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Lyotropic lamellar phase doped with a nematic phase of magnetic nanorods

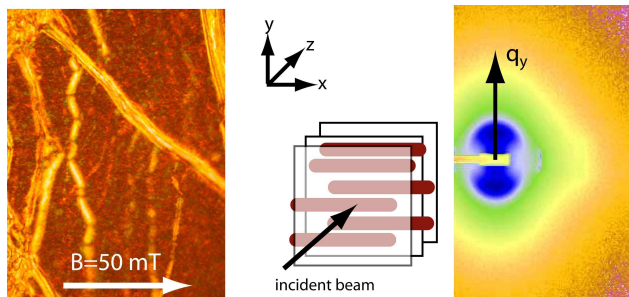
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Abstract

We report the elaboration of a hybrid mesophase combining the lamellar order of a lyotropic system of nonionic surfactant and the nematic order of a concentrated solution of inorganic nanorods confined between the surfactant layers. Highly aligned samples of this mesophase can be obtained by thermal annealing, and the orientation of the nanorods is readily controlled with a magnetic field. High-resolution synchrotron x-ray scattering and polarised optical microscopy show that, compared to their isolated counterparts, both the nematic and lamellar orders are altered, demonstrating their interplay.



Hybrid soft-matter systems, combining at the nanometric scale two components with different types of order, have recently been the focus of a fast-increasing body of research. Indeed, such systems raise interesting fundamental questions about the interaction of the different kinds of order involved and also offer new perspectives of applications, for example in drug delivery.¹

In particular, lamellar phases doped with anisotropic inclusions received sustained attention since their experimental realization in DNA/lipid complexes.^{2,3} Since then, various other organic dopants have been used, such as viruses⁴ and peptides.⁵ These experimental achievements also prompted extensive theoretical efforts,^{6–8} concentrating on the interplay of the two types of order (the lamellar one of the matrix and that of the inclusions within it), and on the characteristics of a possible 2D-smectic phase formed by the inclusions.

These systems are generally obtained by electrostatic complexation through a precipitation process; as such, their texture is very hard to control and they usually occur in the form of multilayered globules with random orientation. It is therefore difficult to discriminate between their molecular organization in the plane of the layers and that along the director of the phase. Furthermore, they are quite concentrated (lamellar spacings of a few nm), which severely restricts the size of the inclusions.

In this Letter, we present a new hybrid system, consisting of a dilute lamellar phase (formed by a

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nonionic surfactant) doped with a nematic phase of inorganic goethite ($\alpha - \text{FeOOH}$) nanorods that differ from the organic dopants used so far by their magnetic properties. The resulting composite (nematic/lamellar) phase is very fluid, and hence easily aligned, which allowed us to study its structure in detail. A notable advantage is that the orientation of the nanorods can be controlled by an externally applied magnetic field of moderate strength.

The degree of order of each component (quantified by the width of the Bragg peak for the lamellar host phase and by the nematic order parameter for the confined nanorods) changes due to the presence of the other component, confirming their intimate interaction.

Furthermore, this system shows promise as template for the production of hybrid materials, e.g. for magnetic storage applications,⁹ shielding,¹⁰ metamaterials¹¹ etc.

The matrix is the C_{12}EO_5 /hexanol/ H_2O system, where C_{12}EO_5 stands for the nonionic surfactant penta(ethylene glycol) monododecyl ether. Its lamellar phase can be diluted down to spacings d in the micron range, while the bilayer thickness $\delta \approx 2.9 \text{ nm}$.^{12,13} We used a hexanol/ C_{12}EO_5 ratio of 0.33 by weight, corresponding to a molar ratio of 1.3 (hexanol molecules for each surfactant molecule). The main role of hexanol is to bring the lamellar phase domain down to room temperature. The surfactant was acquired from Nikko and the 1-hexanol from Fluka; they were used without further purification. For all the samples discussed in this paper, the fraction of membrane $\phi_m = (V_{\text{C}_{12}\text{EO}_5} + V_{\text{hexanol}})/V_{\text{total}} = 6.26 \text{ vol } \%$.

