Universiteit Utrecht
Soft Condensed Matter Group

Mutual structures of colloidal rods and spheres

Bachelorthesis

Abstract

As much as there is known about the phase behavior in systems of rods and systems of spheres, not much is known about systems in which both particles exist. Such systems, containing both rods and spheres, are experimentally studied by making samples containing 3µm by 0.6-0.7µm silica spherocylinders and silica spheres of diameters of 470nm and 1µm. These samples are imaged using a confocal microscope.

Two structures that are characteristic for phases in systems of rods were found to have been influenced by the presence of spheres, also a structure has been found that is not characteristic for systems of either of the separate colloids; the lamellar structure.

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1. Introduction

Colloids are everywhere; from being contained in bottles in chemical labs to being the essential component in some of our everyday materials. The moment you will get bored with reading this thesis (highly unlikely) chances are great you'll be looking at a colloidal system, as the paint on the wall you're blankly staring at consists of many colloids. In short, a colloidal system is a dispersion of colloids in a solvent.

Colloids come in many different forms, shapes and sizes; they can be made of many different materials and can be of any phase. There are solid colloids like the ones in paint, liquid colloids like the ones that are contained in milk and gaseous colloids like the bubbles in foam. Colloids are can be of any imaginable shape, but are restricted in their size. Colloids are particles that are larger than the solvent particles in which they're dispersed and small enough to be subject to Brownian motion. Therefore colloids range from nanometers to several micrometers. Brownian motion is random motion invoked by the constant collisions with solvent particles.

The particular colloids I use are spherocylinders and spheres. These are two shapes that are also quite common in nature. Spherical colloids are, for example, present in milk and one will find rod-shaped colloids when looking at certain viruses; a filamentous bacteriophage is shaped like a rod.

2. Background

2.1 Phase behavior

When looking for structures I'm also looking for phases. The reason structures are found (for example, a row of rods lying side to side) is usually because they are characteristic for some kind of phase (the smectic phase, in this example). Having some basic knowledge of the phase behavior of rods and spheres separately could be useful for understanding the phase behavior of rods and spheres together. I will therefore briefly discuss the phase behavior of the two separate colloids. I will not be able to give very detailed descriptions because not everything about phase behavior is already known. Giving a very detailed description will also not be necessary, for reasons to follow.

2.1.1 Phase behavior of spheres

Compared to rods, the phase behavior of spheres seems not very complicated. Approximating the spheres that are used in this research to be a purely hard sphere system there would only be 2 phases; the fluid and the crystal phase. Like in many colloidal systems the phase behavior is entropically driven, meaning the system urges to do whatever is necessary to increase its entropy. The Helmholtz free energy is a function of entropy in the following way:

$F = U - TS$

Where F is the Helmholtz free energy, U the total internal energy of the system, T the temperature and S the entropy.

As can be seen from this equation the free energy gets lowered when the entropy increases. It turns out the system can maximize its entropy by minimizing the free energy. The free energy of a hard sphere is lower when it has more volume to wriggle around in, as:

$F = -k_B T \ln(V^N)$

Where V^N is the canonical partition function for a system of N hard spheres. V is the volume each hard sphere can wriggle around in.

Wanting to maximize the wriggle space of each hard sphere leads to the system assuming different phases at different densities. It turns out that a system of hard spheres is in the fluid phase at packing fractions of $\eta < 0.494$ [3] and assumes the crystal phase at $\eta > 0.545$ (packing fraction is related to density by $\rho = \frac{6}{\pi}\eta$). Between these values the fluid and crystal phase coexist. The phase diagram as a function of packing fraction and temperature can be seen in figure 1.

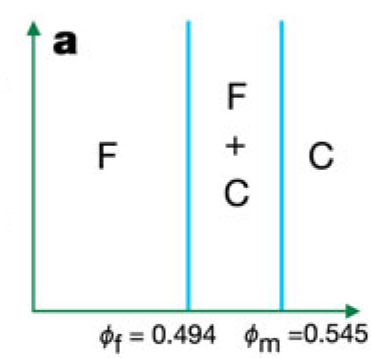


Figure 1. Phase behavior of hard spheres in the T,η-plane.

What's interesting about this plot is the independence of T on the phase behavior. Although this is certainly the case for ideal hard spheres, my samples are not necessarily independent of temperature. The solvent is affected by temperature which in turn subjects the spheres to Brownian motion. This effect is most apparent when comparing large and small spheres; crystal-like structures in samples with small spheres have not been observed, whereas large spheres seem to have no problem forming crystals if the above conditions are met (i.e. high packing fraction).

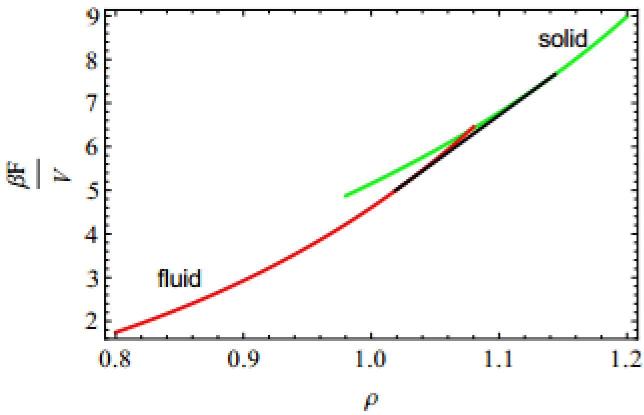


Figure 2. Common tangent construction for a suspension of hard spheres. The red and green lines are the free energies of respectively the fluid and solid phase.

These models are useful for determining parameters in my samples. Because colloids in the samples sediment there are different parameters like pressure and packing fraction at different heights in the samples. Packing fraction can be determined using the confocal microscope, plugging this into the equation of state of the hard sphere model will then give the pressure. Cell theory for hard spheres [4] can also be used to construct a phase diagram (figure 2). If there would be, for example, an interesting structure somewhere in a sample at the same height as a hard sphere nucleus (indicating phase coexistence), the pressure at which this structure forms could be determined from the phase diagram of the hard spheres.

2.1.2 Phase behavior of rods

Whereas a sphere can only have a certain position, rods can also have a certain orientation. Because of this additional ‘feature’ rods have a different phase behavior than spheres. Rods show phases comparable to the fluid and crystal phase of the rods; called the isotropic and crystal phase, and also show liquid crystal phases. A very nice overview of these phases is presented in “Fluorescent colloidal silica rods” by A. Kuijk (figure 3).

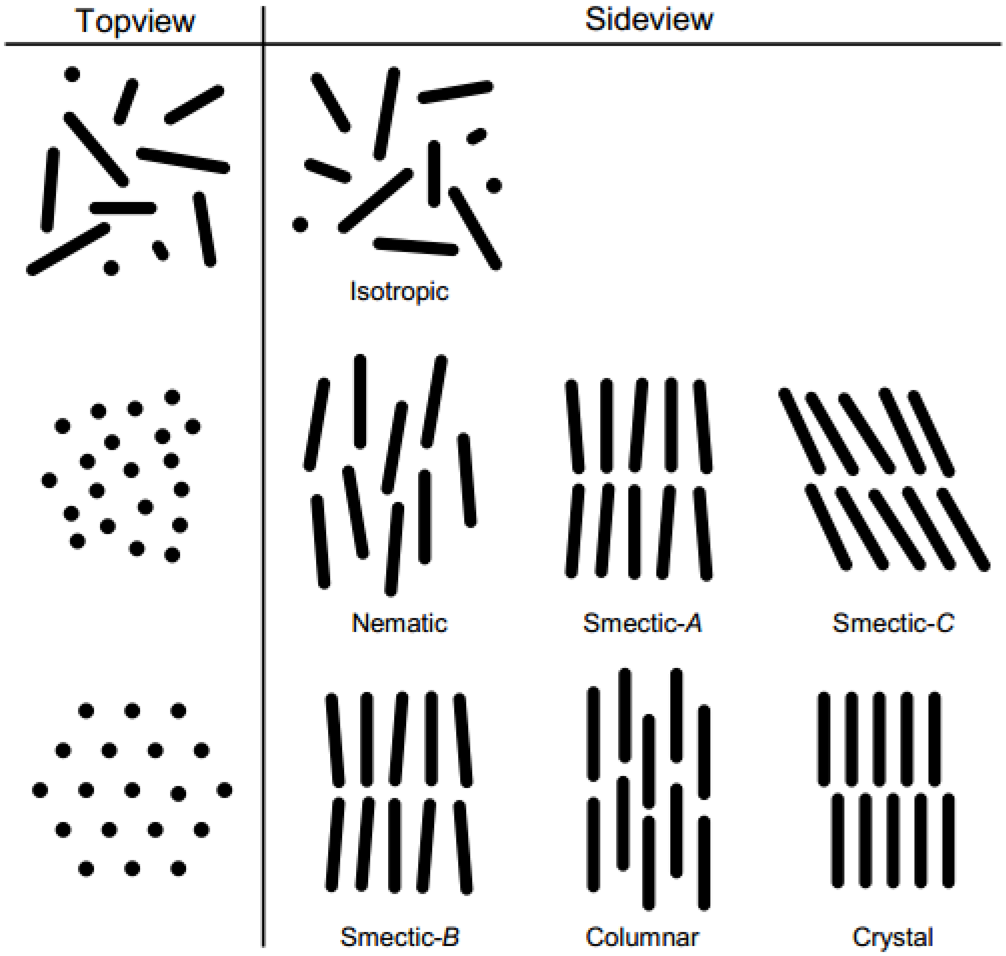


Figure 3. A schematic representation of the various phases exhibited by rods

As can be seen from this overview, the isotropic phase would most resemble a fluid phase. The first step a system of rods will take to look more like a crystal is make its orientation more uniform; the system goes into the nematic phase. In the nematic phase the rods all have positional freedom, but are all oriented in a common direction. The nematic phase is still much like a fluid and is called a liquid crystal phase. If the system wants to look even more like a crystal there is a whole variety of liquid crystal phases it can assume. All smectic phases have in common that they all form layers of rods with aligned main axes. The smectic-A phase is essentially a 2-dimensional liquid; the rods have positional freedom within a layer. The same goes for the smectic-C phase except that common orientation of the rods is tilted with respect to the normal of the layers. The smectic-B phase has no positional freedom inside a layer, as can be seen from the top view. The smectic-B phase looks a lot like the crystal phase; the difference between the two is the way the layers are positioned with respect to each other. In the crystal phase rods from different layers have a certain position with respect to each other, whereas these positions in the smectic-B phase are not correlated. This makes the smectic-B phase basically a crystal phase with the layers weakly attached to each other [1]. The columnar phase is also a liquid crystal phase in which the rods have positional freedom along one direction (the direction of the columns) but are limited to some kind of lattice (hexagonal in the above figure) in the other two directions. Very short rods (rods with low aspect ratio L/D, length to diameter) also have a plastic crystal phase.

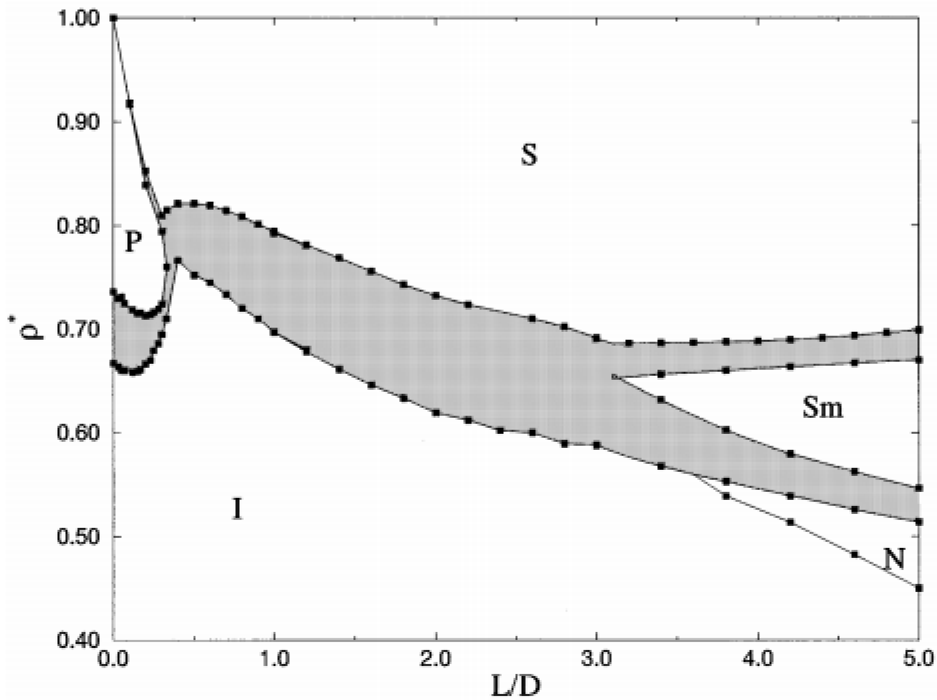


Figure 4. Phase diagram for spherocylinders. This includes the plastic crystal (P), the isotropic (I), solid (S), smectic (Sm) and nematic (N) phases. ρ* is the fraction of the ideal packing fraction for rods, L/D is the aspect ratio of the cylinder, the aspect ratio of a spherocylinder is therefore L/D+1 in this diagram.

All these phases are phases that could be observed in certain systems of rod particles. This does not mean that all these phases will be observed in any such systems. The ability of the system to form certain phases depends on many parameters such as density and possibly temperature if the system contains a solvent. Also shape and aspect ratio play an important role. Rods that are shaped like cigars (ellipsoids) cannot form any smectic phase whereas spherocylinders can. The rods I use resemble spherocylinders. Spherocylinders have been studied in the past by Bolhuis and Frenkel [5] who computed a phase diagram (figure 4).

Similar to the hard sphere model, this phase diagram can be used for determining certain parameters in the sample. The narrow range at which the nematic and smectic phases form for rods with an aspect ratio of 6 means that the density can be determined within a respectable range if either of these phases is found.

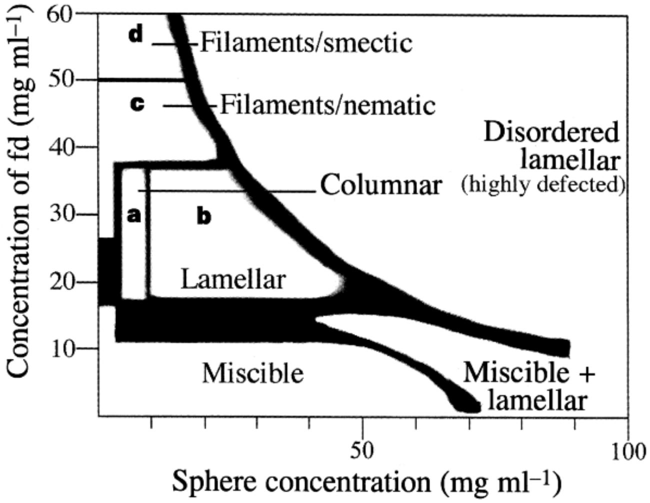


Figure 5. Phase diagram of the fd-virus and 0.1µm spheres, as computed by Adams, Dogic, Keller and Fraden[6].

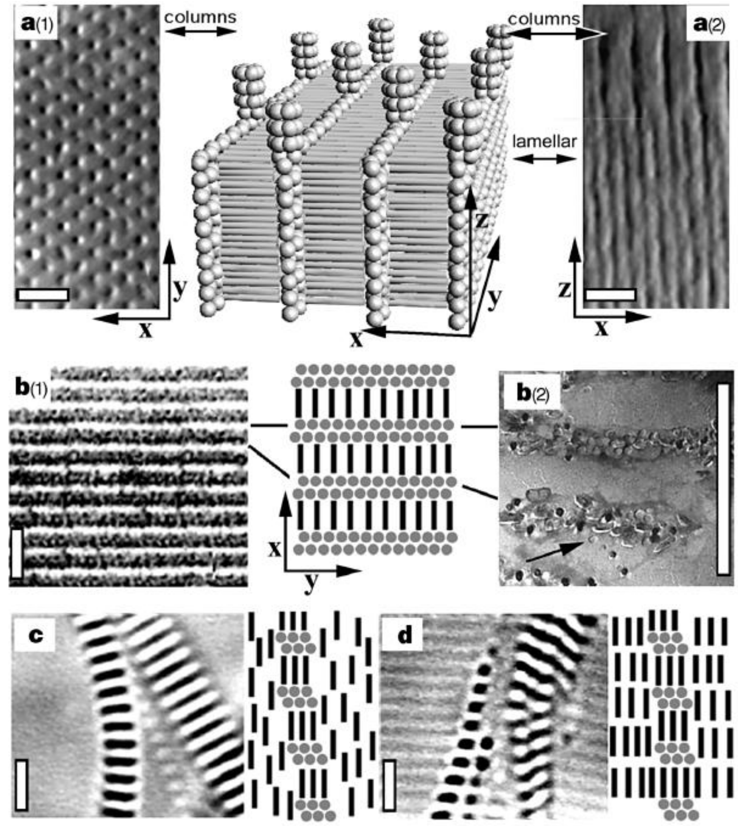


Figure 6. Images of mutual structures by Adams, Dogic, Keller and Fraden [6]

2.1.3 Phase behavior rods and spheres

There is not much known about the phase behavior of rods and spheres together, but it's not a completely unexplored area. Some research has already been done on this subject in a paper by Adams, Dogic, Keller and Fraden [6]. Two distinct phases have been presented in this paper; the columnar and lamellar phase. The columnar phase here is not the columnar phase as found in pure rod systems. A construction of these phases looks like the ones in figure 6.

The lamellar phase is much like the smectic phase in pure rod systems but with spheres between each layer with distinctive positions with respect to the rods. The columnar phase would occur in the region where the sphere concentration is lower and the spheres form columns on top of the lamellar phase in the direction perpendicular to the rods main axes. These columns form a 2-dimensional hexagonal lattice when viewed from above. The concentration of rods and spheres with which these phases would form is shown in figure 5.

2.2 Imaging colloids

The most convenient way to image colloids for my purpose is through confocal microscopy. Different ways of imaging would be using an electron microscope or a conventional optical microscope. However these microscopes lack certain properties that are required for imaging colloids. The electron microscope does not offer the ability to look inside the sediment, whereas the other microscopes do have this property. Comparing the confocal microscope to the conventional optical microscope, the confocal microscope produces the sharpest images. I have only used the optical microscope to see if the synthesis or the coating procedures were successful, because a very detailed image is not required to see this, and this microscope is a lot easier to operate than the confocal microscope. When looking at my samples I used the confocal microscope.

The confocal microscope was developed by Marvin Minsky in the 1950s [2]. The idea of the confocal microscope is based on a conventional optical microscope with some additions to block out of focus light. An optical microscope, when used to look at optically dense samples, produces a lot of out of focus light in addition to the light coming from the focal plane. This makes the image blurry. In a confocal microscope the light source is not put behind the sample (with respect to the photomultiplier) but at the side, directing the light at the sample using a dichroic mirror so the light comes from the same side of the sample as where the light detector is. The combination of a pinhole, a high intensity light source and a high aperture lens reduces the reflection light. This comes down to reducing the area of the focal plane (the plane perpendicular to the optical axis) to a diffraction limited point. The light coming from a point outside the focal plane (further away from- or closer to the lens) is blocked by a pinhole which is placed in the conjugate focal plane. A schematic overview of this setup is presented in figure 7a. By scanning point by point in the plane perpendicular to the optical axis a 2D image is constructed. The result is an image in the plane perpendicular to the gravitational force, which is convenient because my samples sediment solely under the effect of gravity.

