN}$ was found to increase quadratically with σ_D of the polydisperse discs (Bates & Frenkel 1999).

Upon increasing the plate volume fraction to roughly twice the I–N coexistence density ($\phi \approx 0.4$), both the suspension of 17% and 25% polydispersity enter a biphasic

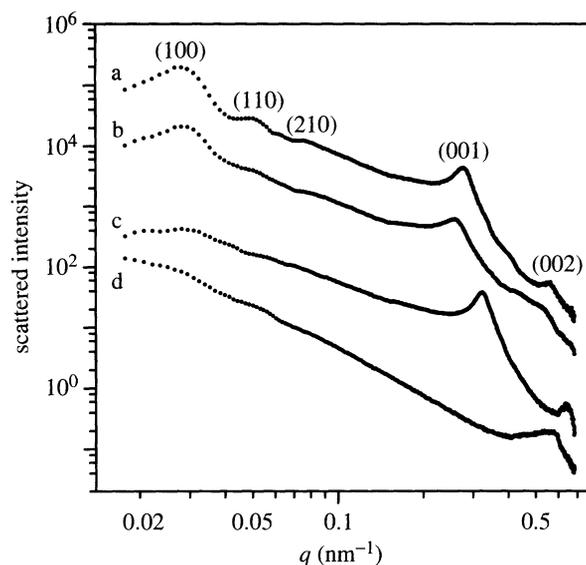


Figure 6. SAXS patterns for samples varying in polydispersity and volume fraction. Curve a is for the case in which $\sigma_D = 17\%$ at $\phi = 0.45$, curves b–d are for the cases in which $\sigma_D = 25\%$ at $\phi = 0.45, 0.5$ and 0.6 , respectively. Curves a and b correspond to columnar ordering, curve c to smectic-like order at densities above columnar stability, and curve d depicts the glassy state encountered upon increasing the density even further. Curves shown are shifted vertically for clarity.

region in which a nematic upper phase coexists with a more concentrated birefringent bottom phase. A columnar signature of the lower phase is suggested by unequivocal Bragg-reflections when illuminated by white light (figure 4). The colour of the Bragg reflections varies from green to yellow to red upon varying the scattering angle. Reflections of blue light can hardly be observed, due to the absorbance by the particles' grafted polymer. The fact that the reflections appear for wavelengths of visible light demonstrates that the crystalline order pertains to a periodicity on a length-scale of the plate diameter (characteristic of columnar ordering) rather than the much smaller plate thickness (as in smectic ordering). By applying Bragg's law to the angle of reflection measured for different wavelengths of light, we identify the characteristic spacing (of the (100) reflection, see SAXS results) as 219 ± 5 nm and 214 ± 5 nm in the cases of the parent and fractionated suspensions, respectively. This corresponds to a typical distance between the centres of the columns of 253 ± 6 and 247 ± 6 nm.

Comparison of the experimentally observed I–N and N–C transition densities with computer simulations for monodisperse hard discs (Veerman & Frenkel 1992), as depicted in figure 5, shows that the transitions in the experiment are shifted to slightly lower densities. The difference in shape of the platelets studied (hexagonal in the experiment versus circular in the simulation) can be expected to be a major contribution to this shift, as shown recently for the I–N transition (Bates 1999). The time-scale for macroscopic phase separation in the N–C biphasic gap varies from a few days to *ca.* 2 weeks, increasing towards the columnar boundary of the coexistence region.

Table 2. q values of the scattering peaks in the radially averaged SAXS pattern

sample	σ_D (%)	ϕ	q (10^{-2} nm $^{-1}$)				
			(100)	(110)	(210)	(001)	(002)
a	17	0.45	2.81	4.88	7.40	27.8	55.5
b	25	0.45	2.89	5.00	7.44	25.6	—
c	25	0.5	(2.88)	—	—	32.3	64.4