Goethite ($\alpha - \text{FeOOH}$) is widely used as a pigment of ochre color.¹⁴ In bulk, its density is $\rho_g = 4.37 \text{ g/cm}^3$. The nanorods were synthesized according to well-established protocols.^{15,16} Stable aqueous suspensions of non-aggregated goethite nanorods are obtained by repeated centrifugation and dispersion in water up to $\text{pH} = 3$, where their surface is hydroxylated, with a surface charge of 0.2 C m^{-2} (the isoelectric point corresponds to $\text{pH} = 9$). Although bulk goethite is antiferromagnetic, the nanorods bear a permanent magnetic dipole $\mu \sim 1200 \mu_B$ along their long axis, probably due to uncompensated surface spins (with $\mu_B = 9.274 \cdot 10^{-24} \text{ J/T}$ the Bohr magneton). Therefore, in suspension, the nanorods are easily aligned

parallel to a small magnetic field. Furthermore, the easy magnetisation axis is perpendicular to this direction so that, at high applied fields, the induced magnetic moment overtakes the permanent one and the orientation of the rods switches to perpendicular to the field at a critical value $B \sim 350 \text{ mT}$.¹⁷ When the rods are confined within the lamellar phase, the reorientation also occurs, at the same field value, and the texture of the lamellar phase follows the orientation of the rods.¹⁸

TEM observations were made on deposits of one drop of dilute nanoparticle suspension on a copper grid covered with a carbon membrane. The morphology is typical for a goethite crystal, elongated along the $[001]$ direction and terminated by $\{210\}$ faces¹⁴ with an aspect ratio of 8.4. The particle size distribution was determined over a population of 200 particles. The average length is $\bar{L} = 315 \text{ nm}$ and the standard deviation $\sigma_L = 88 \text{ nm}$. For the transverse dimension, $\bar{D} = 42 \text{ nm}$ and $\sigma_D = 12 \text{ nm}$. The polydispersities are relatively low, $\sigma_L/\bar{L} = 0.28$ and $\sigma_D/\bar{D} = 0.3$. More precisely, the particles are lath-shaped and from powder X-ray diffraction line-broadening we infer that they have a mean width of 38 nm and a mean thickness of 18 nm, in good agreement with the TEM results.

Small angle x-ray scattering (SAXS) experiments were performed at the ID02 station of the European Synchrotron Radiation Facility synchrotron in Grenoble, France. The incident beam had a wavelength $\lambda = 0.0995 \text{ nm}$, and the sample-detector distance was 5 m. The scattered x-rays were detected with a specially developed CCD camera. A detailed description of the experimental setup can be found in reference 19. The q range over which the data could be reliably collected was $0.02 < q < 0.6 \text{ nm}^{-1}$. The samples were held in flat glass capillaries, 50 μm thick and 1 mm wide (Vitrocom, NJ, USA). The flat faces of the capillaries were set perpendicular to the x-ray beam. The magnetic field was applied using a motorized variable-gap setup available at the beamline.

To determine the order parameter of the nematic phase, azimuthal sections $I(\theta)$ through the scattered signal at the radial position $q_{max} = 2\pi/(80 \text{ nm})$ of the nematic peak were fitted with a profile derived from the Maier-Saupe theory, as discussed in detail in references 20–22.

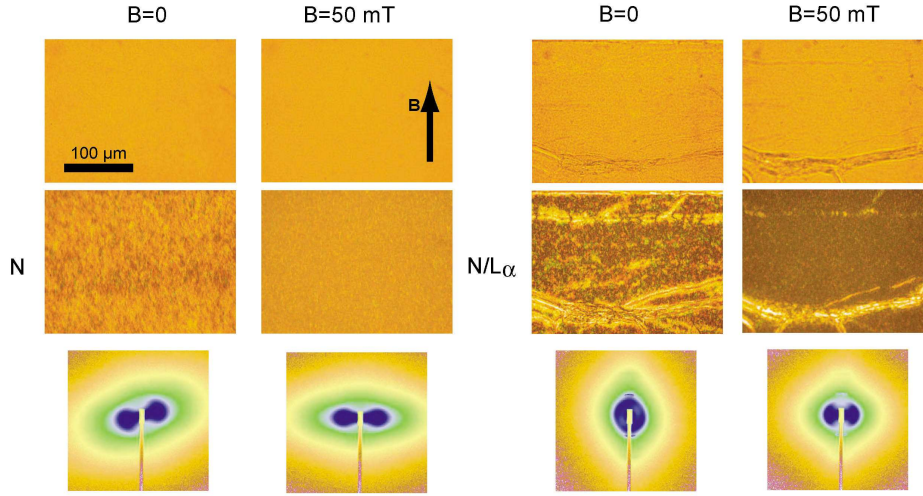


Figure 1: Optical microscopy textures (top) and SAXS signal (bottom) of the nematic phase of goethite, at a concentration $\phi_g = 8$ vol %, in water (left) and contained within the lamellar L_α phase (right). The lower microscopy images are taken between crossed polarizers, parallel to the image sides. In both cases, the nematic phase is very well aligned along the magnetic field, even at a relatively weak value of 50 mT. In the panel on the right, the lamellar phase is almost completely aligned in homeotropic anchoring (bilayers parallel to the flat faces of the capillary), with the exception of a few oily streak defects, visible in the microscopy images and which give rise to the very weak and sharp peaks along the vertical axis in the SAXS images.