In Minsky's original design a regular light source was used to make the sample visible. The light that is eventually detected is the result of reflection from the sample. Nowadays a laser is used to excite atoms in the sample, which then emit light. This emitted light is then detected using a photomultiplier tube (PMT). Exciting atoms to emit light allows for different species of colloids (rods and spheres in my case) to be imaged simultaneously if they have been dyed using different types of dye. The rods are dyed with FITC (fluorescein isothiocyanate) that gets excited at energies corresponding to light of wavelengths near 490 nm, and emits light with a wavelength of about 520 nm. The confocal microscope system uses laser light with a 488 nm wavelength targeted at exciting FITC. The spheres are dyed with TRITC (tetramethyl rhodamine isothiocyanate) that gets excited near wavelengths of 550 nm and emits light with a wavelength of around 600 nm. The 543 nm laser is targeted at exciting TRITC.

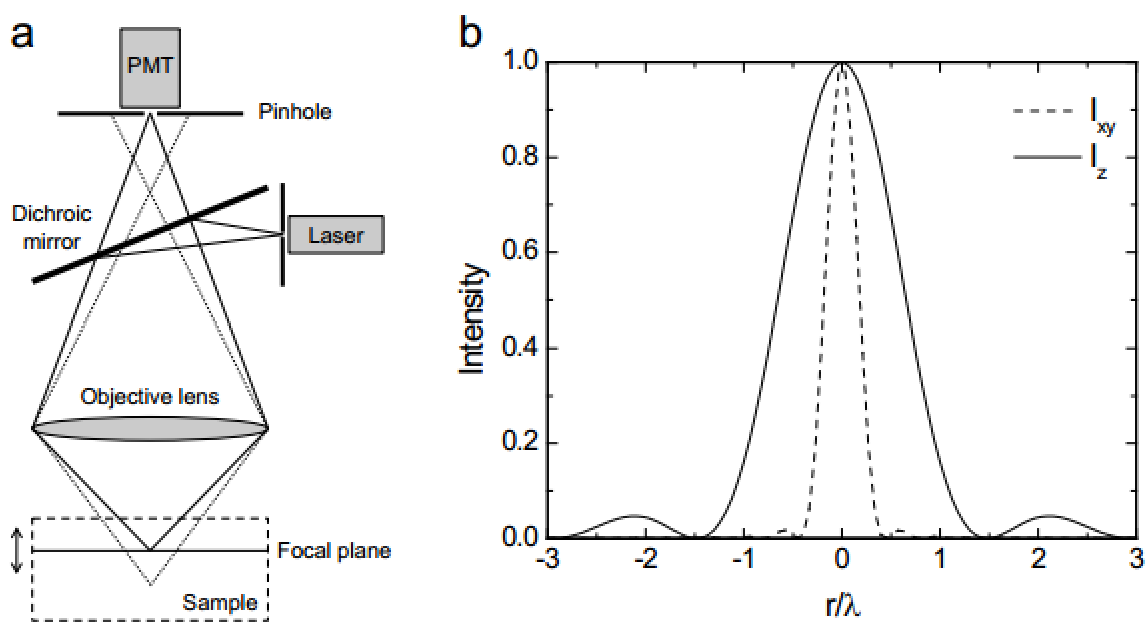


Figure 7. a) A schematic overview of the confocal microscope. b) Diffraction in the z- and x,y-direction.

2.2.1 Limited sharpness

Because light is a wave, the sharpness of the image is limited by the diffraction limit. Refraction in the sample can also play a role in limiting sharpness but there is a simple solution for this problem. When silica (n=1.45) colloids would be dispersed in a liquid with a lower refractive index, for example water (n=1.33), the focal plane would not be at a single z-coordinate, but depend on the coordinates of the colloids. A schematic picture of this effect is given in figure 8. This effect can be counteracted by dispersing the colloids in a solvent with the same refractive index as that of silica. For this solvent I use a mixture of dimethyl sulfoxide (DMSO) and water at a ratio of 10/0.85 (DMSO/water).

The limiting of the sharpness by diffraction cannot be reduced, so it has to be kept in mind when interpreting images. The diffraction is different in the z-direction and the x,y-plane (figure 7b). These intensity functions are given by [1]:

$$I_{xy}(v) = \left(\frac{2J_1(v)}{v}\right)^2 \quad (1) \qquad\qquad I_z(z) = \left(\frac{\sin\frac{u}{4}}{\frac{u}{4}}\right)^2 \quad (2)$$

with v = 2πrNA/λ and u = $2\pi(NA)^2z/(\lambda n)$, r and z are distances from the center point, λ is the wavelength of the laser, NA the numerical aperture of the objective lens, n the refractive index of the medium and J_1 the first-order Bessel function.

The diffraction limit in the z-direction gives the images a certain thickness; particles that are below or above the focal plane get smeared out into the focal plane. This means not every particle in one image is at the same z-coordinate and images get a certain thickness. Filling in the proper values into equation 2 gives a thickness of about 750nm.

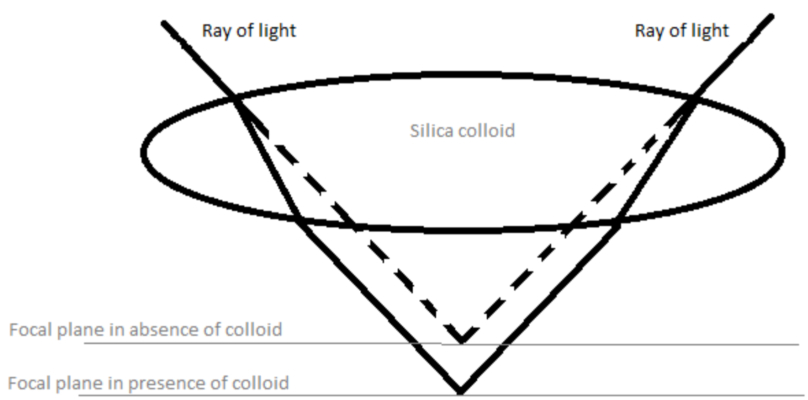


Figure 8. The focal plane shifts as it passes through material with different refractive index than the solvent.

3. Experiment

3.1 Goal

The goal of this research is finding structures that can be formed by silica rods and silica spheres together, and finding the conditions under which these structures form. Such structures shall be called "mutual structures" and the structures that are found will be verified for being actual mutual structures, other than just rod- or spherestructures. What a "mutual structure" exactly is will become apparent when reading this thesis, just like how this became apparent to me while doing the research. I did not want to define "mutual structure" too well right at the start of the research as I didn't know what to expect. The reason for doing research on rods and spheres together is because there is not much known about their mutual properties, unlike the properties of rods and spheres separately. Something that could be found from researching rods and spheres together would, for example, be a crystal with interesting optical properties. One could think of Bragg reflection for multiple wavelengths simultaneously in one direction, or manipulating the polarization of light. However, finding applications for binary crystals is not the goal of this research.

3.2 The sample

The structures that are observed using the confocal microscope reside in samples. Each sample is a piece of glass with a small glass capillary glued to it, filled with a colloidal dispersion. The samples are made by mixing rods and spheres in the right ratio in a separate bottle, from which the capillary is filled. The filled capillary is glued to the glass which will then dry upside down under UV-light with a wavelength of 350nm. When the glue has dried the sample it is turned right side up so the colloids will sediment. A picture of a sample is presented in figure 9.

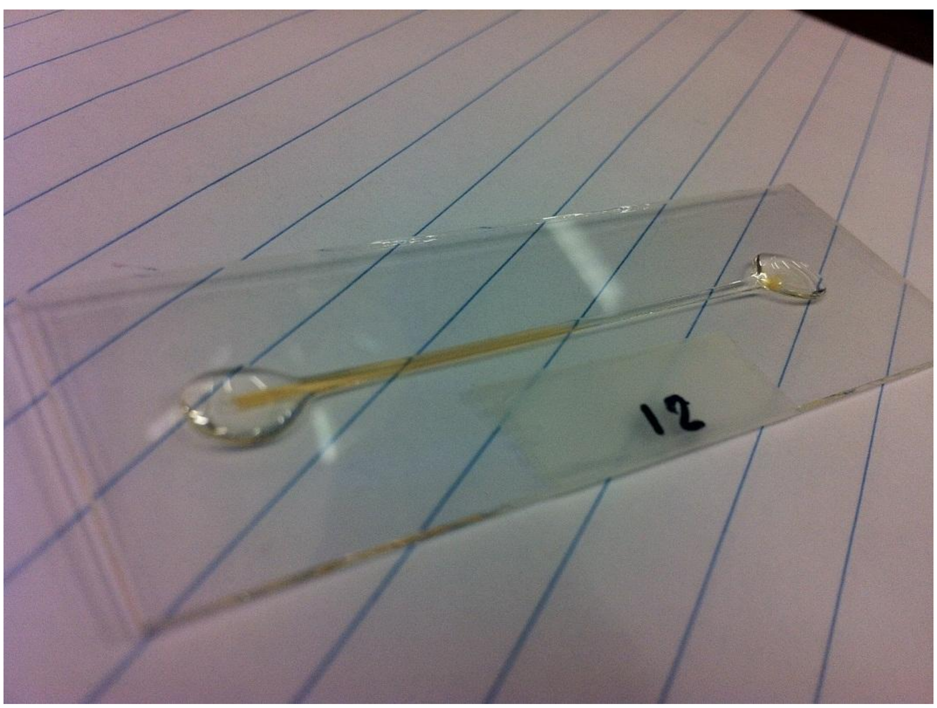


Figure 9. A sample consists of a labeled piece of glass and a glass capillary containing the colloidal suspension glued together.

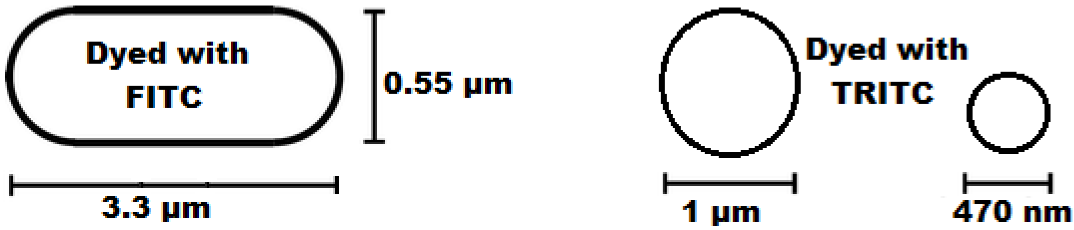


Figure 10. A schematic representation of the different species of colloids that are used.

3.3 Plan/Setup

This research is focused around looking at the behavior of colloidal rods and spheres. The colloidal rods and spheres that are used were made through synthesis in the chemical labs at the Ornstein laboratory. The rods are about 3.3µm in length and about 0.55µm in diameter, so their aspect ratio (L/D) is about 6. For the spheres I used two kinds, one that I call “small spheres” and one that I call “large spheres”. The small spheres have a diameter of about 470nm and the large spheres have a diameter of about 1µm.To be able to tell the rods apart from the spheres, each colloid is given a different dye. The rods have been dyed with FITC and both spheres have been dyed with TRITC. Light emitted by FITC turns up as green and light emitted by TRITC turns up as red on the images that will be presented in the results section. There are no samples containing both large and small spheres so it’s not necessary to give each type of sphere a different dye. A schematic representation of these colloids is given in figure 10.

When I just started the research I only had some theoretical knowledge of what rods and spheres might do, but how this would work out in my samples I did not know. I decided to just make some samples and see what would happen. In this time I tried to develop a feeling for the behavior of colloids and the ability to interpret future samples. I didn’t want to make a big set of data right away, as I wouldn’t have known what this data would have to consist of. I started by making 10 samples, and looked at them at irregular times:

Label	Rods %	Spheres % (large/small)	Checked after (in days)
1	5	5 L	1, 2, 15
2	2.5	2.5 L	1, 5
3	5	2.5 L	5, 14
4	2.5	5 L	5, 14
5	5	0.6 S	1, 8
6	2.5	0.3 S	1
7	5	0.3 S	1
8	10	0	7
9	>10	0	6
10	5	5 S	6

I will not go over the results from these samples in detail, as the differences in times I looked at them make it difficult to properly compare the samples.

After these samples were made I decided to focus mostly on samples containing a high rods/spheres-ratio. I wanted to make some samples containing more spheres than rods, but I thought samples in which the rods 'smother' the spheres would make mutual structures easier than samples in which the spheres 'smother' the rods.

The samples that would be made are as follows:

Label	Rods %	Large spheres %	Small spheres %
15	5	0.1	-
14	5	0.5	-
13	5	1	-
3	5	2.5	-
1	5	5	-
11	5	7.5	-
12	5	10	-
2	2.5	2.5	-
21	5	-	0.1
20	5	-	0.5
19	5	-	1
18	5	-	2.5
10	5	-	5
17	5	-	7.5
16	5	-	10
5	5	-	0.6
7	5	-	0.3
6	2.5	-	0.3

Because this scheme includes samples of the time before this scheme was made, the names are in a seemingly random order. The samples were imaged at 1, 3, 7, 14 and 21 days after each sample was made. This should give me a good set of data to start with and hopefully produce some nice structures for further examination.

3.4 Rodsynthesis

The rods that are used are made as described in "Fluorescent colloidal silica rods" by Anke Kuijk. Turning bottled chemicals into viewable rods is done in three steps:

3.4.1 The core

In a 500ml glass bottle, 30g (PVP, molar weight M_n=40.000) is dissolved in 300ml 1-pentanol. The PVP forms big clumps when put into the 1-pentanol so this is then sonicated for one or more hours until the mixture looks homogeneous. Next 30ml of absolute ethanol is added, then 8.4ml pure water and 2ml 0.18M sodium citrate. The bottle is then shaken for a minute or so to make everything mix properly. Then 6.75ml ammonia (NH_3 in 25% OH) is added. The bottle is then gently shaken again and 3ml of tetraethyl orthosilicate (TEOS) is added. After shaking again, the mixture is left to react for 6 hours before adding another 2ml of TEOS. The bottle is then shaken once more and the reaction is left to proceed overnight.

The next day the reaction has to be stopped by washing the freshly made rods. This is done by centrifuging the solution for one hour at 1500g. The mixture is now split in 2 parts; a sediment of rods on the bottom of the bottle and the supernatant on top of it. The supernatant (with the unreacted chemicals in it) is taken out and the rods are redispersed in ethanol. The rods are then washed in ethanol again, 3 times, by centrifuging for 15 minutes at 1500g and redispersing the rods in ethanol afterwards. These washing steps are repeated 2 times using water instead of ethanol and centrifuging for 15 minutes at 1500g, and then 3 times in ethanol again, centrifuging for 15 minutes at 500g.

The resulting rods are quite polydisperse, so before proceeding with the synthesis reducing the polydispersity is desired. Rods that are too small are removed by centrifuging the solution of rods at a certain acceleration and amount of time. After centrifuging the solution, the supernatant is checked for monodispersity using the optical microscope (Leica DMRE).

3.4.2 The first coating

The rods have to be coated with dye in order to be able to see them on the confocal microscope. In a dried flask the rods are redispersed in 150ml absolute ethanol, to which 12ml H_2O is added. After sonicating for 15 minutes 10ml ammonia is added. After waiting 15 minutes a solution of 5ml absolute ethanol, 0.6ml TEOS, 20µl (3-aminopropyl)triethoxysilane (APS) and 13mg of fluorescein isothiocyanate (FITC) is added to the rods. This is left to react overnight and is then washed 3 or 4 times in ethanol, centrifuging at 300g for 20 minutes each time.

3.4.3 The second coating

When the rods would be looked at using the confocal microscope, it will be hard to tell the rods that lie next to each other apart. The outer shell of the rods is fluorescent so when a couple of rods lie side to side they would blur together. The solution to this is adding a non-fluorescent shell to the rods so fluorescent cores of adjacent rods don't touch anymore. This procedure is similar to the procedure of adding a dye to the rods:

The rods are dispersed in 150ml of ethanol in a round bottom flask while being gently magnetically stirred. 12ml H_2O is added to the solution which is then sonicated for 15 minutes. Then 10ml ammonia is added and after waiting 15 minutes, 0.8ml TEOS is added. This is left to react overnight again, after which it is washed 3 or 4 times again using ethanol and centrifuging at 300g for 20 minutes.

4. Results

4.1 Influence of the sample

The way the samples are made and the material they're made of have a clear influence on the structures of the colloids. The influence of the sample can be attributed to 2 different features; the walls of the sample and the axes of the sample. I will shortly discuss the possible effects each of these features.

4.1.1 The wall

The walls on the side of the sample and especially the bottom have a very big influence on the local structuring of the colloids. When colloids sediment they're pulled towards the bottom, a rod that arrives at the bottom will then orient itself parallel to the x,y-plane. The walls on the side of the sample also have an influence on local structures. For example, the chemical composition of the capillary tube may cause the wall to be charged when it is filled, making the wall attract or repulse the colloids or direct their orientation. Such an effect can translate itself into demixing of rods and spheres or demixing into differen phases, significantly altering the conditions at the wall with respect to conditions in the rest of the sample. What the effect of the walls exactly is, is not known, therefore no images of the walls will be included in the results.

4.1.2 The axes

The axes of the sample, defined as drawn in figure 11, have a quite self-explanatory effect. The z-axis is the axis that is aligned with the gravitational force. The parameters in the sample show the most variation in this direction; the colloid density for example is much higher near the bottom than it is at the top of the capillary, where it is approximately zero. Sufficiently far from the walls there is assumedly no x,y-dependence whatsoever, as long as the sample has not been tilted.

4.2 Interpretation

A lot can be seen from the images of the confocal microscope if looked at it correctly; you have to know what to pay attention to. In this section I will discuss what I set myself to look for, in order to prevent myself from overlooking anything in the samples. I will also explain terminology here that I will use when discussing my results.

4.2.1 Structures

My goal is finding structures, so this is what I pay most attention to. When looking for structures I always start at the bottom of the sample. The reason for this is the fact that structures usually start forming at the bottom, because gravity pulls the colloids against a flat surface. The bottom also offers the clearest pictures; it is the only place where you can see no overlapping colloids from different heights.

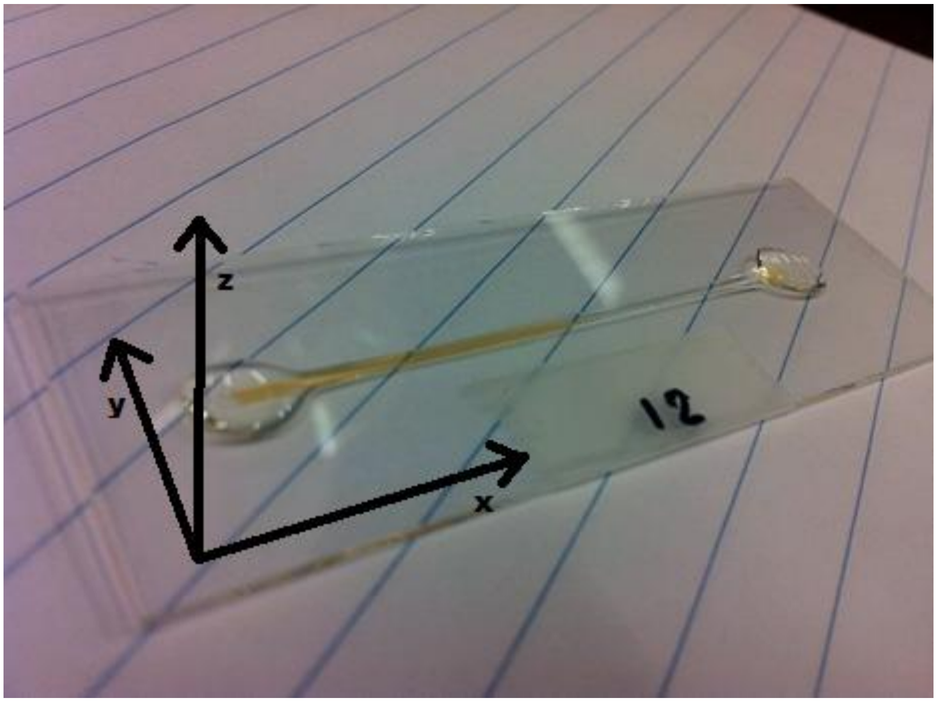


Figure 11. The axes of the sample; the x- and y-axes lie in the plane of the glass and the z-axis points towards the sky.