SAXS experiments provide further proof for the columnar signature of the dense liquid-crystal phase. Curves a and b in figure 6 correspond to the columnar phase in the case of 17% and 25% polydispersity, respectively. These curves show practically identical features. In the small- q regime, where the spacing $d = 2\pi/q$ is of the order of the diameter of the plates, we can distinguish one major peak and two additional peaks. The q values of these three peaks (table 2), whose q ratio is approximately $1 : \sqrt{3} : \sqrt{7}$, reveal that ordering in the plane of the plate diameters is hexagonal, with the peaks corresponding to the (100), (110) and (210) reflections. Apparently, the (200) reflection is relatively weak compared with its neighbouring (110) and (210) peaks, such that it is not (clearly) resolved in the scattering profile. From the q values of the (100), (110) and (210) peaks we obtain the typical distance between the centres of the columns as 251 ± 4 and 258 ± 1 nm in the suspension with $\sigma_D = 25\%$ and 17%, respectively, in good agreement with the values found with light scattering. This distance is hence practically equal to $(1 + \sigma_D)\langle D \rangle$ in the case of both suspensions. The two peaks at much larger q correspond to 1 and 0.5 times a spacing of roughly the plate thickness, such that we identify them as (001) and (002) reflections. These peaks may therefore relate to (liquid-like) order between the plates along the z -axis of a column of plates.

Although the observed scattering patterns are consistent with a columnar structure, they could also stem from a structure in which particles are hexagonally ordered in layers without lateral correlations between adjacent layers. These structures can be distinguished by considering the effect of tilting the sample with respect to the X-ray beam (Brown *et al.* 1999; Guinier 1994). If the structure is indeed columnar, tilting the sample will not result in a change in q values of the scattering peak maxima, similar to the case of a three-dimensional crystal lattice of spheres. This argument only applies if there is a common axis of alignment of the columns throughout the scattering volume that is roughly parallel to the beam. In the experiment we obtain such a strongly oriented sample by inserting the suspension in a flat 0.2 mm path-length cell. The resulting two-dimensional scattering patterns are shown in figure 7, which depicts two different configurations, the beam being either perpendicular to the flat face of the cell or at an angle of 20° . In contrast to the scattering pattern at 20° , the perpendicular configuration gives an almost negligible intensity of the (001) reflection (corresponding to a spacing of the order of the plate thickness). This means that there is a strongly preferred orientation of the platelets, their faces being parallel to the wall of the cell. On the other hand, the small- q reflections are rings, rather than a hexagonal pattern of spots, and the large- q reflections are also more radially smeared out than the two-fold symmetric scattering that is to be expected for a single domain of a columnar phase. We therefore conclude that the scattering volume comprises several domains, having a common axis of alignment perpendicular

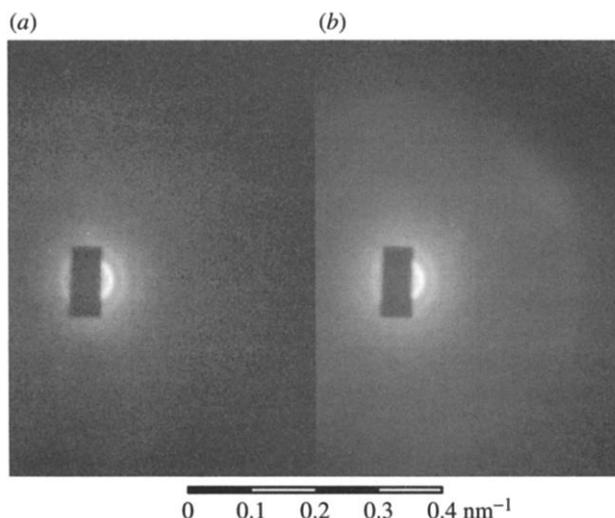


Figure 7. Two-dimensional SAXS patterns of a sample with $\sigma_D = 17\%$ at $\phi = 0.45$ in a flat (0.2 mm thick) capillary. The angle between the incident beam and the normal to the capillary is (a) roughly zero and (b) 20° . The position of the beam-stop is slightly out of the centre to broaden the accessible q space.

to the wall of the cell, which are nevertheless only slightly correlated with respect to orientation in the lateral direction. Comparison of the radially averaged scattering patterns at 0° and 20° demonstrates that the q values of the (small- q) peak maxima do not differ significantly (less than 1%). Leaving aside the unlikely (though not excluded) possibility of a three-dimensional crystal structure, the tilting experiment thus confirms that the dense liquid-crystal phase is a columnar phase.