Microscopy observations were done using an Olympus BX51 microscope (at $5\times$ – $40\times$ magnification) using linearly polarized light and, when specified, an analyzer perpendicular to the incident polarization. For birefringence measurements we used a Berek compensator (U-CBE from Olympus) and a green band-pass filter (480–580 nm.) The magnetic field was applied using a home-made setup based on permanent magnets with a variable gap. One can thus reach field intensities of up to 0.9 T.

Figure 1 presents a comparison between an aqueous nematic suspension N of goethite nanorods (left) and the hybrid nematic/lamellar (N/L_α) mesophase (right), with and without an applied magnetic field. For the N/L_α system, in the absence of a magnetic field, the texture of the phase as observed between crossed polarizers (middle row) exhibits both the oily-streak defects due to the smectic symmetry of the lamellar component and textures typical for a nematic phase (in-between the oily streaks). Applying a modest (50 mT) magnetic field aligns the nematic component, so that only the lamellar defects remain visible.

Using SAXS, we studied the orientation of the

goethite nanorods confined in the N/L_α phase. The SAXS patterns (Figure 1, bottom row) show that the confined nanorods are easily aligned along the magnetic field direction, without disrupting the texture of the lamellar phase. The particles remain aligned when the magnetic field is switched off, showing that the nematic uniform alignment of the confined nanorods is stable. Moreover, we measured by SAXS the order parameter S in the N and N/L_α phases at the same particle concentration $\phi_g = 8$ vol %, on samples aligned using a moderate magnetic field (50–200 mT). While the aqueous nematic phase N has $S \simeq 0.75$, the hybrid system exhibits lower nematic order, with $S \simeq 0.45$ (Figure 2A). This decrease could be due to the weakness of orientational correlations between the particles confined between different surfactant bilayers. Above the reorientation threshold, the order parameter of the rods varies continuously and reaches saturation at about 700 mT (Figure 2A). No significant effect was observed above this value. Also, the magnetic field has no detectable effect on the undoped lamellar phase, even at the highest field values we could reach.

Another noteworthy characteristic of the hybrid system is the enhanced susceptibility of the

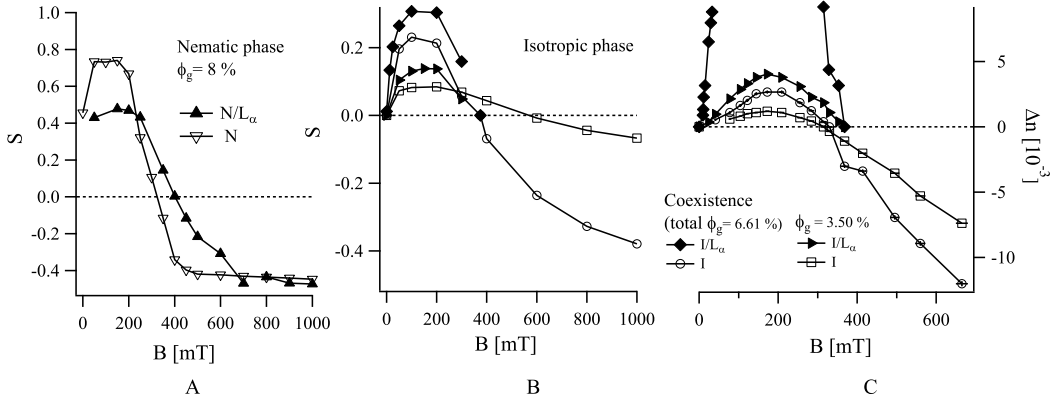


Figure 2: A – Order parameter S (calculated from the SAXS patterns) of the nematic phase of goethite nanorods, in the lamellar phase (\blacktriangle) and in water (∇) as a function of the applied magnetic field. At field values $B \gtrsim 350$ mT the nanorods align perpendicular to the field, resulting in negative values of the order parameter. B – Induced order parameter and C – induced birefringence of the isotropic phase of goethite nanorods as a function of the applied magnetic field, for two concentrations ϕ_g . The symbols are the same in subfigures B and C. The optical birefringence measurements cannot be performed in the lamellar phase above the reorientation field value due to the change in texture (homeotropic to planar).