4.2.1.1 Rod structure

A structure of a colloid is characteristic for one of its phases. These phases can be used for qualifying structures in the samples; when I'm talking about a "smectic structure", I'm talking about a structure characteristic for the smectic phase. Determining the magnitude of these structures is also important; whereas some samples may show a complete smectic phase, another may show small clusters of smectic structures here and there.

4.2.1.2 Sphere structure

As with the rods, I compare the sphere behavior to already known sphere structures. However the criteria I use for spheres are not as sophisticated as those I use for the rods. I only make the distinction between structured or not structured. The structure I talk about here is a (2-dimensional) hexagonal structure. I usually don't care for quantifying sphere structure, because if a structure forms anywhere it usually forms everywhere; the conditions in my sample are (ideally) independent of the x- and y-coordinates. Another reason is that quantifying the magnitude of the structure, if one appears, usually says something about the rods/spheres ratio in the sample, which I already know beforehand.

4.2.1.3 Mutual structure

Compared to looking for rod and spherestructures, looking for mutual structure is usually quite difficult. When looking at rods or spheres, I know what to expect, so I know what to look for. In order to know what to look for here, I need to define for myself what I mean with "mutual structure".

I make the distinction between 2 types of mutual structure: large and small scale mutual structure. With small scale structure I mean the behavior of single rods with respect to single spheres and vice versa; how they position and orient themselves with respect to each other. With large scale structures I mean all other behavior that cannot be observed in samples with solely rods or spheres, including phase behavior.

Looking for mutual structure goes much like looking for rod and sphere structure; if I want to see small scale mutual structure I look at the bottom. When I want to know the exact relative location/orientation of colloids the bottom is the only location I can use as this is the only place where colloids don't blur together. For large scale structures I look through the whole sample (all z-coordinates; conditions are usually constant for x,y-coordinates).

4.2.1.4 Discs

Even though most structures form at the bottom, I would be missing a lot if I would only look here. An often recurring structure that usually formed multiple micrometers above the bottom is a structure I call "discs". Discs are big groups of rods lying next to each other, usually extending in the directions perpendicular to the main axis of a rod more than at least one rod-length (so the structure is more flat than thick; a disc). The disc is in principle a microphase of the rods but I will use the term disc for convenience.

4.2.2 Layers

Every sample is layered; there is always (assuming I have waited a sufficient amount of time) a sedimentation layer under a much more dilute layer. Some samples have more layers, like separate rod- and sphere layers. Layers are important for referring heights to; saying that something happens at 18µm above the bottom may mean something completely different in a sample with a sedimentation layer of 20µm than in a sample with a sedimentation layer of 100µm. The thickness of the sedimentation layer can also be used as a measure for structure in the sample. A large scale smectic sedimentation layer can have half the thickness of a sedimentation layer that is mostly isotropic.

4.3 The first samples

Getting the results I want for my research I did 2 things; make samples in the lab and observe them using the confocal microscope. Therefore my results consist solely of the red-green images the confocal microscope produced. The research is very visual, and as such the results will be presented accompanied by many images of the samples. I will discuss each sample separately and present a general discussion at the end.

When looking at the images, keep in mind that the rods are 3.3µm long. Because there are rods in each of the images I will not include scale bars.

4.3.1 Large spheres

4.3.1.1 Sample 15

This samples volume consists of 5% rods and 0.1% spheres. Because of some issues I had to remake this sample after 1 week. Figures A, B and C are the first version and figures D, E and F are a duplicate.

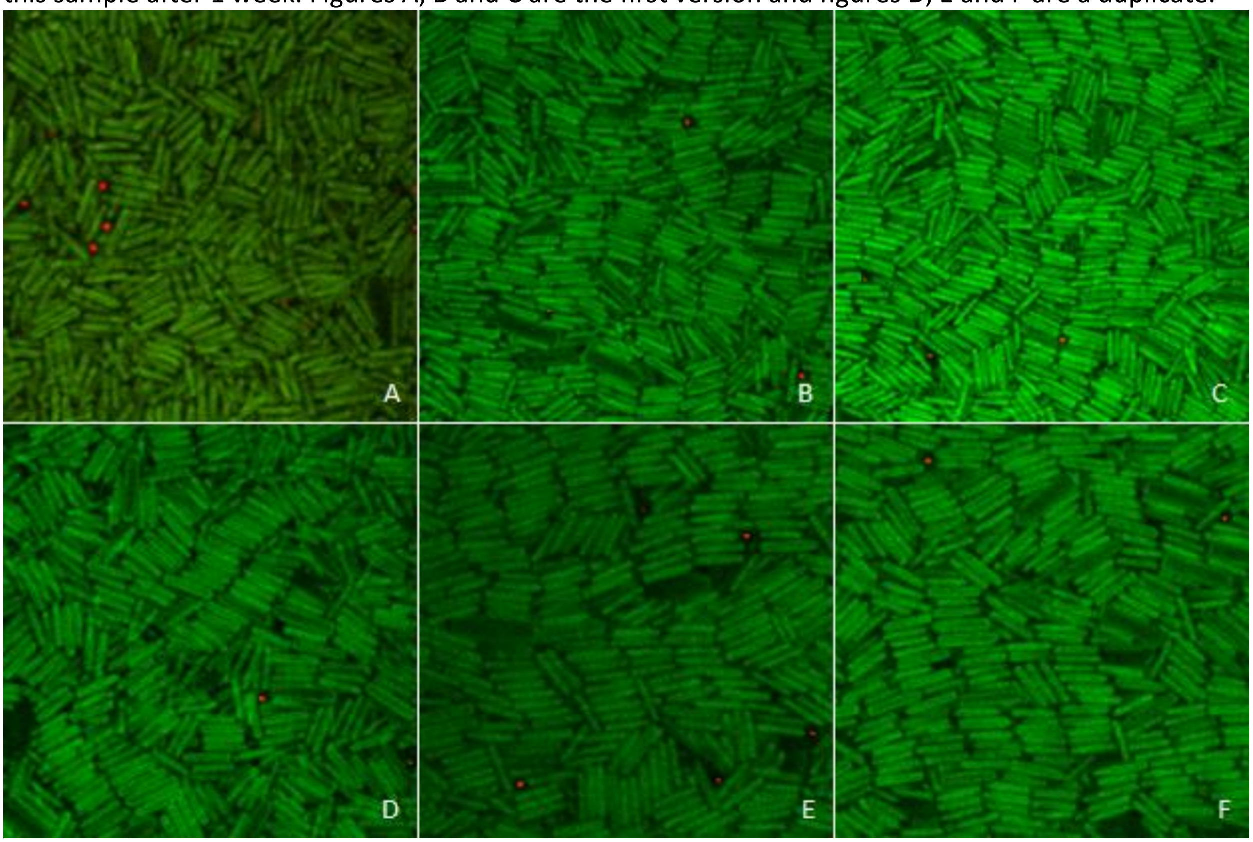


Figure 12. The sedimentation process over 2 weeks. A After 1 day; B 3 days; C 7 days; D 7 days; E 14 days; F 21 days. Each image is made at the bottom of the sample.

After one day the colloids don't seem to form any interesting structure. After three days the sediment seems to resemble the nematic phase. Over the next weeks the sample doesn't change too much, what is nematic after 3 days becomes more and more smectic after 1 or 2 weeks. Note that the duplicate sample (figures D, E and F) form their structure somewhat slower than the first sample; the duplicate sample at 7 days looks most like the first sample after 3 days. The spheres don't seem to play much of a role in the formation of structures, let alone there be mutual structures. Where there are spheres they usually position themselves at the tip of a rod. One might expect the smectic structures to become neater after waiting a longer time, but this doesn't happen. This could be an influence of the spheres on the rod-structure, which would disturb the structure too much. The disturbed structure can also be attributed to the polydispersity of the rods, there are a couple of larger rods which appear slightly darker and larger on the images.

The sample doesn't change much along its z-axis; the sedimentation layer is about 18μm thick and the structures that can be seen in figure 12 persist to heights of about 2-3μm. Higher than this the rods are isotropic and there are a little more spheres in this part than on the bottom.

4.3.1.2 Sample 14

This samples volume consists of 5% rods and 0.5% spheres.

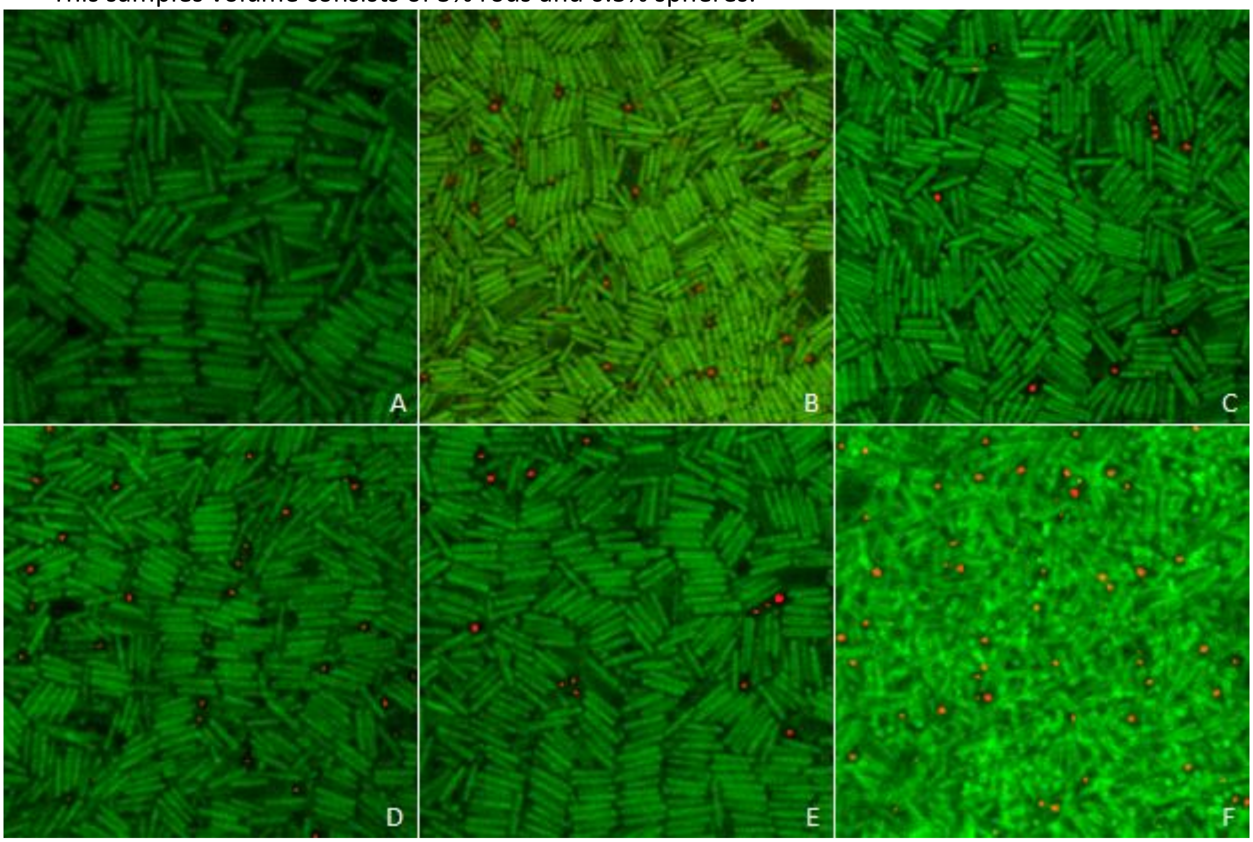


Figure 13. Sample 14. A is sample 14 after 1 day; B after 3 days; C 7 days; D 14 days; E 21 days; F is sample 14 after 21 days at a height of 10μm.

The rods show smectic structures where the general orientation extends over a couple of rod lengths as soon as after one day. However, the structure doesn't become much better after waiting longer; the sample still shows a lot of disturbed structures after 21 days, as can be seen in figure E. The rods seem to be able to form smectic structures which are most apparent in the lowest part of figure E, but like I said this also shows disturbances. I could attribute this to the presence of spheres. I cannot say much about behavior of spheres other than just disturbing the rods. The spheres put themselves at the tips of rods sometimes, but put themselves between rods just as often. The spheres don't seem to have a preferred location with respect to the rods.

Looking at behavior at different heights I find that the spheres are mostly in the isotropic part of the sample, which can be seen in figure F. The isotropic part ranges from ~2μm above the bottom to about ~20μm above the bottom, which is also the height of the sedimentation layer. Figure F is made after 21 days, but this behavior does not depend on time; images like this appear at all times between 1 and 21 days around the same height.

4.3.1.3 Sample 13

This sample contains 5% rods and 1% spheres, and deserves some extra attention. I've made 2 versions of this sample, because the first version became unusable after 2 weeks. The first four pictures are from the first version, the next four are from the other version.

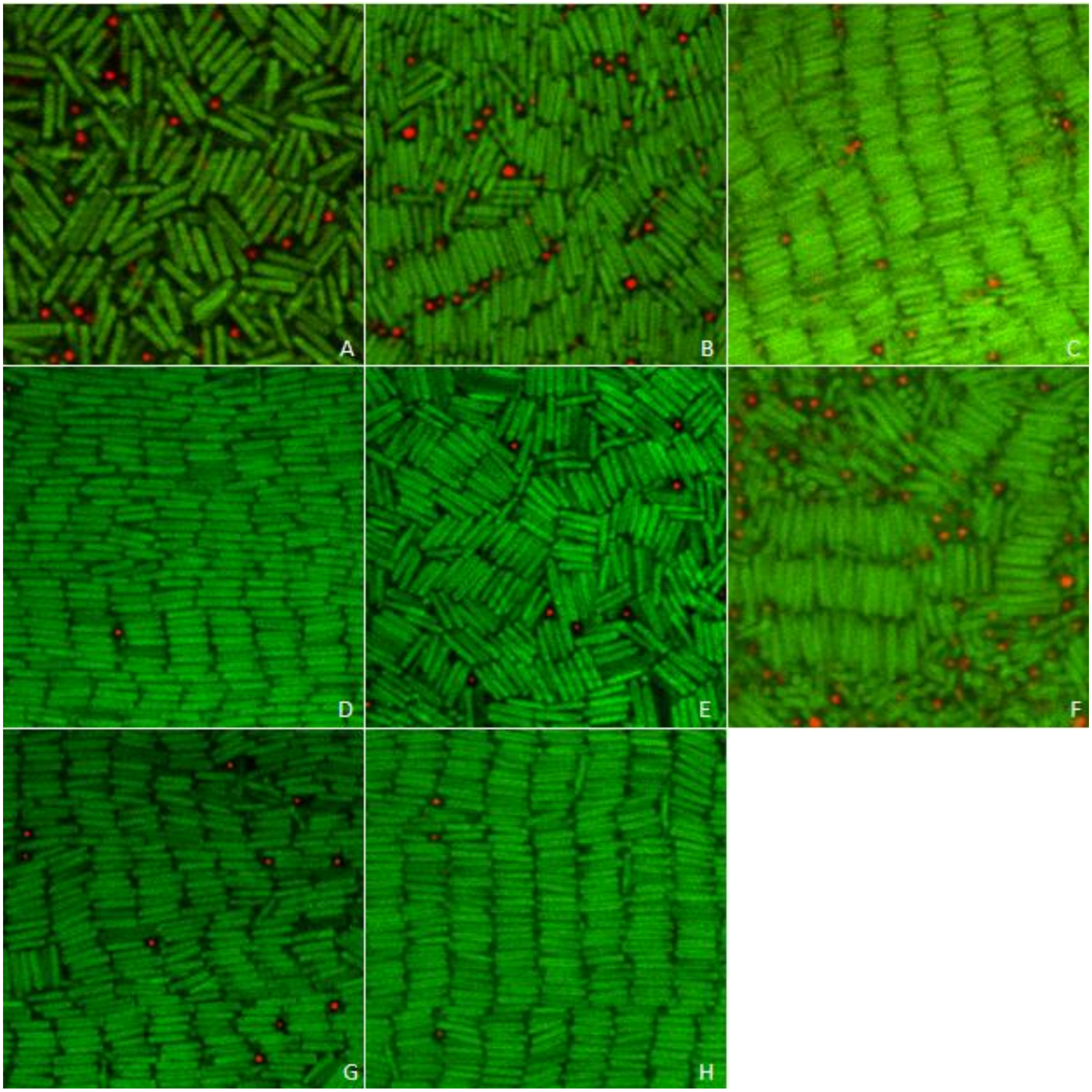


Figure 14. A through D are the first version of the sample after respectively 1, 3, 7 and 14 days. E through H are the second version after respectively 7, 14, 14 and 21 days. C is taken at a height of 4μm above the bottom and F is taken at 7μm above the bottom.

The biggest difference in both versions is the difference in their early stages. The first version after 3 days looks more structured than the second version after 7 days. Eventually both versions became similar, which can be seen by comparing figures D and G with each other. Both versions contained large scale smectic structures with rods oriented in the x-direction which persisted to great heights, up to 8µm at some places. The orientation did not necessarily persist to this height, as can be seen from figure F. Notice also how the orientation redirects itself along the x-axis, which could be an influence of the walls of the sample; the first version started y-oriented (figure B) but became x-oriented later.

The spheres seem to play a minor role in the formation of structures and I cannot speak much of mutual structures. The layer of spheres between the smectic layers in figure B come close to what I would call a mutual structure, but this behavior wasn't seen as explicitly at different times.

This sample also showed some structure at heights other than just the bottom. The structures that were on the bottom were still visible much higher (figure C) and there were also some discs (figure F). However, it is difficult to say whether the discs in figure F are actually discs or structures influenced by the bottom; everything below this picture was structured into these layers of rods as well. The sedimentation layer is about 17µm thick on average, but this strongly depends on where you look; the thickness ranges from 13 to 23. The sedimentation layer was 23µm thick where figure C was taken and 16µm thick where F was taken.

4.3.1.4 Sample 3

This sample contains 5% rods and 2.5% spheres.