A remaining question concerns the origin of the observed columnar stability in these systems, where polydispersity must be a major factor. In analogy with computer simulations' predictions for crystallization of polydisperse hard spheres, stabilization of the ordered phase may emanate from fractionation, lowering the polydispersity in the ordered phase at the expense of the polydispersity in a coexisting disordered phase. The present experiments allow us to determine the extent of fractionation, by TEM examination of small samples of a coexisting nematic and columnar phase. Fractionation indeed gives rise to a reduction in the polydispersity in the columnar phase, as we find $\sigma_D = 18$ and 14% in the columnar phase of the two systems studied (table 1). This indicates that at least in the case of the pre-fractionated system ($\sigma_D = 17\%$), we may expect a monophasic columnar state beyond the N-C coexistence region. In fact, the fully columnar state is observed for both suspensions. This demonstrates that even in the case of $\sigma_D = 25\%$, fractionation is not an absolute condition for columnar ordering, and that this polydispersity in diameter is therefore still below the terminal value. One may wonder, however, if the columnar phase remains stable upon increasing the volume fraction of such fully columnar samples, i.e. if interparticle distances decrease such that the disruptive effect of polydispersity in diameter becomes more pronounced. For $\phi = 0.50$ (curve c in figure 6), the columnar (100), (110) and (210) peaks in a sample of $\sigma_D = 25\%$ become markedly suppressed, while, at the same time, the (001) and (002) peaks become more distinct. Bragg reflections for visible light (which pertain to the (100)

reflection) almost completely disappear. One may speculate that the suppression of the columnar peaks and the simultaneous structuring with a periodicity of the order of the plate thickness are indicative of a crossover to smectic-like ordering. Unlike the columnar phase, a smectic phase is not sensitive to polydispersity in diameter, since ordering within the smectic layers is liquid like. Instead, a smectic phase will be suppressed by polydispersity in thickness. Hence, the stability of a nematic, columnar and smectic phase depends on a suspension's polydispersity in both thickness and diameter. Our observations that a system with a diameter polydispersity as high as 25% forms a columnar phase, and crosses over to a smectic-like structure at higher ϕ , are the first exhibitions of such a mechanism in the case of plate-like particles. Illustrative in this respect is that, in the case of $\sigma_D = 17\%$, the columnar phase is still stable at $\phi = 0.53$, as demonstrated by strong Bragg reflections for visible light.

4. Conclusions

In addition to an isotropic-to-nematic phase transition at lower densities, suspensions of sterically stabilized gibbsite platelets are found to undergo a nematic-to-columnar transition even if the diameter polydispersity is as high as 25%. While fractionation at the nematic-columnar transition is pronounced, the suspensions also exhibit a fully columnar state. Such a tolerance for polydispersity is remarkable in light of the terminal polydispersity reported for hard-sphere crystallization and hard-rod smectization. As for the latter, however, the effect of the rods' length polydispersity has been considered, while assuming a monodisperse thickness. Hence, the stability of the columnar phase in the presently studied platelet suspensions may very well be connected with the fact that the platelets possess a polydispersity in thickness too. Further insight into the relationship between diameter polydispersity and thickness polydispersity on the one hand, and the liquid-crystal phases formed in such suspensions on the other, requires further study by experiment, theory and simulations.

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Discussion

A. YODH (*Department of Physics and Astronomy, University of Pennsylvania, PA, USA*). Has anyone in the liquid-crystal community tried to mix discotics (plate-like) and nematic (rod-like) liquid crystals?

H. N. W. LEKKERKERKER. That is a very good question but I am afraid that I do not know the thermotropic-liquid-crystal literature well enough to answer it.

A. RENNIE (*Department of Chemistry, King's College, London, UK*). As I have seen the phase separation in your sample myself, I have been impressed by the structures that you observe. The domains extend over quite large distances. Is it possible that the walls of the sample cells influence the structure?

H. N. W. LEKKERKERKER. Your suggestion that boundaries may influence the structures is certainly a valid one. Both the rigid walls of the sample cells and the free interfaces between the various phases affect the liquid-crystal textures.