isotropic confined particle phase (I/L_α), quantified by the induced order parameter $S(B)$ (Figure 2B) and birefringence $\Delta n(B)$ (Figure 2C) under an applied magnetic field B . The experiments were performed for two different goethite concentrations, $\phi_g = 3.5$ vol % and at coexistence with the N/L_α phase, at an overall concentration $\phi_g = 6.61$ vol %. Due to the presence of the lamellar phase, we were not able to determine precisely the goethite content in the two coexisting phases, but it appears to be roughly similar to that in aqueous solutions (approx. 4.5 : 7.5 vol %).

Both parameters are clearly higher in the hybrid system. This feature is extremely strong for the field-induced birefringence (diamonds in Figure 2C) of a confined isotropic phase of volume fraction $\phi_g = 6.61$ vol %, within the biphasic domain of aqueous goethite suspensions. At this concentration, there is coexistence between the isotropic- and nematic-doped lamellar phases (I/L_α and N/L_α), which were identified optically, within the same capillary, by their distinct textures. The gap between 33 and 350 mT corresponds to birefringence values that cannot be reliably determined using our setup. The corresponding microscopy and SAXS images are shown in Figure 3, where the strong birefringence is revealed by the color shift and the progressively increasing order parameter of the nanorods by the horizontal lobes

in the scattering pattern.

Both the lower order parameter in the nematic phase and the higher susceptibility in the isotropic phase are compatible with a second-order phase transition (predicted in the literature for a 2D nematic phase^{23,24}), as opposed to the first-order transition in the aqueous system.¹⁷

Finally, the presence of the inclusions affects the structure of the host lamellar phase, which becomes stiffer, as seen by the decreasing width of the Bragg peak with increasing goethite concentration. This effect is displayed in Figure 4. We can tentatively attribute it to a strong interaction between the nanorods and the surfactant bilayers, leading to the formation of hydrogen bonds.²⁵ The nanorods are thus adsorbed onto the bilayers and increase their stiffness.

We emphasize that the two components (the surfactant layers and the nanorods) are intimately mixed. While the lamellar order is of course imposed by the surfactant bilayers, it also applies to the nanorods confined between these bilayers. As a result, there is only one repeat distance, giving rise to the single set of Bragg peaks, discussed in Figure 4.

It is noteworthy that the overall X-ray signal is mainly due to the nanorods (at this dilution, the contribution of the surfactant bilayers is negligible). Indeed, the structure factors are obtained di-

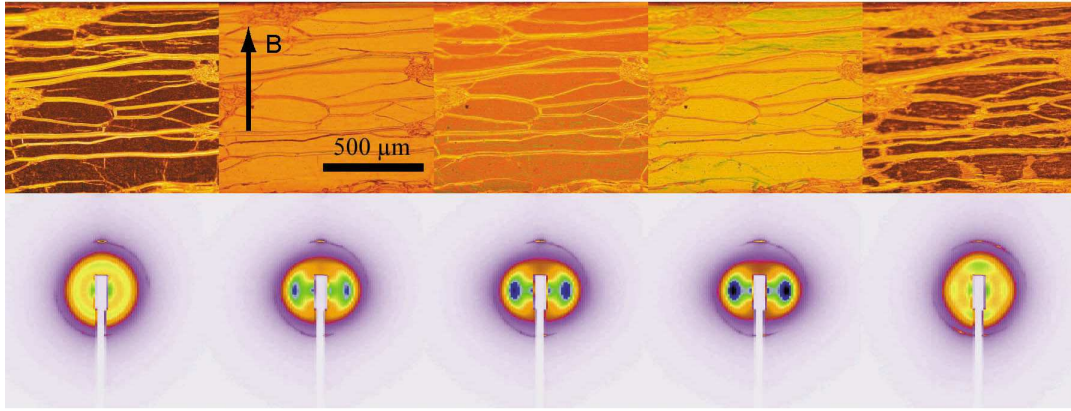


Figure 3: Optical microscopy textures (top) and SAXS signal (bottom) of the lamellar L_α phase doped with the goethite isotropic phase (I/L_α) at coexistence with the nematic-doped phase N/L_α for different values of the applied field. The microscopy images are taken between crossed polarizers, parallel to the image sides. From left to right, the field values are: $B = 0, 27, 52.5, 104$ and 370 mT.

viding the measured intensity by the form factor of the nanorods.²⁶ No peak can be detected for goethite concentrations $\phi_g < 2$ vol %.