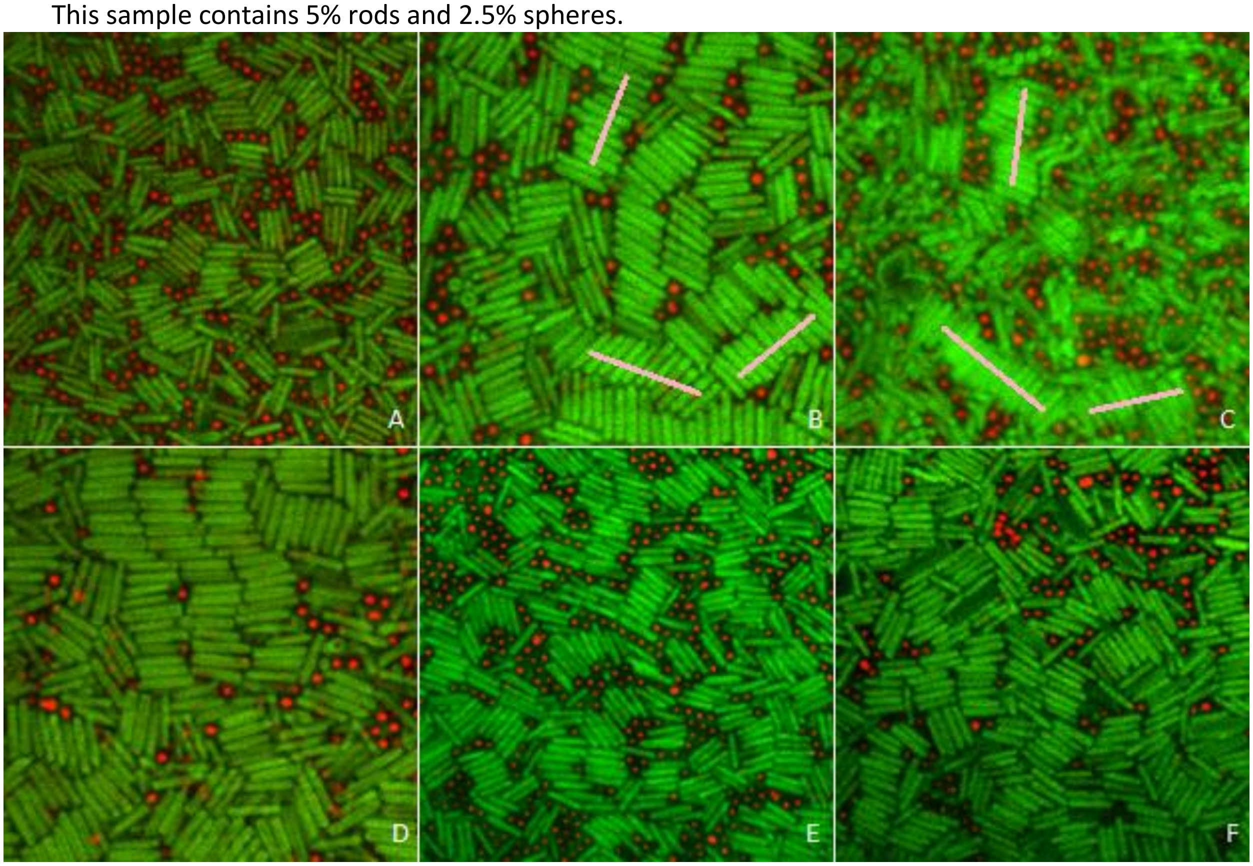


Figure 15. These images are taken after respectively 1, 3, 3, 7, 14 and 21 days. Figures B and C have the same x,y-coordinates but where B is taken at the bottom, C is taken 5µm higher.

Although the sample has contained clusters or rows of multiple rods, this never seemed to turn into a nice large scale structure at the bottom. There were discs at some times; I found most discs after 3 days but not so much at other times. Such discs can be seen in figure C. This disc in particular might also be formed under the influence of the bottom; figure B shows very similar structures and having seen the images between B and C shows that the layers I accentuated with a pink line are part of the same cluster. However, there were more discs in this sample after 3 days so the discs in figure C are probably formed through a combination of 'bottom influence' and 'disc conditions'.

The spheres in this sample don't really seem to meddle with the rods. Where there is sufficient space the spheres want to form their characteristic hexagonal structure. Because there the rods don't form very neat structures I would say there is not much mutual structure either; not the lamellar or columnar structure, that is. I won't exclude the possibility of the discs to be formed under influence of the spheres, and therefore be a mutual structure.

At heights other than the bottom the sample is always somewhat structured, unlike what the chaos on the bottom suggests. This could be because of the existence of discs very close to the bottom. The sedimentation layer extends to about 22µm above the bottom.

4.3.1.5 Sample 1

Sample 1 contains 5% rods and 5% spheres.

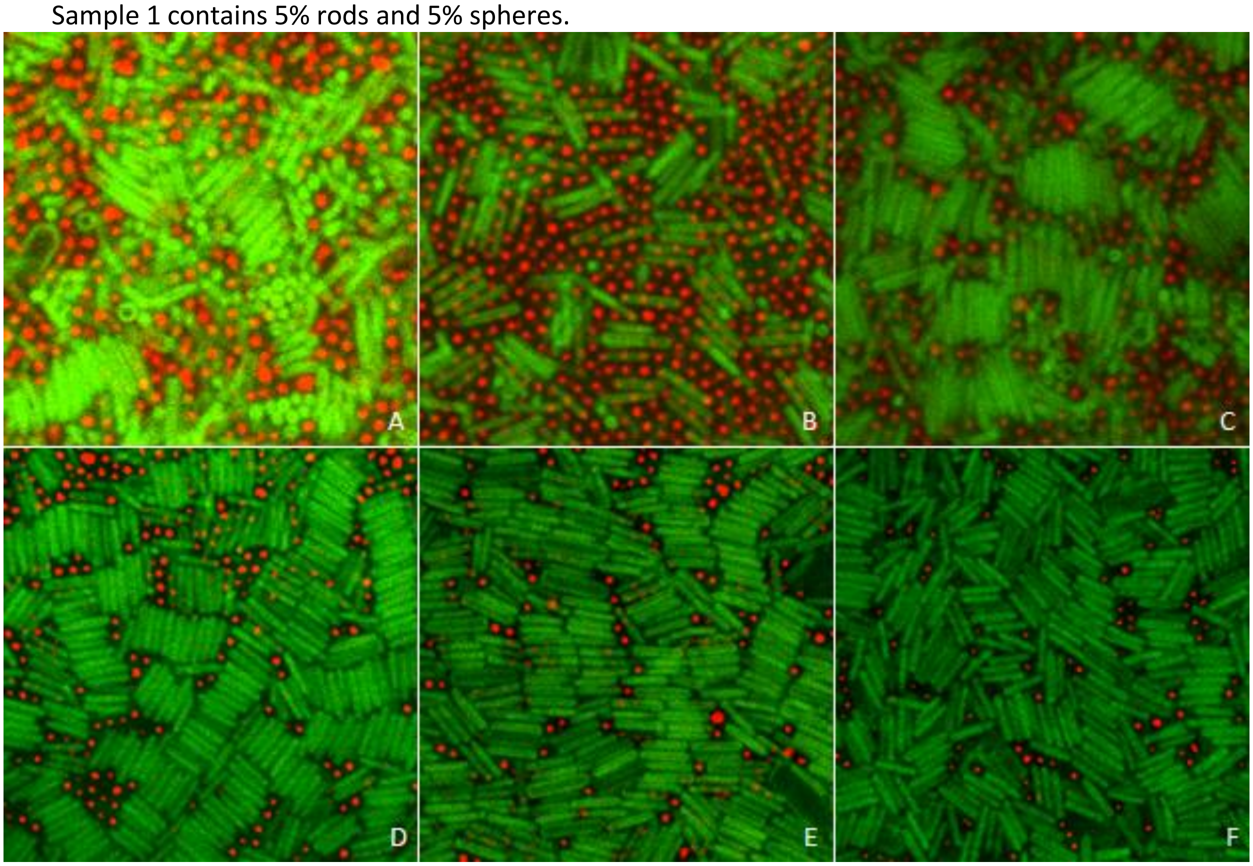


Figure 16. Sample 1 after respectively 1, 3, 3, 7, 14 and 21 days. A is taken at 14µm above the bottom, C is taken at 8 µm above the bottom and the rest is taken at the bottom.

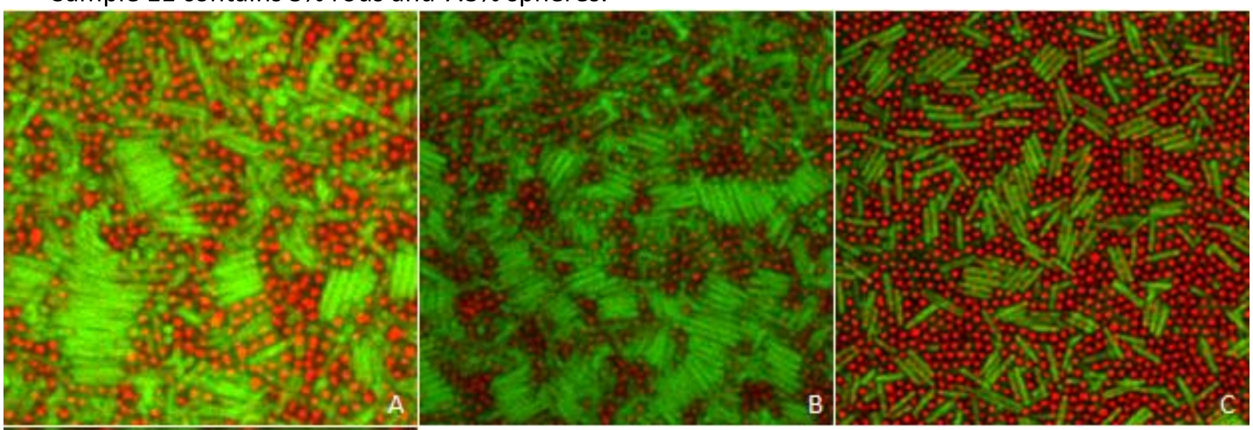
At the early stages of this sample the bottom wasn't the most interesting place to look. After one day and after 3 days most rod structure was located a few micrometers above the bottom. Figure B and

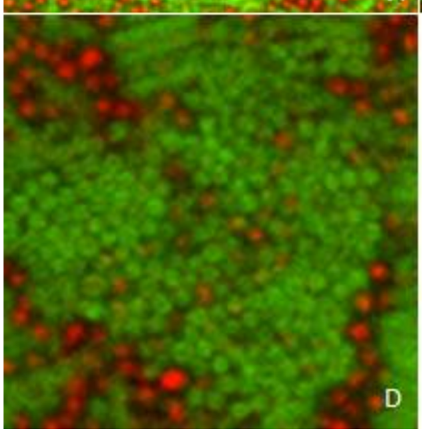
C are both at the same x,y-coordinates but at different heights, notice the difference in the amount of rods. After a few more days the discs were nowhere to be found and the on the bottom long rows of rods started to form. After 14 days the sample started to look quite promising; the spheres between the layers of rods here and there may indicate that the lamellar phase can be formed. After 21 days none of this behavior was found.

Looking at the height in the sample I noticed that the sedimentation layer was becoming thinner. After one day the sedimentation layer was about 28µm thick and eventually became about 20µm thick. The discs also seemed to sink; after one day they were at about 14µm, two days later at about 8µm and 4 more days later I didn't find any discs, meaning they may have reached the bottom.

4.3.1.6 Sample 11

Sample 11 contains 5% rods and 7.5% spheres.





Before I was able to look at this sample 3 weeks after it was made, the sample appeared to have been tilted; there was a lot of movement and the sedimentation layer was much thicker in one end of the sample. Therefore I will not include data from this sample after 21 days.

Figure 17. Sample 11 after respectively 1, 3, 7 and 14 days.

When looking for structures in this sample, the bottom is not the right place to look. The bottom usually looked somewhat like figure C; isotropic rods with a lot of spheres amongst them. Going up in the sample one will only find more isotropy up to around 15µm above the bottom. At this point discs start to form which can be seen in figures A, B and D. Going up to around 24µm the discs disappear again and from here on the sedimentation layer consists mostly of just spheres. The sedimentation layer was about 35µm thick at all times. Figures A, B and D are taken at about 20µm above the bottom.

Because the discs do not lie on the bottom, their internal structure is usually difficult to see; rods from different heights blur into one image. When I come across a disc with rods aligned in the z-direction the structure in a disc becomes much better visible, like in figure D. The disc structure appears to be characteristic for the smectic-B phase; the rods seem to be organized on some kind of 2-dimensional lattice (mostly hexagonal it appears) indicating they have no translational freedom in the x,y-plane.

4.3.1.7 Sample 12

Sample 12's volume consists for 5% of rods and 10% of spheres.

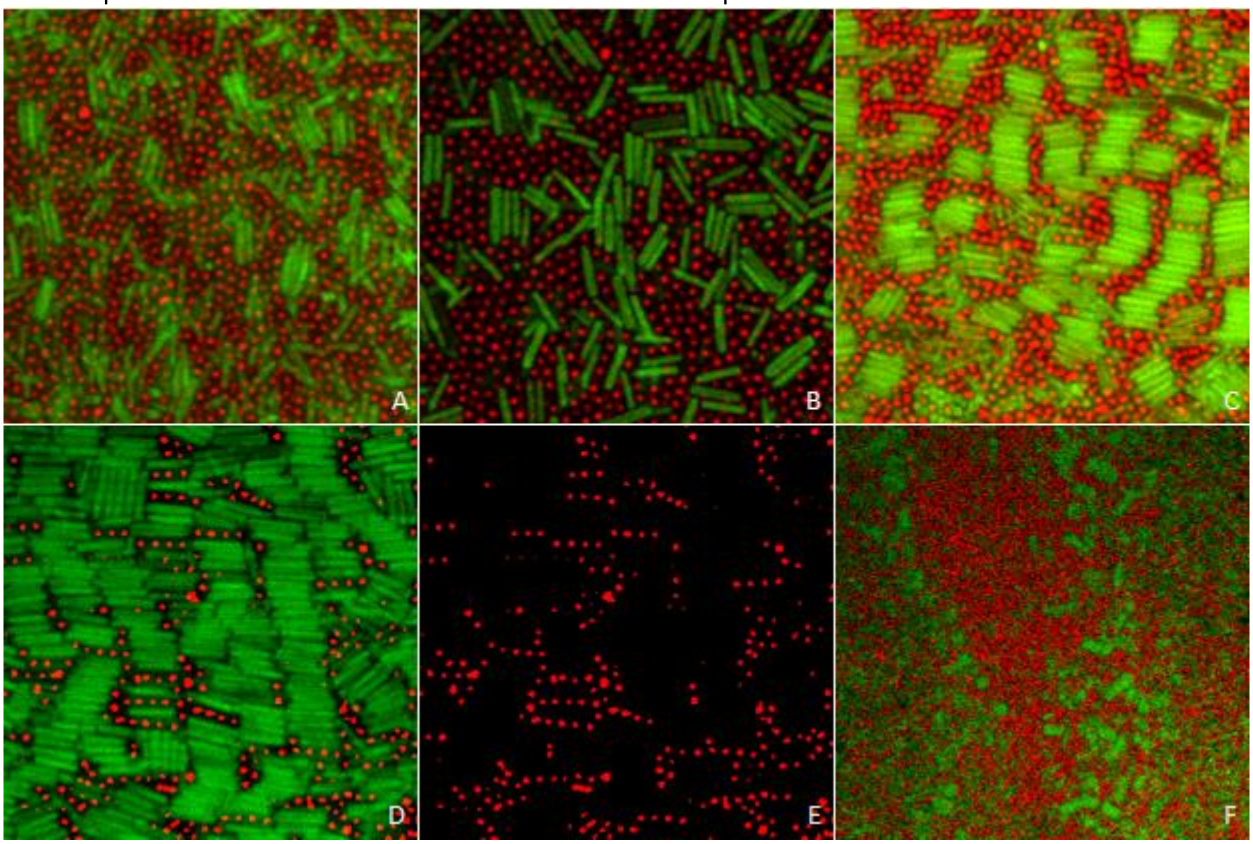


Figure 18. Sample 12 after respectively 1, 3, 7, 14, 14 and 21 days. F is a different version of sample 12 than A-E.

Many different behaviors were found in this sample. Starting at one day after the sample was made, the sediment was mostly isotropic. Figure A was taken at 11µm above the bottom, there are a few small discs in this sample, but what I thought was interesting here is the orientation of the rods even without the direct presence of discs (it may not seem very obvious, but the mean orientation is y-directed). After 7 days a lot of discs were formed, from the bottom up. Figure C is taken at 5µm high, in a layer of discs of 10µm thick. Note how the discs are all oriented in the same direction.

The disc structuring I just described is one behavior that occurred in this sample. Another structure I found can be seen in figures D and E. At this point I made 2 versions of sample 12 (I made a 3rd version later on) and the first version is the only version in which I found this structure, and there wasn't even a lot of it. The structure I'm talking about here can best be seen when you take away the rods, as has been done in figure E; the spheres form little chambers for the rods to lie in. Looking at different heights the chambers seem to arrange themselves on a hexagonal lattice –like a honeycomb, when viewed from the side (y,z-plane) or above (x,y-plane). Because I didn't find much of this structure, and have never found it again as clearly as I did here, I cannot say too much about it. I don't know if it's a stable structure, or what the conditions are under which it forms. I can make a guess about these conditions however; as

I’ve also found signs of this structure in sample 1 (5% rods, 5% large spheres), I could say that this structure would form if the rods-to-spheres ratio is about one; this is the case in sample 1 and possibly also the case here, as the rod concentration seems locally higher where the structure appeared. This wouldn’t make sense number-wise; you need a lot more spheres to form walls with than you need rods to surround, but it might make sense density-wise as the conditions for structures to form usually has something to do with density (phase diagrams are often plotted with density on one axis).

Another interesting behavior I found in this sample, and the reason I presented figure F, is demixing between rods and spheres. I’ve seen this in the first version of sample 12, but not to the same extend as in the version from figure F. In the first version demixing occurred only in the direction along the walls, so I thought this was just the influence of the wall, even though the demixing interface was quite far from the wall. In the second version the rods and spheres demixed into separate ‘fields’; the sample looked like a giraffe’s skin. Note that the demixing is not “pure”; there are still rods in the sphere fields and vice versa. This demixing can be seen in figure F, where a sphere field is surrounded by a rod field. There are more obvious pictures of this demixing but I chose to show this picture because it shows 2 things at once; there are also discs in this picture. The demixing happens at all heights; at the bottom and at 65µm above the bottom where figure F was taken. The sedimentation layer was about 95µm thick. At the bottom the demixing was the clearest, but at increasing heights, discs started to appear near the interfaces of the rod- and sphere fields. From this I could conclude that the rods need to be near a sufficient amount of spheres to be able to form discs, and have to be in a certain density (or possibly pressure-) range. This seems to agree with other samples where discs were found; discs are usually not found on the bottom but float around at a certain height.

4.3.1.8 Sample 2

This sample contains 2.5% rods and 2.5% spheres.

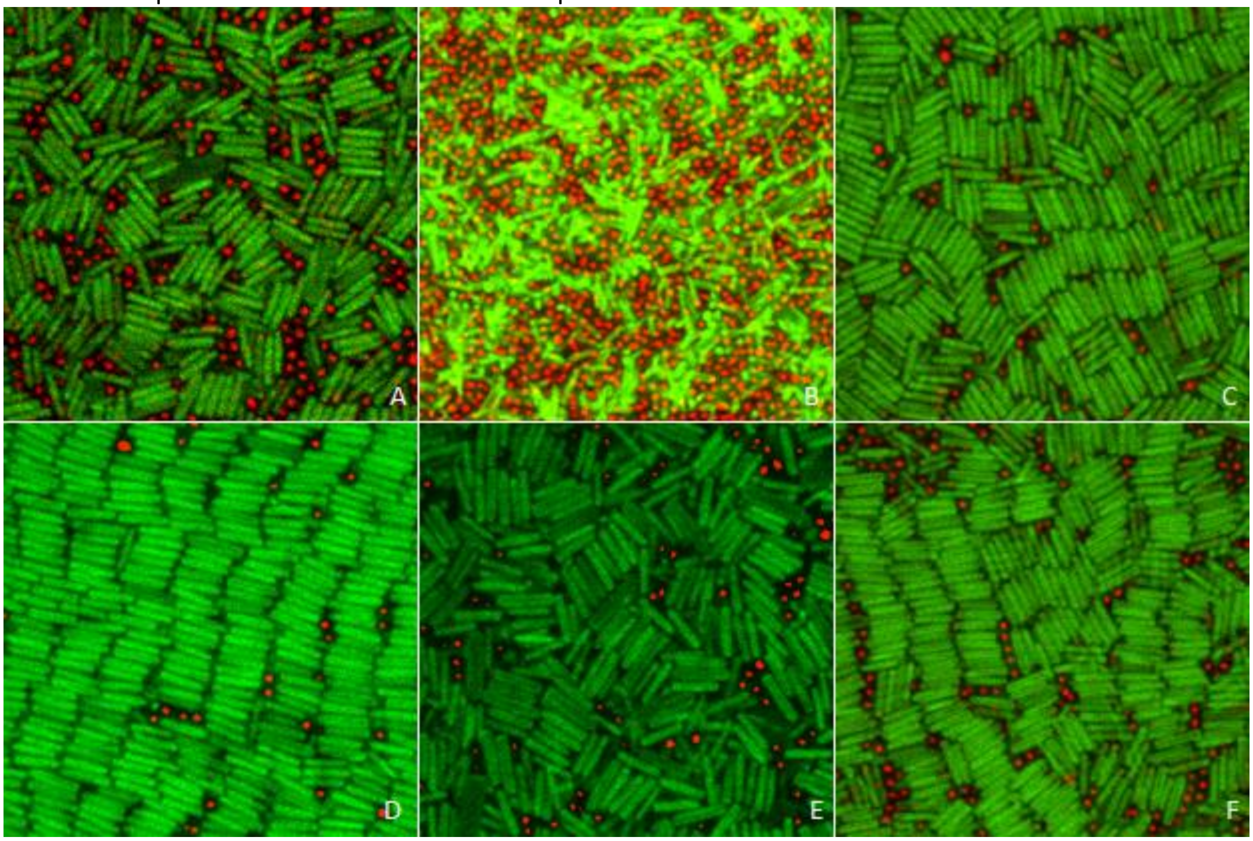


Figure 19. Sample 2 after respectively 1, 3, 7, 14, 21 and 28 days. E and F are from a different version than A-D.

The odd concentrations in this sample are a relic from when I just started the research. I still include this in my results because it's a nice change from just differing amounts of spheres; this sample also differs in total density and therefore the pressure of one of my samples (sample 1 (5% rods, 5% large spheres)). Like a few other samples I had to remake this sample after the first version became unusable. The second version was by far not as well structured as my first version, but the longer I waited the more it started to look like the first version.

Starting with one day after I made the sample, I didn't find any structure at all. After 3 days the sample looked just like it did after 1 day. I took figure B at 4µm above the bottom to show the difference in sphere concentration at the bottom and a little above the bottom; the spheres seem to be pushed out of just the very lowest layer of colloids. Right on top of the lowest sedimentation layer (the one imaged in figure A) the amount of spheres is significantly higher than the layer below. After 7 days the rods started forming long rows of aligned rods and after 14 days the sediment started to look quite smectic, with spheres positioned at tips of rods or forming groups of 3 that align themselves along the rods (figure D).

The next version of sample 2 didn't form it's structures as fast as the first version did, but it seemed to eventually get there; figure E looks similar to figure A and figure F (7 days after figure E) looks similar to figure C (7 days after figure A).

Figure D showed the most signs of mutual structure in the way that spheres tend to lie at the tips of rods. Looking at different heights in this sample I found such rows of spheres between layers of rods to actually be small planes of spheres; the mutual structure extended to about 3µm in the z-direction and about 3-4 spheres (which is about 3-4μm) in the x- or y-direction. This can prove that spheres favor lying at the tip of rods and that they didn't just randomly end up there. However, it is not possible for the spheres to lie one-to-one at tips of rods; the radii of the rods and spheres differ by a factor of about 0.7 so in the planes between smectic layers one would find a ratio of about 2 rods to 1 sphere.

4.3.2 Small spheres

4.3.2.1 Sample 21

This sample contains 5% rods and 0.1% spheres.

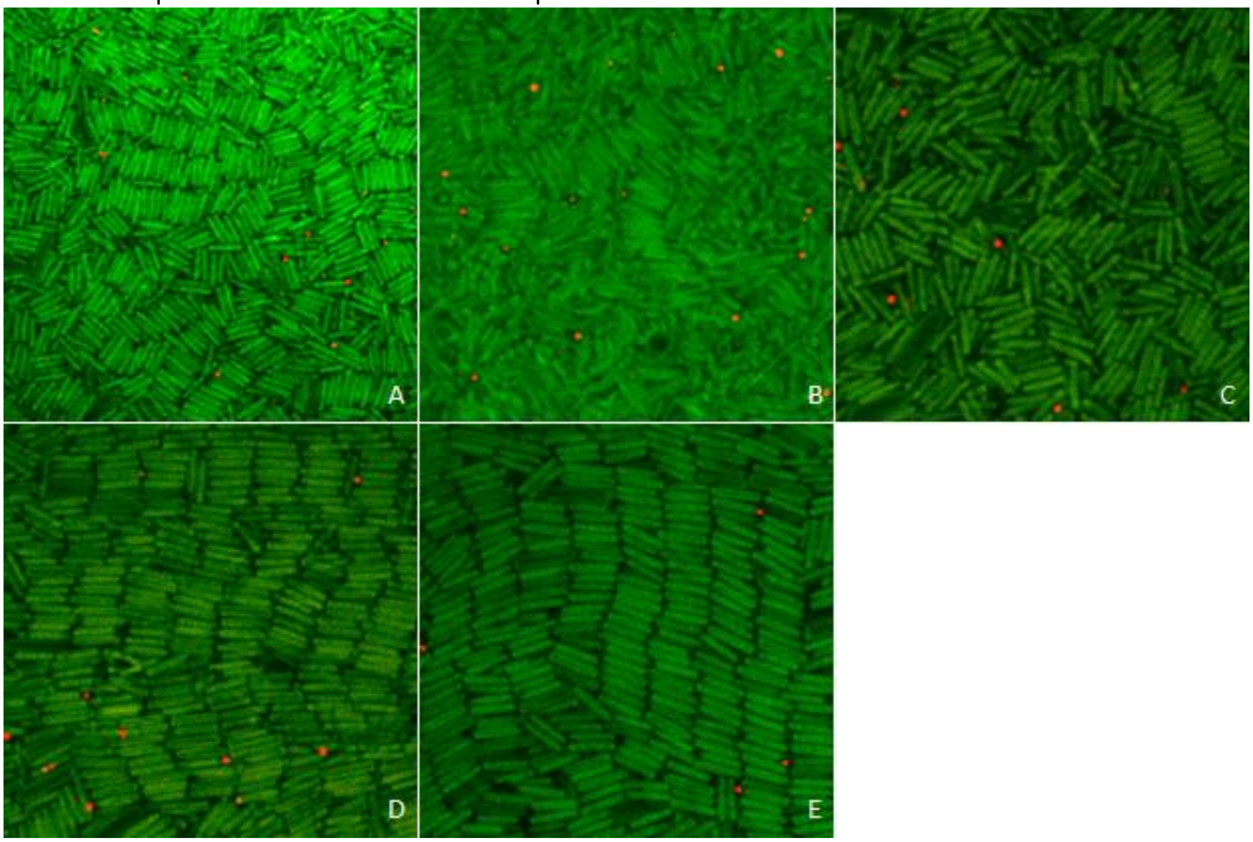


Figure 20. Sample 21 after respectively 1, 3, 7, 14 and 21 days. B is taken at 8µm above the bottom.

The very low concentration and small size of the spheres make this sample almost a purely rod sample. If I assume the spheres have no effect on the structure of the rods at all the spheres show me what a single sphere would do if it were somehow placed in the middle of an already existing rod structure (already existing, because the spheres assumedly have no influence on the formation of this structure). It turns out that most spheres tend to position themselves at the tip of a rod, as can be seen from figures D and E. In other words, a sphere will find the most available volume between smectic layers; remember that the free energy contribution of a sphere is minimal when it has maximal wrigglespace. To be certain I can assume the structures to form as if it were a pure rod sample, I would have to compare it to a pure rod sample. However, I don't have any pure rod samples at this point.

Now let's look a bit more objectively at the sample; after one day it has already formed some traces of smectic structures, and after 3 days I found a disc. There were multiple discs located between 4µm and 10µm above the bottom after 3 days (the sedimentation layer is about 20µm thick). At any other time I couldn't find any discs. After 7 days the sample still doesn't look very structured anywhere but after 14 and 21 days a large scale smectic structure has formed.

So far the sample shows nothing too unexpected. Further conclusions should follow if I can compare this sample to a purely rod sample.

4.3.2.2 Sample 20

This sample contains 5% rods and 0.5% spheres.

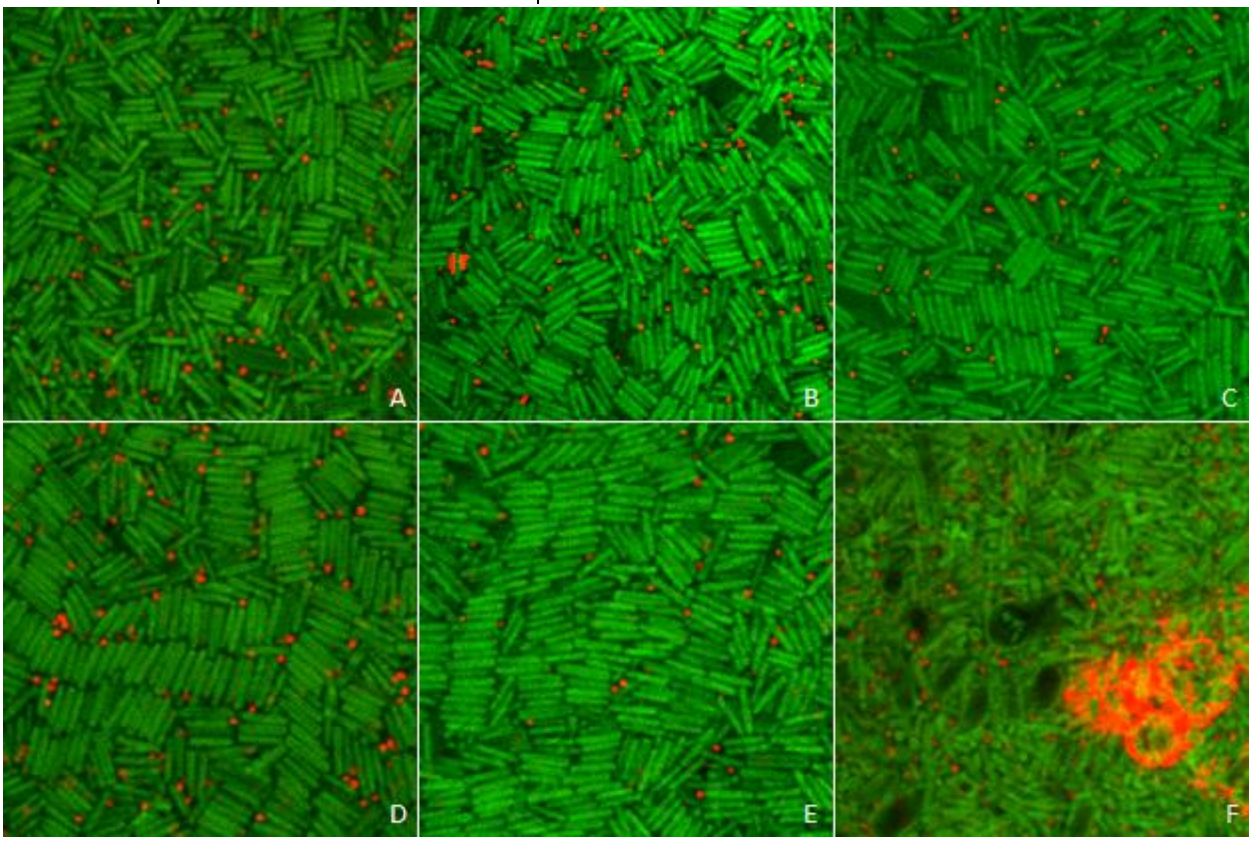


Figure 21. Sample 20 after respectively 1, 3, 7, 14, 21 and 1 day(s).

This sample starts off fairly isotropic, 1 day after it's made as can be seen on figure A. Clusters of rods with aligned axes have formed after 3 days and slightly longer clusters after 7 and 14 days. Eventually nematic-like structures appear in the sample as can be seen in figure E. The structures in these figures definitely do not appear everywhere in the sample, but still give a good representation of what is possible in the sample.

This sample also had a layer of very small discs (~10 rods) at most times (after 1, 3 and 21 days for certain) at a height of 5 to 8µm above the bottom, or from the bottom to about 10µm higher. The sedimentation layer is about 20µm thick at each time.

What I also want to point out in this sample is the difference between a theoretical sample and the real sample. In such a "theoretical sample" all the rods are exactly the same size and there would be only 3 things in my sample; rods, spheres and solvent. Of course, in reality this is never the case; there are giant rods in my sample that are the result of imperfections in the synthesis procedure (the dark shapes in figure F). There also appeared to be some kind of bubble that probably originates from something in my bottle with spheres. Although this red bubble is quite rare, the giant rods appear in many other samples and are likely to have some effect on the structures.

4.3.2.3 Sample 19

This sample contains 5% rods and 1% spheres.

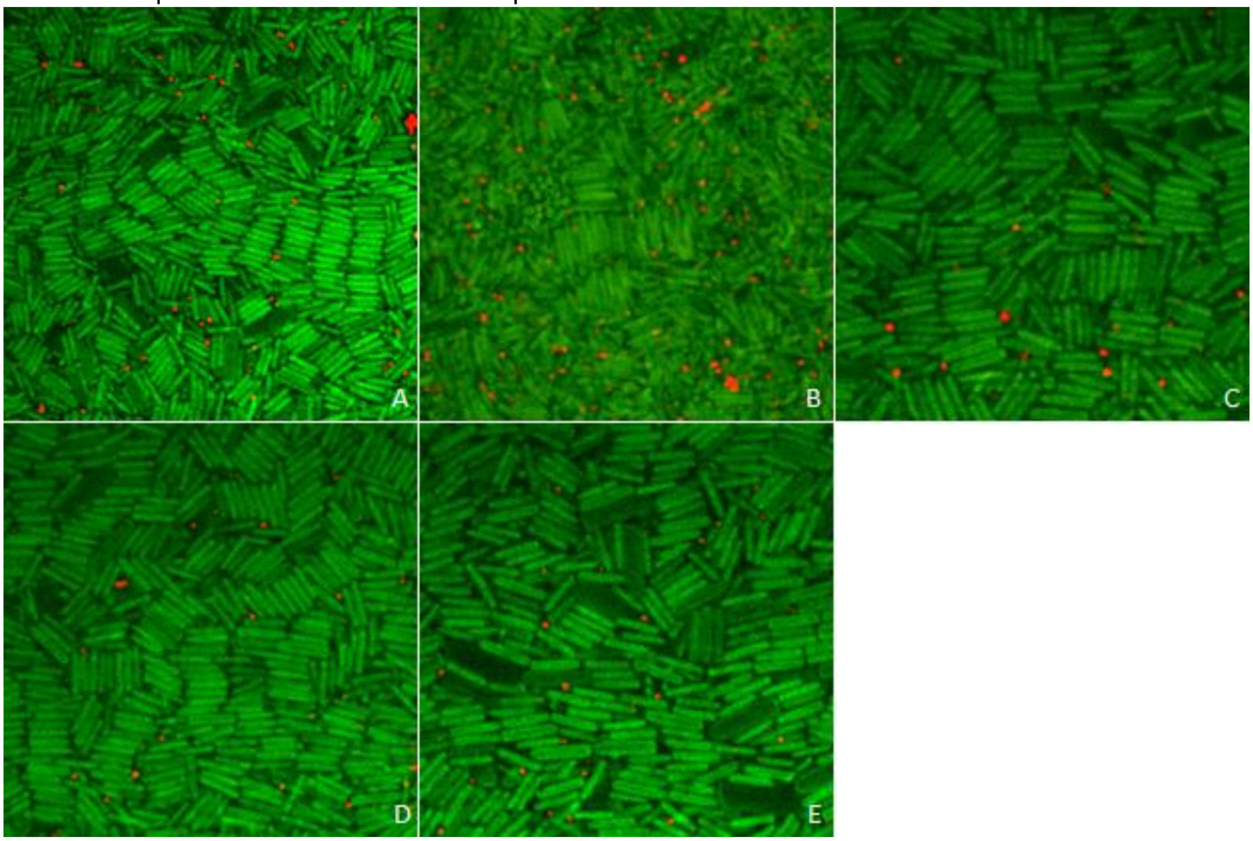


Figure 22. Sample 19 after respectively 1, 3, 7, 14 and 21 days. B is taken at a height of 4µm.

One day after I made the sample the rods showed mostly the isotropic phase with some smectic and nematic structures here and there. Seeing images like figure A after just one day, one might expect to see the sample turn into a big smectic phase after some time. This appeared not to be the case. After 3 days the bottom of the sample seemed just as isotropic as after one day, with the exception that I didn't find the bits of nematic/smectic structure that I found after one day. There were some discs however (figure B), at heights between the bottom and 8µm above. After 7 and 14 days (figures C and D) the clusters of rods became longer and after 21 days the sample was mostly nematic, oriented in the x-direction (figure E). The structures that were found on the bottom were usually still recognizable at about 4µm above the bottom, especially structures such as the ones in figures A and E. The sedimentation layer is about 20µm thick at each time.

The spheres don't seem to play a very big role in any of the structures in this sample at first glance; the spheres are quite randomly positioned with respect to the rods, sometimes between them, sometimes at their tips. However the spheres could be the reason the rods don't form the kind of structure we saw in sample 21 (p. 28), but this could also be attributed to the amount of giant rods in this sample. Another reason that there are no structures in this sample like the ones in sample 21 is that it could be a game of chance; it may be possible that even 2 identical samples would still form different structures.

4.3.2.4 Sample 18

This sample contains 5% rods and 2.5% spheres.

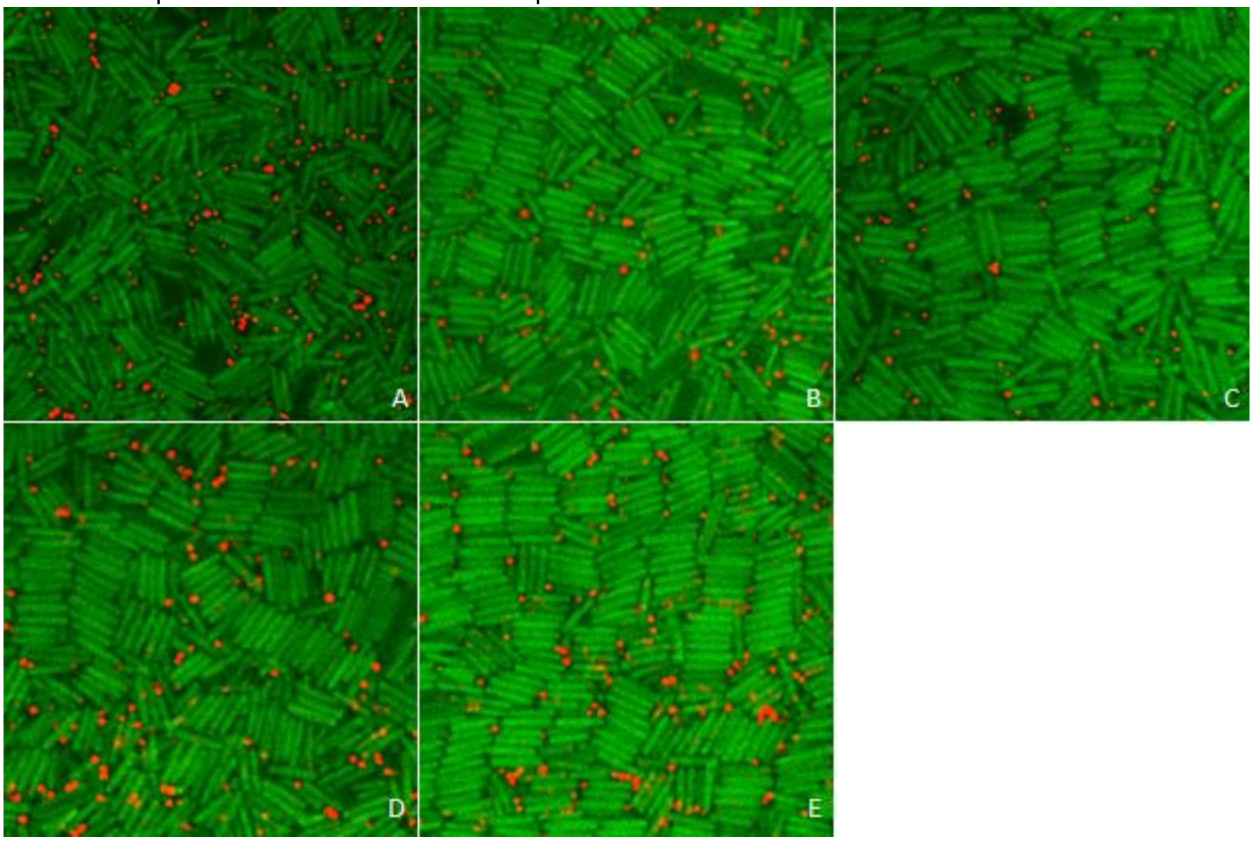


Figure 23. Sample 18 after respectively 1, 3, 7, 14 and 21 days.