The two components of the hybrid mesophase interact in non-trivial ways, as demonstrated by the enhanced magnetic field susceptibility of the nanorods (Figure 2, B and C) and by the increased stiffness of the lamellar phase (Figure 4). For the most concentrated system, the nanorods exhibit both nematic order (also encountered in aqueous solutions) and a lamellar order imposed by the confining surfactant bilayers. In this respect, the phase is similar to those encountered in complexes formed by DNA with cationic lipids, with the important distinction that we use a dilute phase of nonionic surfactant, which is easily aligned by thermal treatment and that the orientation of the nanorods couples to an external magnetic field. As such, this hybrid phase could provide an ideal testing ground for the hypothesized “sliding phases”,²⁷ stacks of weakly-coupled layers with a certain degree of two-dimensional (in-plane) order within the layers.

From a practical point of view, the combination of these two types of order makes the system a promising candidate for the formulation of composite materials with controlled periodicity and anisotropy, ordered over macroscopic distances. Moreover, the magnetic properties of the goethite nanorods are particularly interesting in this respect.

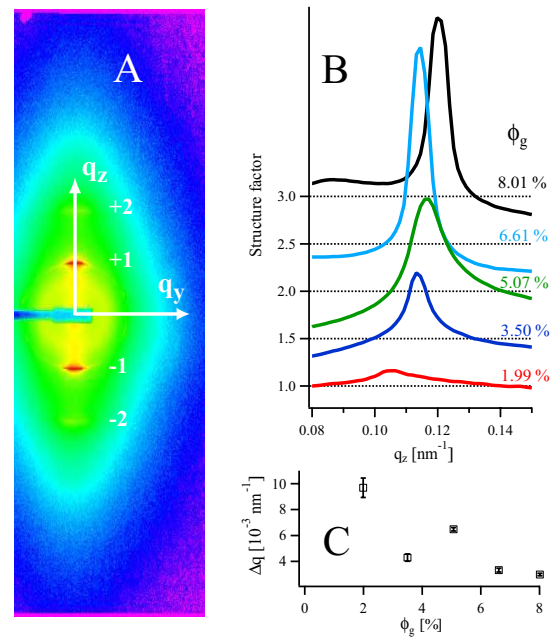


Figure 4: A – SAXS image (taken without magnetic field) of a lamellar phase containing $\phi_g = 6.61$ vol % goethite, aligned in planar anchoring (the layer normal is along $z.$). Several Bragg peaks are visible, labelled by their index. B – Structure factors of the lamellar phase doped with increasing amounts of goethite, indicated alongside the curves. The curves are shifted vertically in steps of 0.5. C – Width of the Bragg peaks in B as a function of the goethite concentration.

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Lyotropic lamellar phase doped with a nematic phase of magnetic nanorods –Supplementary Information–

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Chemical

The goethite nanorods are formed by a dissolution-crystallization process from 2-line ferrihydrite, a poorly defined highly hydrated phase. 400 ml of a 0.1 M aqueous solution of $\text{Fe}(\text{NO}_3)_3$ were hydrolysed by addition of base solution (NaOH , 1M) at $\text{pH}=11$ and room temperature, leading to a brown precipitate. After ageing for 15 days, the solution is ochre in color and contains rod-shaped nanoparticles (see below for the size analysis). The solid is isolated by centrifugation and then dispersed in a 3M solution of nitric acid for 2 hours in order to charge the surface positively. Stable aqueous suspensions of non-aggregated goethite nanorods are obtained by repeated centrifugation of this mixture and dispersion in water up to $\text{pH}=3$.

Particle morphology: TEM analysis

Figure 1 presents a representative TEM image and the particle size distribution. The subsequent analysis was described in the text.