In each figure I present the bottom of the sample, because apart from some small discs after 21 days this is the only place where the rods are not isotropic. After one day the sample is just isotropic everywhere, 2 days later (figure B) the rods assume a common direction here and there so it becomes more nematic. Over time the sediment becomes more and more nematic/smectic. This is not very apparent from the images, as figure C and E look quite similar. The small scale structures don't become very neat –E looks somewhat smectic but has many disturbances –but become larger scaled. Zooming out on figure C one would see some patches of structure (like the one in figure C) surrounded by isotropic rods. Zooming out on figure E would reveal a large scale (although disturbed) smectic structure; many rows of rods all having the same orientation.

Another interesting thing about this sample is the distribution of each species of colloid. The rods are in the lowest part of the sample, from 0-20µm above the bottom. The spheres are less numerous in this part than they are above 20µm, from here on up the concentration of spheres first becomes higher before gradually declining up to a height of about 60µm. At 60µm there are still quite some spheres but sufficiently less than in lower parts of the sample.

4.3.2.5 Sample 10

This sample contains 5% rods and 5% spheres.

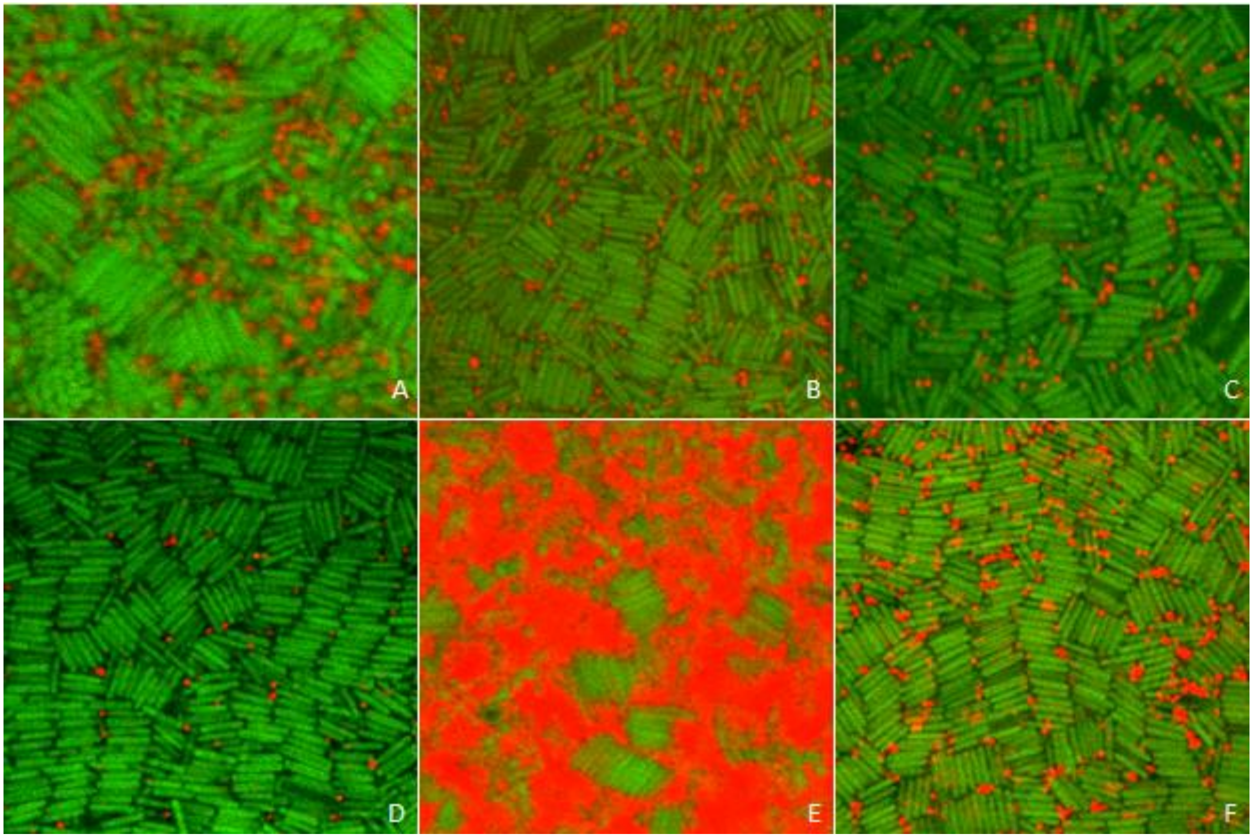


Figure 24. Sample 10 after respectively 1, 3, 7, 14, 14 and 21 days.

This sample has 2 distinct types of structure in it; discs and bottom structure. After 1 day there was no structure on the bottom (just isotropy) and at a heights between 6 and 11µm above the bottom there were small discs like the ones in figure A. Three days after I made the sample the discs were smaller and less numerous than before. So I present an image of the bottom (figure B), which became more structured into clusters/rows of aligned rods. After 7, 14 and 21 the discs became even smaller and less numerous and the bottom a little more structured yet. At 14 days I came across the image in figure E; I've noted before that discs sometimes tend to form near the boundary between high/low concentrations of rods/spheres on one side and the opposite on the other. Figure E is a very nice example of this phenomenon; in the lowest part of the 'spheres layer' the only kind of rods are rods that form discs.

The thickness of the sedimentation layer in this sample was quite constant for most times. The rods layer was about 18µm thick but there were still a lot of spheres around 50µm above the bottom. It seems that in samples with a lot of small spheres it becomes harder to give a definite thickness for the sedimentation layer because of this vertical demixing. Note that when I say there are a lot of spheres around 50µm above the bottom, I don't mean that the spheres layer is this thick. I cannot say where exactly the spheres layer begins or ends, there are definitely spheres at the bottom and above this 50µm. I could say the boundaries of the spheres layer are where the spheres concentration is a certain fraction of the maximum concentration in the sample. In practice this is difficult, because I cannot determine the exact concentration by just looking at images from the microscope. So keep in mind that when I say 50µm, someone else might say it's really 40 or 60µm, which is just as correct.

4.3.2.6 Sample 17

This sample contains 5% rods and 7.5% spheres.

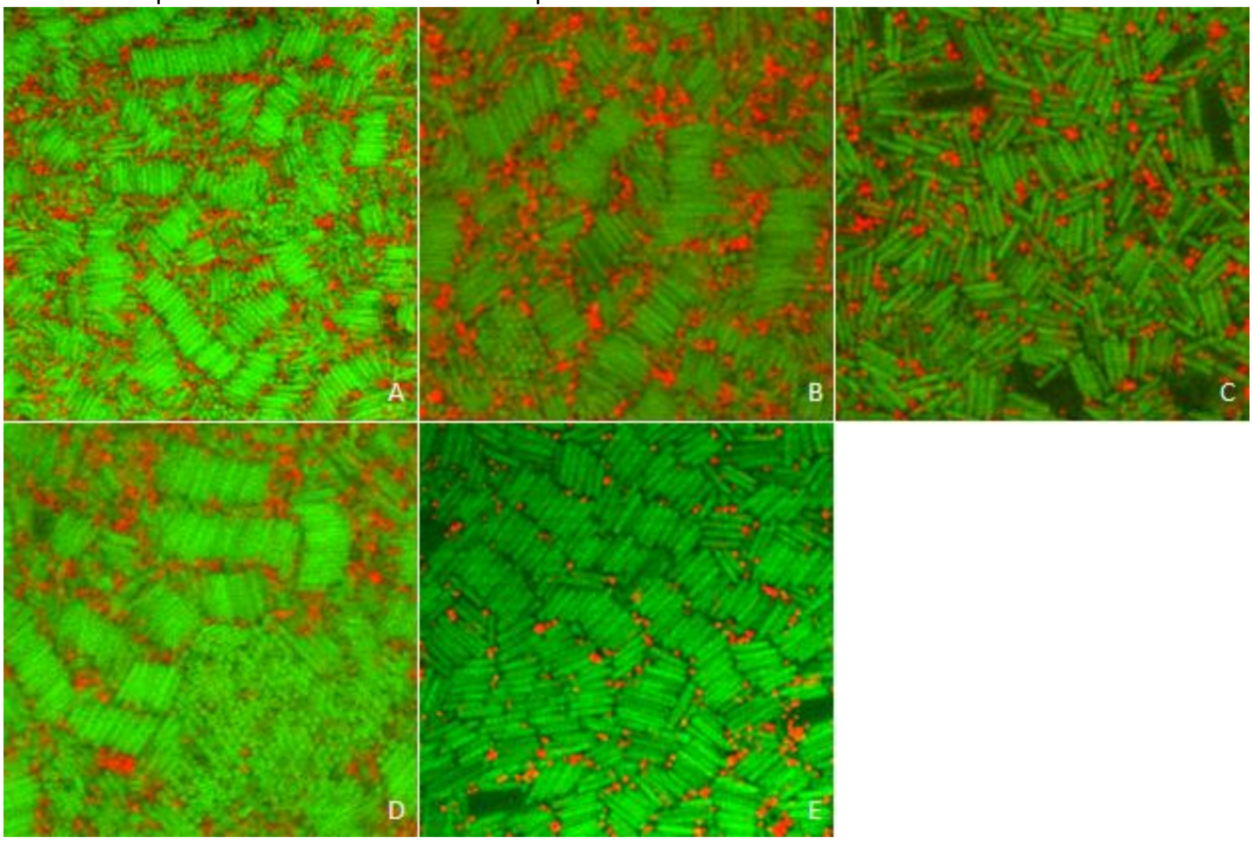


Figure 25. Sample 17 after respectively 1, 3, 7, 14 and 21 days.

This sample is all about discs. For the first 2 weeks (after 1, 3, 7 and 14 days) the sample hardly changed; there was a distinct range of heights at which discs would occur and the sedimentation layer stayed the same thickness. Figures A, B and D were taken in the discs layer, which is between 5 and 12µm above the bottom. These images are quite zoomed out to get a good idea of the size and amount of discs. The size is usually not so apparent when looking at a disc from the side, but figure D shows a good example of the size of a disc. After 21 days things changed a little. There were still lots of discs but they seem to have sunk somewhat; the discs layer is now between 0 and 8µm above the bottom and the discs are not as large and numerous as before. The rods layer was about 15µm thick and the spheres layer ended around 60µm above the bottom.

4.3.2.7 Sample 16

This sample contains 5% rods and 10% spheres.

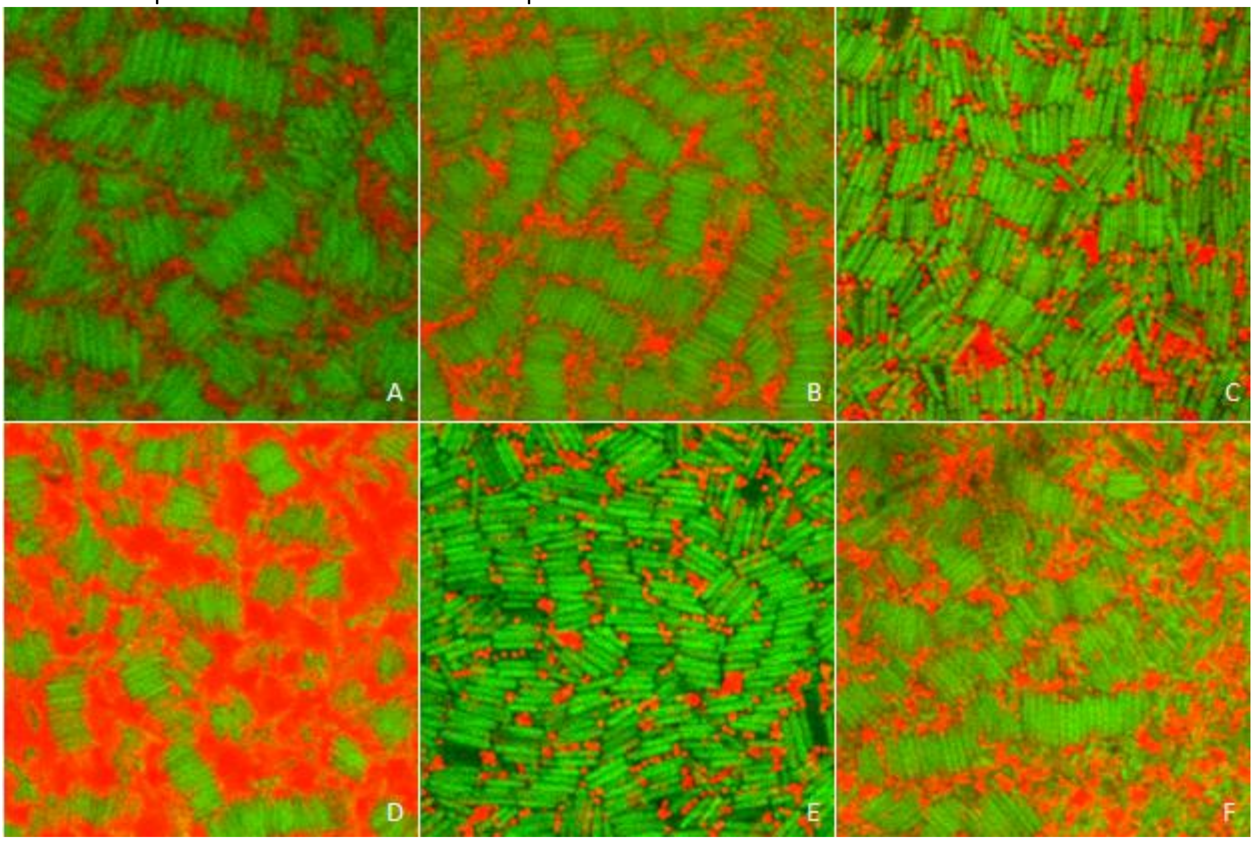


Figure 26. Sample 16 after respectively 1, 3, 7, 14, 21 and 21 days.

This sample contains lots of discs near the boundary of the rods layer and spheres layer. At 1 and 3 days the bottom was isotropic everywhere and about 10µm to 20µm above the bottom discs had formed (figures A and B). Later (7 or more days after the sample was made) the rods on the bottom started to order, like in figure C. At this point there were 2 structured regions in the sample; at heights 0-2µm was the bottom structure and at heights 8-16µm were the discs. These two regions are separated by an isotropic region. The bottom of the spheres layer is usually at about the same height as the bottom of the discs layer, and the top of the rods layer is usually the same as the top of the discs layer (figure D). Figures E and F are images from the 2 structured regions; the bottom and the discs. The spheres layer didn't end till about 70µm above the bottom.

4.3.2.8 Sample 5

This sample contains 5% rods and 0.6% spheres.

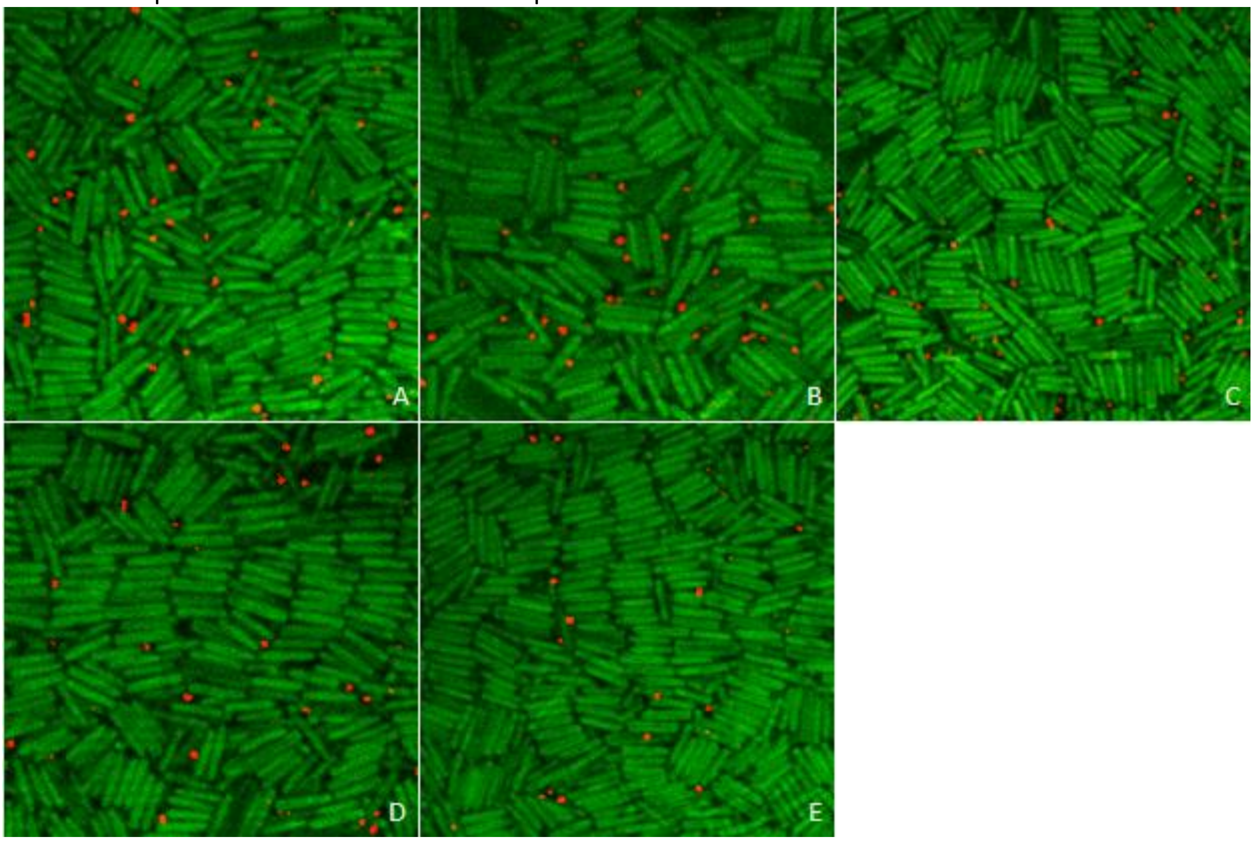


Figure 27. Sample 5 after respectively 1, 3, 7, 14 and 21 days.

This sample, with these specific concentrations, was the first sample I made containing small spheres. The idea behind these concentrations was to replicate the number ratio of that of sample 1 (5% rods, 5% large spheres); these spheres have half the diameter of the large spheres so they have $1/8^{th}$ of their volume, so the volume concentration had to be 5/8%. It turns out that small spheres don't sediment like large spheres so the number ratio in the sedimentation layer of sample 1 is not the same as the number ratio in this samples' sedimentation layer.

Looking at the structures in the sample I found that the rods start off quite isotropic and gradually become more smectic. Although the nematic phase could be seen as the 'bridge' between the isotropic and the smectic phase (going from complete freedom in the isotropic phase to only positional freedom in the nematic phase to only restricted positional freedom in the smectic phase) the rods in this sample seem to skip the nematic phase. This is not too surprising as we've seen that rods of this aspect ratio (~6) have to be in a narrow density range in order to form the nematic phase. The intermediate phase for these rods seems to be one in which ~4 or more rods form clusters in which the rods lie parallel to each other. These clusters do not necessarily share orientations, so I could call this phase 'cluster-isotropic' (figures A-C). Going through this cluster-isotropic phase the clusters become bigger and start sharing orientations, which leads to the smectic phase, albeit with disturbed/curved smectic layers (figures D and E).

4.3.2.9 Sample 7

This sample contains 5% rods and 0.3% spheres.

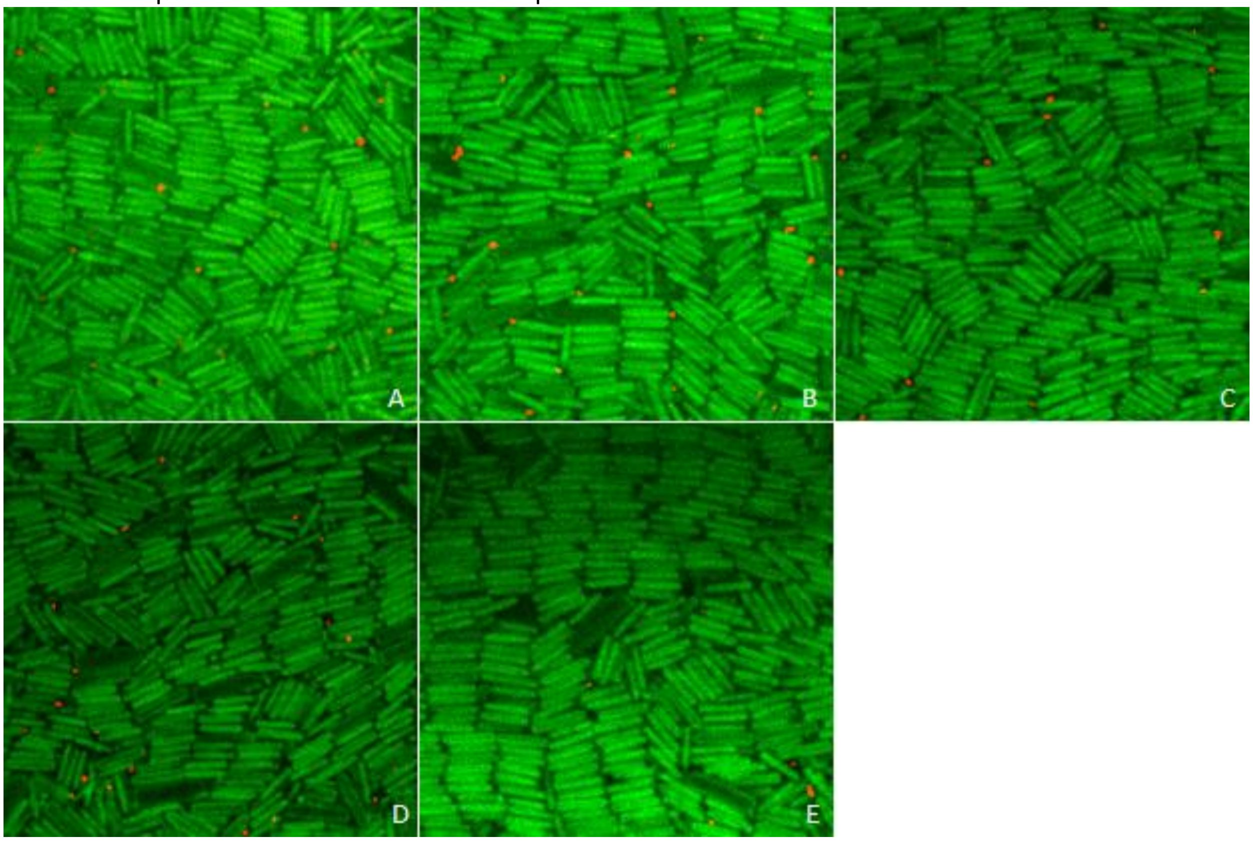


Figure 28. Sample 7 after respectively 1, 3, 7, 14 and 21 days.

This sample started mostly isotropic and became smectic over time. Although figure A doesn't seem very isotropic, most of the sediment was at this moment. The smectic structures that eventually turned up in the sediment are not very neat; figure E still looks much like images taken at earlier times like figure C and even figure A. The giant rods that appear a bit darker in the images might be the reason for this. Giant rods usually lie a little above the bottom (2µm or so) so only a few are visible in these images, but they may still have an influence on the structures on the bottom. Of course there could be another reason; the density might not be right for the smectic phase. Excluding one of these possibilities is difficult, because the density is difficult to measure by counting colloids on the screen, and making the rods more monodisperse takes a lot of time.

Looking up in the sample doesn't show much; everything above the bottom is isotropic. The colloids demix somewhat in the z-direction. The sample becomes very dilute of rods at a height of about 18µm and at about 30µm for the spheres.

4.3.2.10 Sample 6

This sample contains 2.5% rods and 0.3% spheres.

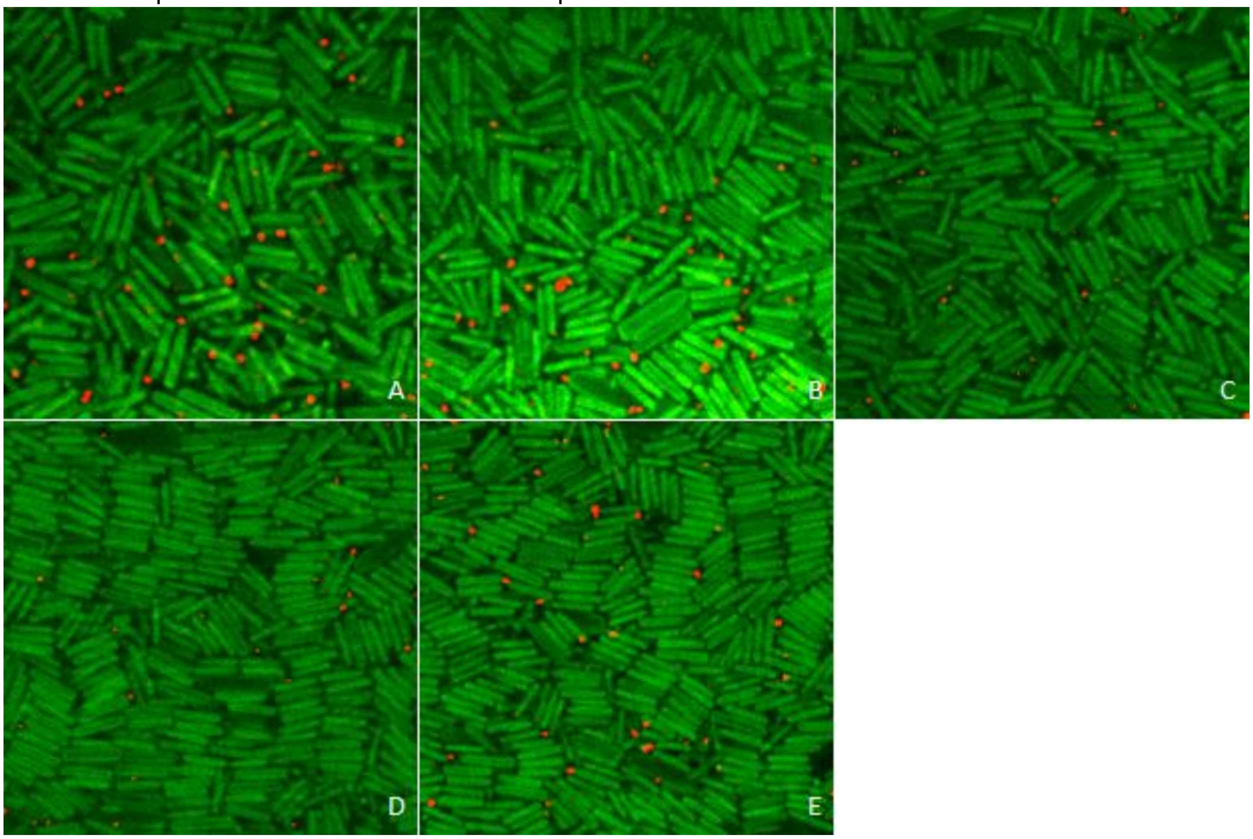


Figure 29. Sample 6 after respectively 1, 3, 7, 14 and 21 days.

Everything in this sample happens at the bottom, so I'll only present images of the bottom. After one day there is not really any structure anywhere; the rods are mostly isotropic and the spheres are randomly mixed amongst them (figure A). After 3 days not much has changed except that the rods seem a bit more clustered (figure B). After 7 days the rods are on average directed in the x-direction and after 14 and 21 days this average direction becomes clearer (figures C-E).

The spheres seem quite randomly distributed in the rod structure at first, but the spheres do have a favored position with respect to the rods. The majority of (if not all) the spheres in figure E are positioned at the tip of a rod and don't sit right in the middle of a cluster or smectic layer.

The odd concentrations in this sample are meant to replicate the number ratio of sample 2 (2.5% rods, 2.5% large spheres), like I described for sample 5 (p. 35) which was meant to replicate the number ratio of sample 1.

4.4 Discussion of the first samples

4.4.1 Categories

Many different samples show many different structures. The reason certain structures were formed can be attributed to many things; distance from the bottom, density, concentration ratio and size of the colloids all seem to play a role. I could, for example, assume that the disc structure depends on the concentration ratio of the species of colloids. If I were to categorize my samples it may become apparent what causes a certain structure to form. I will therefore categorize my samples by structure. Such a categorization would look like this:

Smectic bottom	21, 2, 13
Large discs	16, 17, 12, 11
Small discs	10, 18, 19, 20, 21, 1, 13
Bottom discs	3, 19, 20
Chambers	12
Other	7, 6, 5, 14, 15

I shall first explain the names I gave the structures:

- Smectic bottom: In this category I put samples that showed very large smectic structures. Many samples have showed some form of smectic structures, but for this category I emphasize the magnitude of the smectic structure. If rods in the sediment that lie, say, 60 smectic layers apart (about the size of the screen fully zoomed out) have the same orientation, and the sediment contains straight smectic layers, the sample belongs in this category.
- Large discs: Samples that show a distinct region of discs that is separated from the bottom by an isotropic region fall in this category, if the discs are sufficiently large and in great amounts.
- Small discs: Samples that show a distinct region of discs that is separated from the bottom by an isotropic region fall in this category. If the discs are large and numerous they belong in the “large discs” category.
- Bottom discs: If a sample contains discs that lie on the bottom, or if the region between the bottom and the discs region is not sufficiently isotropic, it belongs in this category.
- Chambers: The structure that was found in sample 12 (p. 24) wasn’t found in any other sample, it also doesn’t fall under any of the other categories. To put this structure in the “other”-bin wouldn’t do justice to the beauty of this structure, so I made a new category. To understand what I mean with “chamber”-structure please see section “Sample 12”.
- Other: Samples that didn’t contain much structure even after 3 weeks fall in this category. None of the samples stayed fully isotropic, but if there were no discs and the bottom was nematic or disturbed/curved smectic the sample falls under none of the above categories.

The names I gave these categories are quite general and the criteria for samples to fall under one of these categories are not very strict. One might wonder how big a disc has to be to fall under the “large discs” category and not under the “small discs” category. I will not worry about this too much, my samples lend themselves pretty well for such a categorizations as there are not many samples that fall between these categories. Sample 11 (p. 23) was the only one I found difficult to categorize, as the discs in this sample were large, but not particularly numerous like the ones in sample 16 (p. 34) or 17 (p. 33).

Having a division like this I can now make general assumptions. The “large discs” category, for example, has all the samples with high sphere concentrations; 7.5% spheres and 10% spheres for both sizes of spheres. I could say that in order to have discs form in samples, I would have to use high sphere concentrations. However, this would be a premature assumption with the results I have at this point as the spheres concentration is not the only way in which samples 11, 12, 16 and 17 differ from other samples. The density or pressure is also higher when more spheres are in the sample, simply because the average mass density is higher in samples with more colloids. I would have to have a reference sample with the same density gradient but a different concentration ratio.

4.4.2 Sphere structures

So far I’ve talked mostly about what rods do, what influences the behavior of the rods, etc. The spheres seemed all very irrelevant. The reason for this is that the spheres seemingly do the same thing every time according to the situation they’re in. If there are a lot of rods in a sample the spheres just fit themselves wherever they can. The way in which they do this has an influence on the behavior of the rods, so such behavior can also be described by the behavior of the rods. If the spheres are in samples with few rods, the large spheres will position themselves on a 2-dimensional hexagonal lattice on the bottom. For large spheres this can be summed up as; if they have enough room they will form their structure, if they don’t have enough room they will not form their structure. This rule applied to all samples containing large spheres. For small spheres the rules seem even simpler; small spheres don’t form structures. There are no samples in which there are many small spheres on the bottom, probably because they’re light enough to be easily pushed away by the rods. The spheres that are present on the bottom move around a lot –much more than their diameter every few seconds –meaning they haven’t formed any kind of lattice. Small spheres are also hard to tell apart using the confocal microscope so they would probably have to form very neat structures before it would clearly show up on the microscope.

All sphere behavior of the rods that I do mention is behavior that might lead to some kind of mutual structure. This can usually be described as some position with respect to a rod, which means the focus of attention will always be towards the rods.

4.4.3 The next step

The two most distinctive structures in the samples are the large discs and the smectic bottom, as these are generally the largest scaled structures. The chamber structure is also quite interesting in my opinion, however it is so rare that I don’t want to spend time searching for something, when I could be finding something. What I’m hoping to find is the lamellar structure [6] as I described in the phase behavior section. I believe I would sooner find mutual structures in samples that already have the conditions to form structures of the separate species of colloids, than I would in samples with different conditions. Samples in which I found the smectic bottom structure and the large discs structure apparently already have the conditions to form structures; the samples with smectic bottom structures obviously have the conditions to form the smectic phase, and samples with large discs have the conditions for rods to nucleate.

To sum it up, I want to do the following things for my next step:

- Make more samples that may form large discs.
- Make more samples that may form smectic bottoms.
- Make samples containing only rods, in various concentrations.

I added this last demand because I constantly let myself trip over the fact that I didn't have any reference samples. Each time I want to call something mutual structure I have to compare it to a sample containing just rods; to make sure a certain behavior would be behavior of rods and spheres together, or behavior characteristic for just rods. The other 2 demands I set for the next step serve multiple purposes. First I hope to find lamellar structure. I can imagine a smectic bottom to turn into the lamellar phase if spheres were forced in the structure; the spheres would have to go somewhere between the rods and hopefully position themselves between smectic layers, as the amount of wriggle space is largest there. The large discs structure may also turn into the lamellar phase. The large discs that were in the previous samples already looked much like the lamellar phase if only the discs would align their orientations; this would lead to alternating layers of rods and spheres in one direction. Second I want to be able to reproduce structures that I claim to have made. If the bottom of a sample shows a large scale smectic structure, like it did in sample 13 (5% rods, 1% large spheres), I don't know for certain that a similar sample will show a similar structure. Possibly the sample was tilted, making the conditions in one end of a sample as if it were a 2.5% rods/0.5% spheres sample. A similar sample that is not tilted would then not show a smectic bottom and the conditions for such structures would not be found.

For the next step I will make samples containing the following amounts of colloids:

Label	Rods %	Spheres %
31	15	-
33	12.5	-
35	10	-
37	7.5	-
39	5	-
41	5	-
43	5	10 large
45	5	7.5 large
47	5	1 large
49	5	10 small
51	5	7.5 small
53	5	0.1 small

The samples with the high concentrations of rods are meant to replicate the densities in samples with both rods and high concentrations of spheres; assumedly the density of the 15% rods sample would be about the same as a 5% rods with 10% spheres sample. I basically copied the samples that I put in the large discs and smectic bottom categories, with the exception of sample 2 (the 2.5% rods, 2.5% large spheres sample).

4.5 The second samples

4.5.1 Only-rods

4.5.1.1 Sample 31

This samples volume consists for 15% of rods.

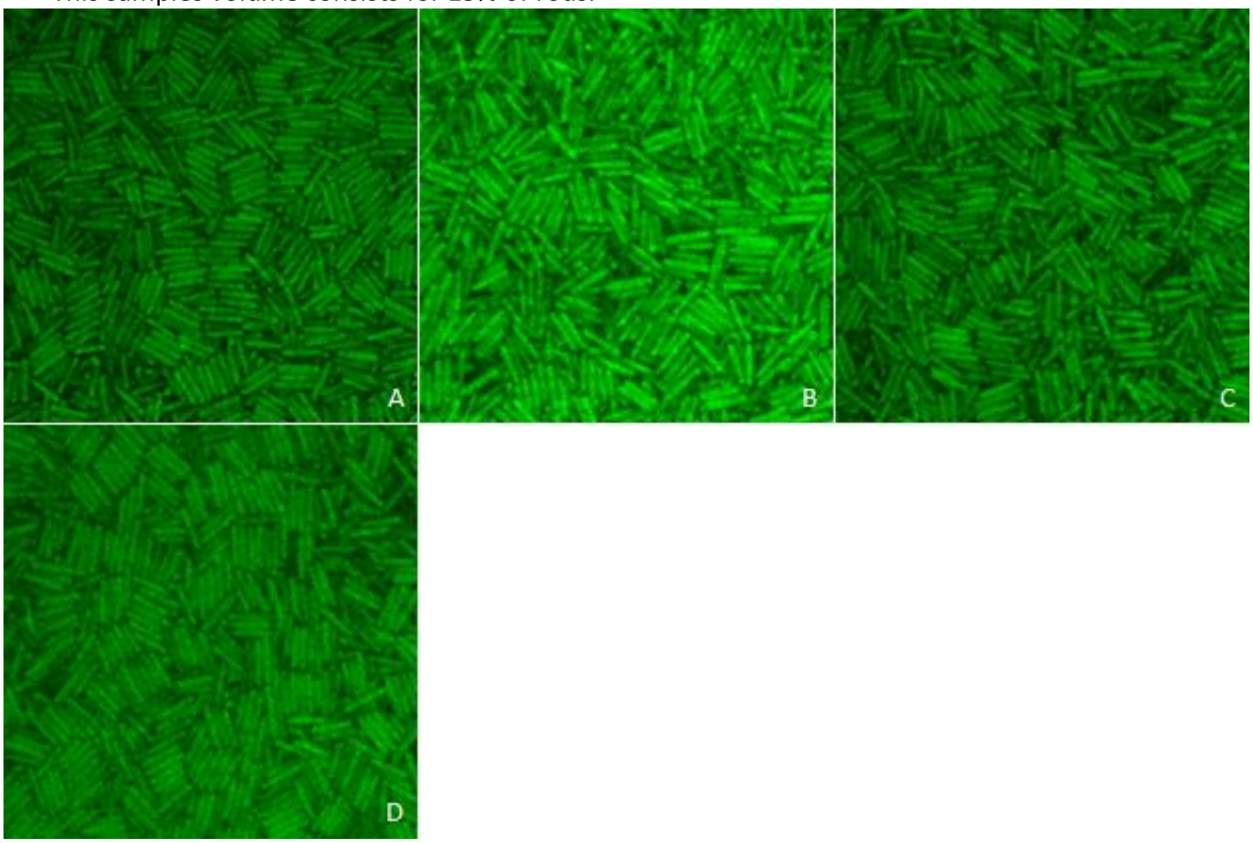


Figure 30. Sample 31 after respectively 1, 3, 7 and 15 days.

The sediment in this sample has not shown any significant change over a period of 2 weeks and has only been isotropic. Literature suggests that if any of my samples would crystallize it would have to be this one, because a high density of rods favors crystallization and this sample has the highest density. Perhaps it is only pressure that's high in this sample, and it will be too big an effort for the rods to adjust their orientation. The fact that there are also no discs in this sample contradicts the previous statement in a way; I would expect the pressure to be lower higher up in the sample, and that there would a point where the rods can adjust their orientations to form discs. The sedimentation layer was about 50µm thick after one day and gradually became about 40µm after 7 and 15 days.