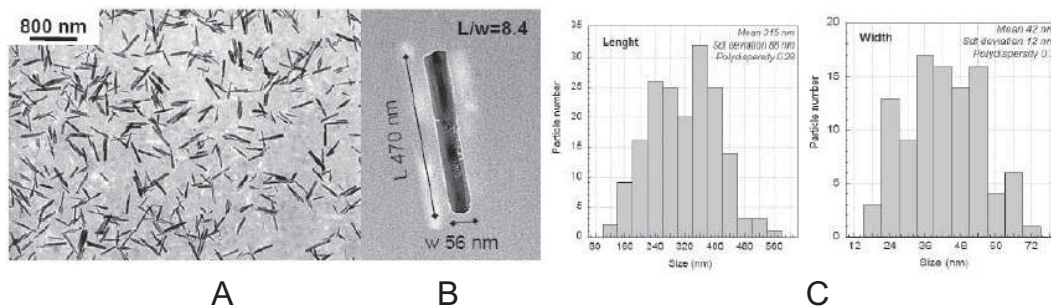


Figure 1: TEM image showing a large quantity of non-aggregated nanorods (A), Zoom on one acicular goethite crystal with typical dimensions (length and width) and an aspect ratio of 8.4 (B), length and width distributions obtained from measurements over 200 particles (C).

Formulation

The volume fractions ϕ_m and ϕ_g are defined with respect to the total volume of the solution. The mass concentrations are determined directly by weighing the components

into vials and the volume concentrations are then calculated using: $\rho_{C_{12}EO_5} = 0.95 \text{ g/cm}^3$, $\rho_{\text{hex}} = 0.82 \text{ g/cm}^3$, and $\rho_{\text{goeth}} = 4.37 \text{ g/cm}^3$.

Two stock solutions were used, one a concentrated lamellar phase with $\phi_m = 62.82\%$ (and with $m_{\text{hex}}/m_{C_{12}EO_5} = 0.35$) and no goethite, and the other with $\phi_g = 9\%$ and no surfactant. Mixing the appropriate amounts of these stock solutions and diluting with a 10^{-3} M HNO_3 solution (to maintain a constant $\text{pH} = 3$) yielded the desired final concentrations of membrane and goethite. We assumed that all the hexanol remains in the membrane, since its water solubility is low.

Schematic of the hybrid phase

depicts the hybrid phase. The surfactant membranes are perpendicular to the z direction (so the Bragg peaks appear along the q_z axis, as shown in Figure 4A of the main text) and the nanorods are confined in the (x, y) plane. For the nematic case, they are also oriented (on the average) along the x axis.

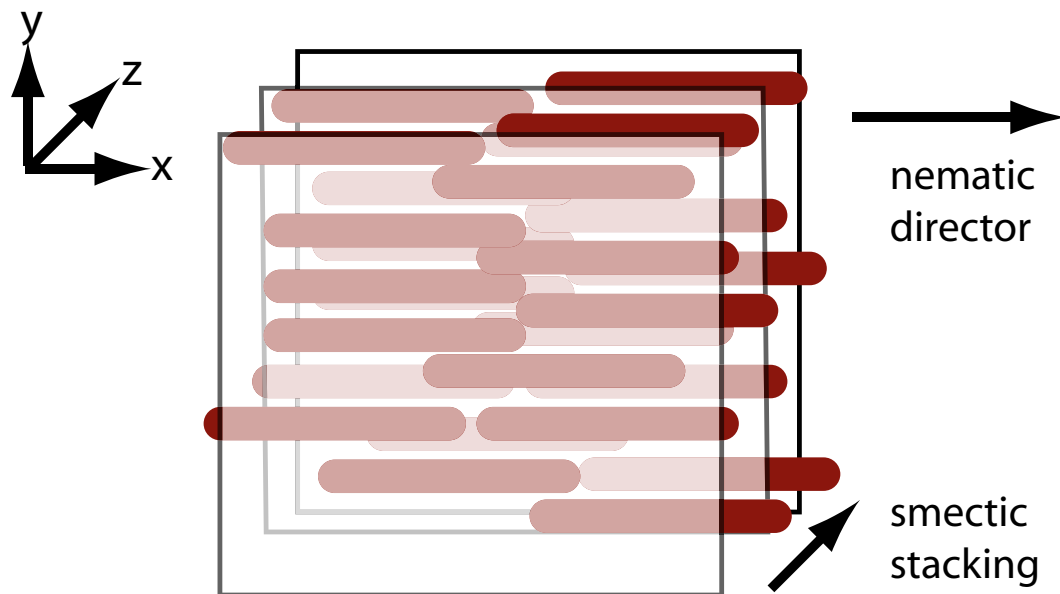


Figure 2: Representation of the hybrid phase. Three surfactant membranes are shown, as well as the two intermediate layers of nanorods.