4.5.1.2 Sample 33

This sample contains 12.5% rods.

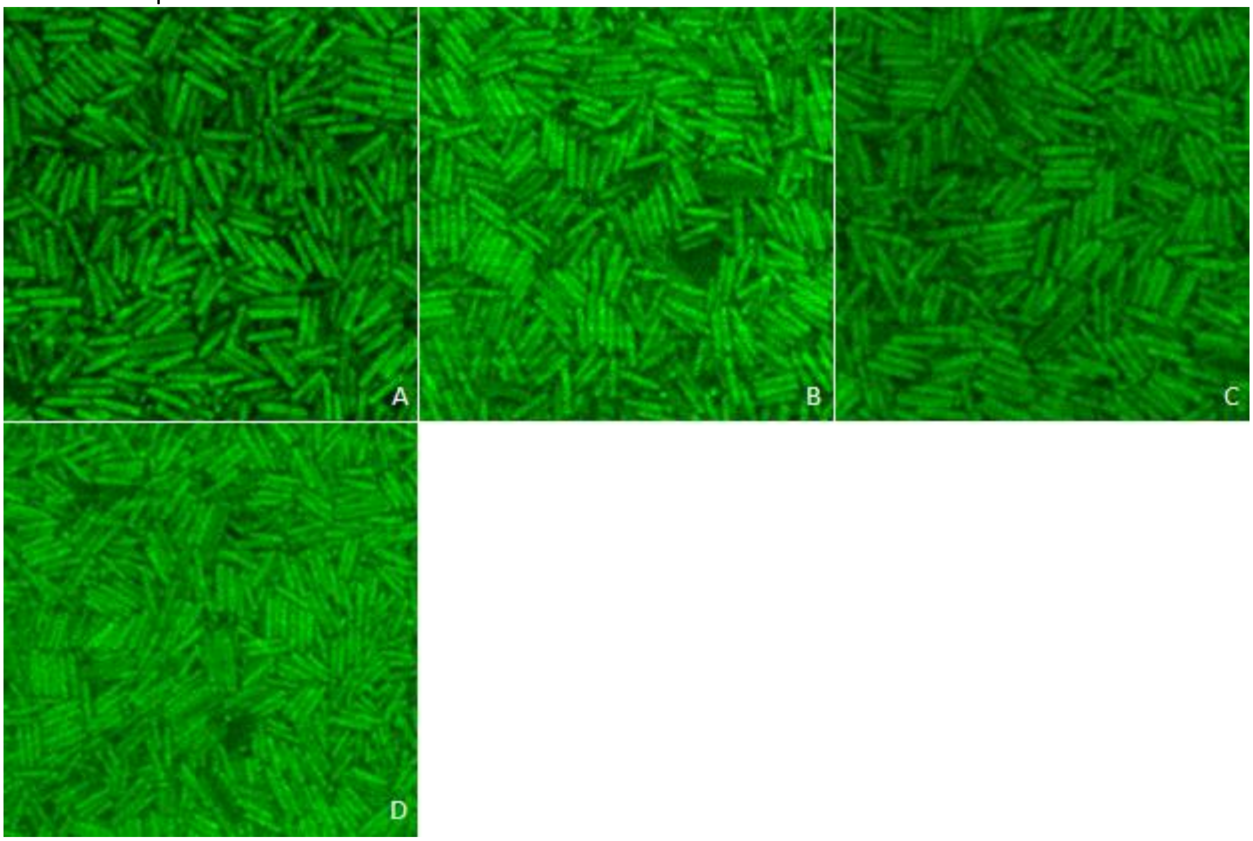


Figure 31. Sample 33 after respectively 1, 3, 7 and 15 days.

This sample started fully isotropic and hardly changed over 2 weeks. There are slightly more clusters after 15 days than after one day but I still cannot call figure D (which is from 15 days after the sample was made) anything other than isotropic. There are also no discs in this sample. The sediment is 40µm thick at each time.

4.5.1.3 Sample 35

This sample contains 10% rods.

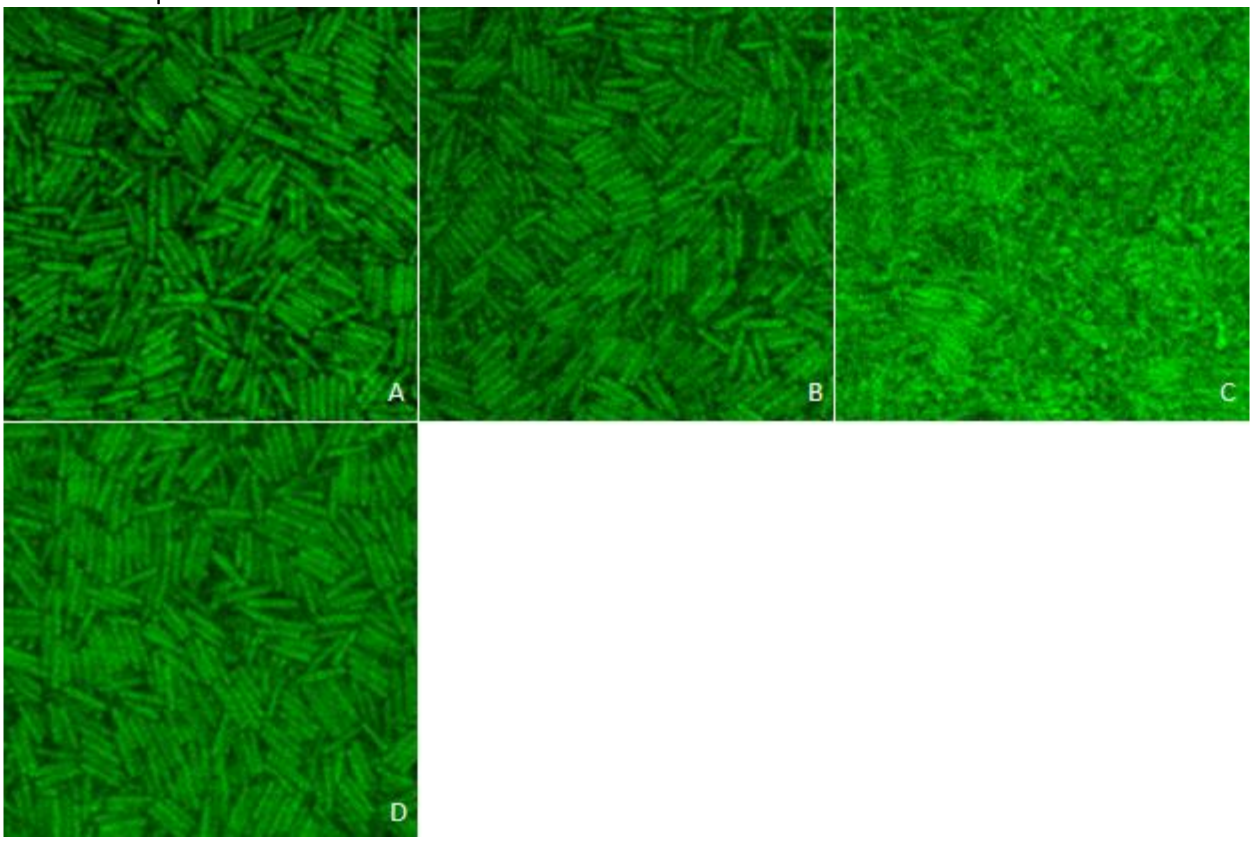


Figure 32. Sample 35 after respectively 1, 3, 7 and 15 days. C is taken at 25µm above the bottom.

This sample has been mostly isotropic each time I looked at it, with some slightly nematic patches. After 7 days I found something that, with a little imagination, could pass for a disc (figure C near the bottom left corner). Other than these small patches of nematic structure and tiny discs there is nothing more of interest in this sample. The thickness of the sedimentation layer is 36µm on average, varying by a few micrometers at some times.

4.5.1.4 Sample 37

This sample contains 7.5% rods.

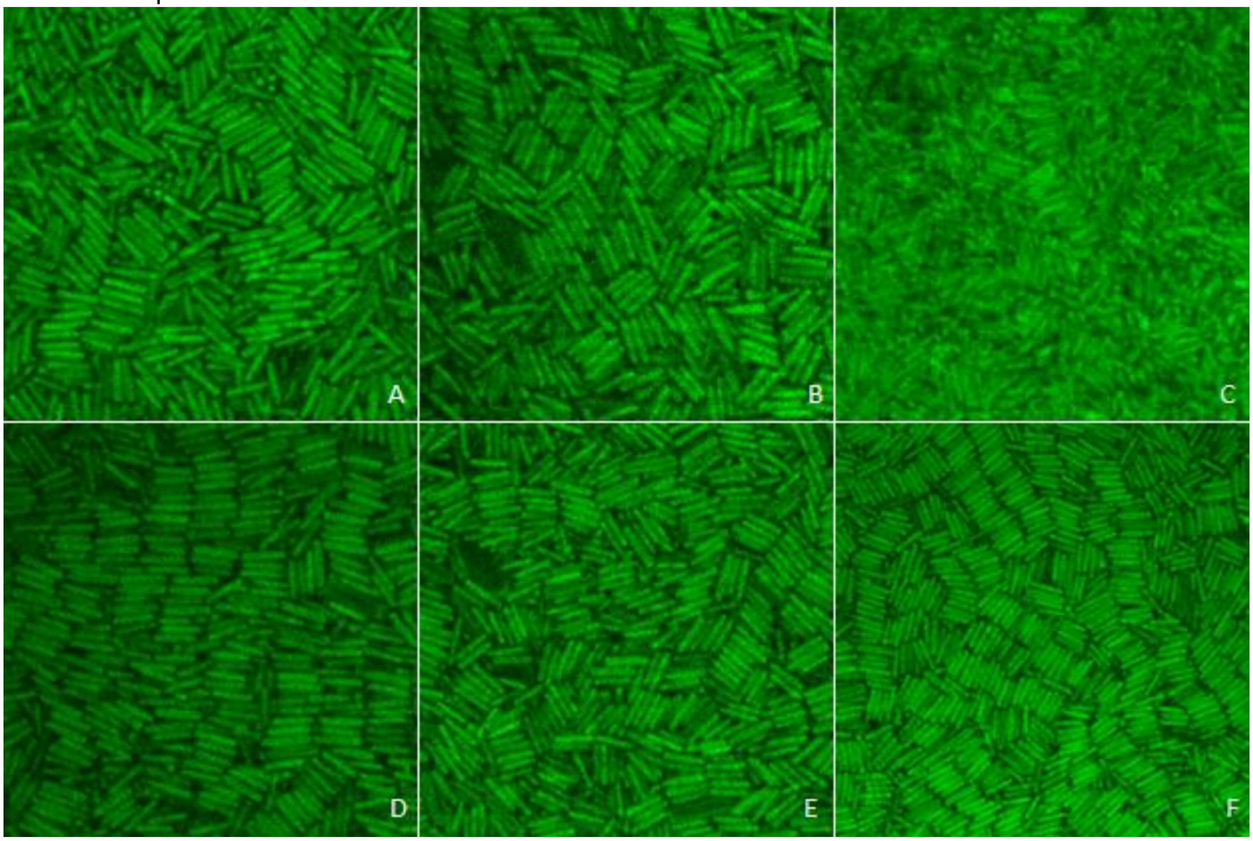


Figure 33. Sample 37 after respectively 1, 3, 3, 7, 7 and 15 days. C is taken at 6µm above the bottom.

One day after the sample was made there were some long rows of aligned rods here and there on the bottom of the sample. Over the 2 weeks the sample became more smectic on increasingly more places. Three days after the sample was made there were also a couple of small discs a few micrometers above the bottom (figure C), however the bottom is where the most interesting structures were. The thickness of the sedimentation layer varied over different x,y-coordinates, the sediment was about 20µm thick on average. The rods lying on the bottom in the thinner parts of the sedimentation layer were more structured (smectic, figure D) than the rods lying in the thicker parts of the sedimentation layer (figure E); the sedimentation layer was 16µm thick where figure D was taken and 26µm where figure E was taken. Structures such as the ones in figures D and F were about 3µm thick.

4.5.1.5 Sample 39

This sample contains 5% rods.

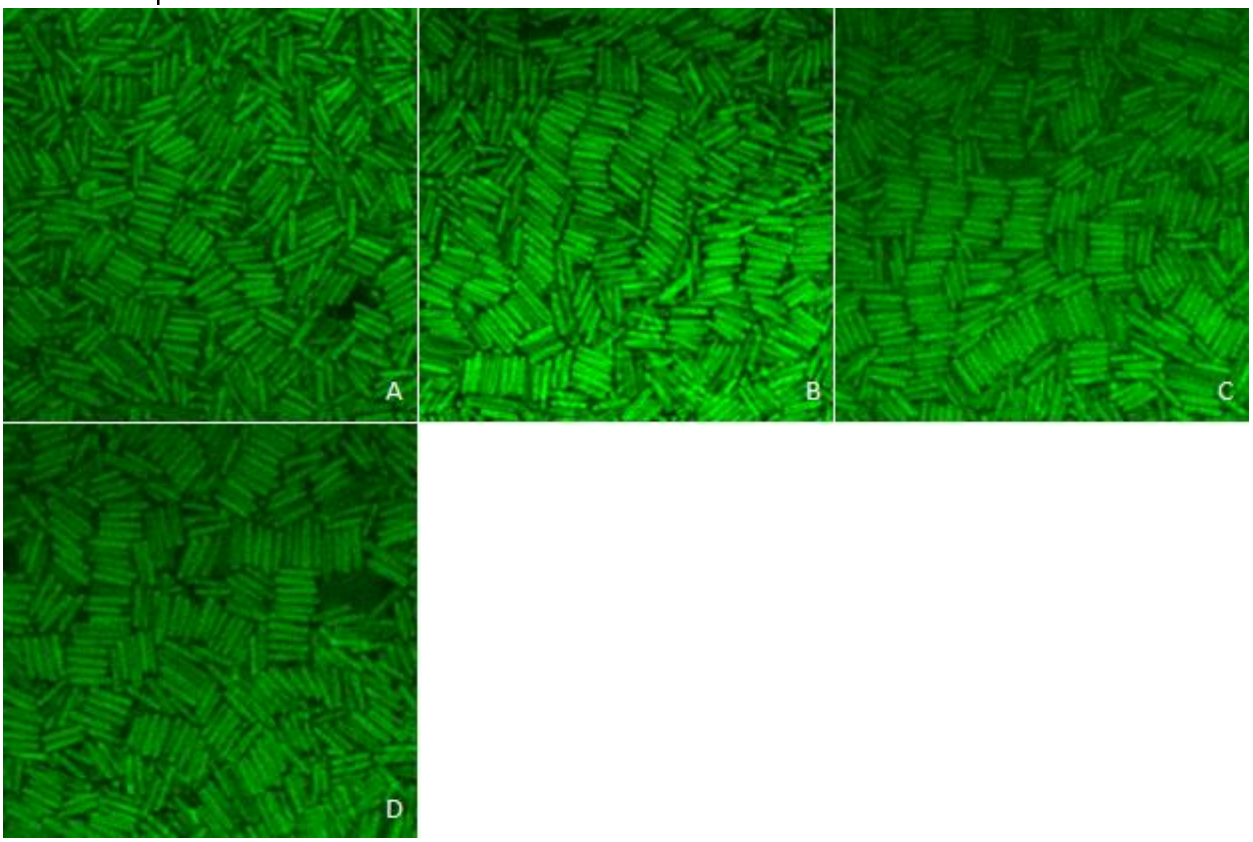


Figure 34. Sample 39 after respectively 1, 3, 7 and 15 days.

Some rows of aligned rods in the sample after 1 day. All the structure at each time is restricted to some small scale structure in the form of a couple of rows lying next to each other on the bottom, there are no discs either. The sedimentation layer is about 15µm thick at each time.

4.5.1.6 Sample 41

This sample contains 5% rods.

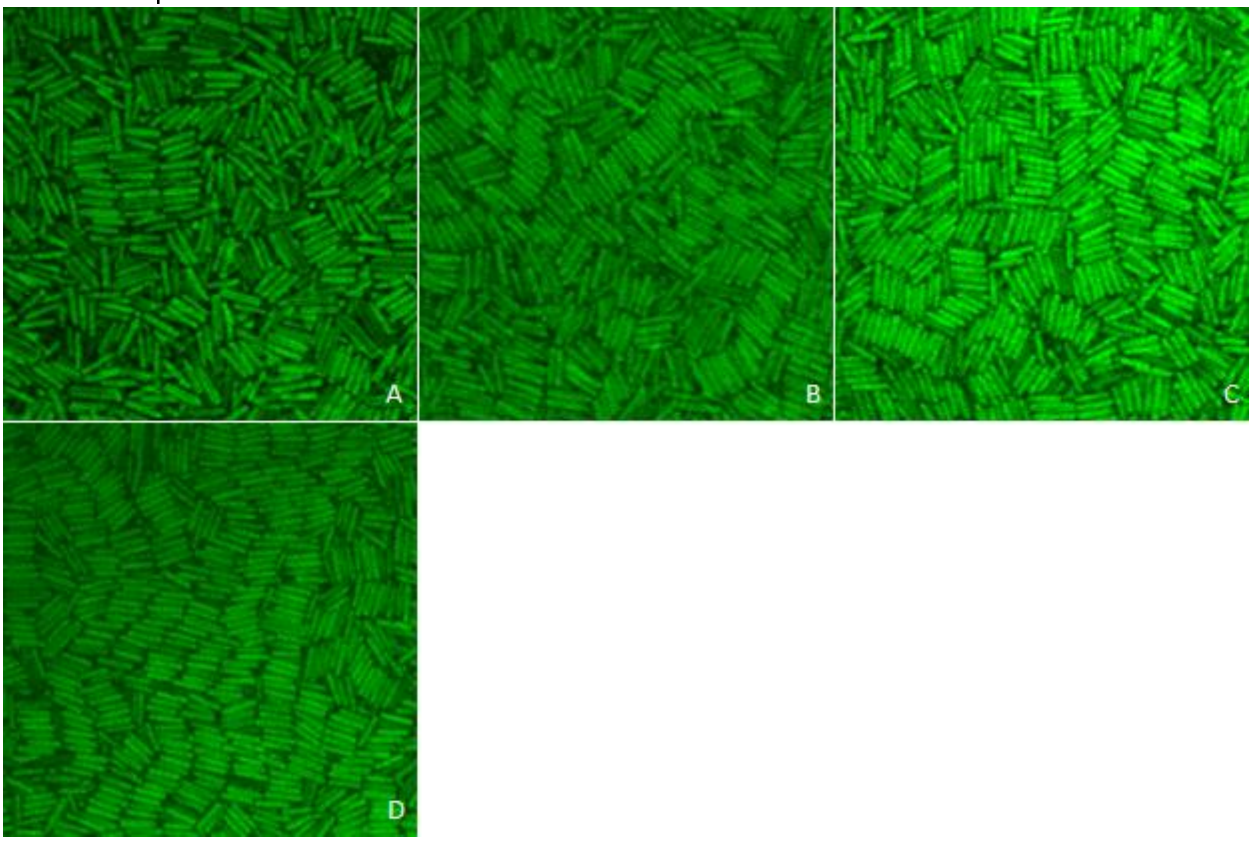


Figure 35. Sample 41 after respectively 1, 3, 7 and 15 days.

This sample gradually became quite smectic over 2 weeks, as can be seen in figure D. However, the structure didn't scale much further than the edges of this image. I found no discs and the sedimentation layer in the sample was about 14μm thick at each time. The structure in figure D was about 2μm thick.

4.5.2 Large spheres

4.5.2.1 Sample 43

This sample contains 5% rods and 10% large spheres.

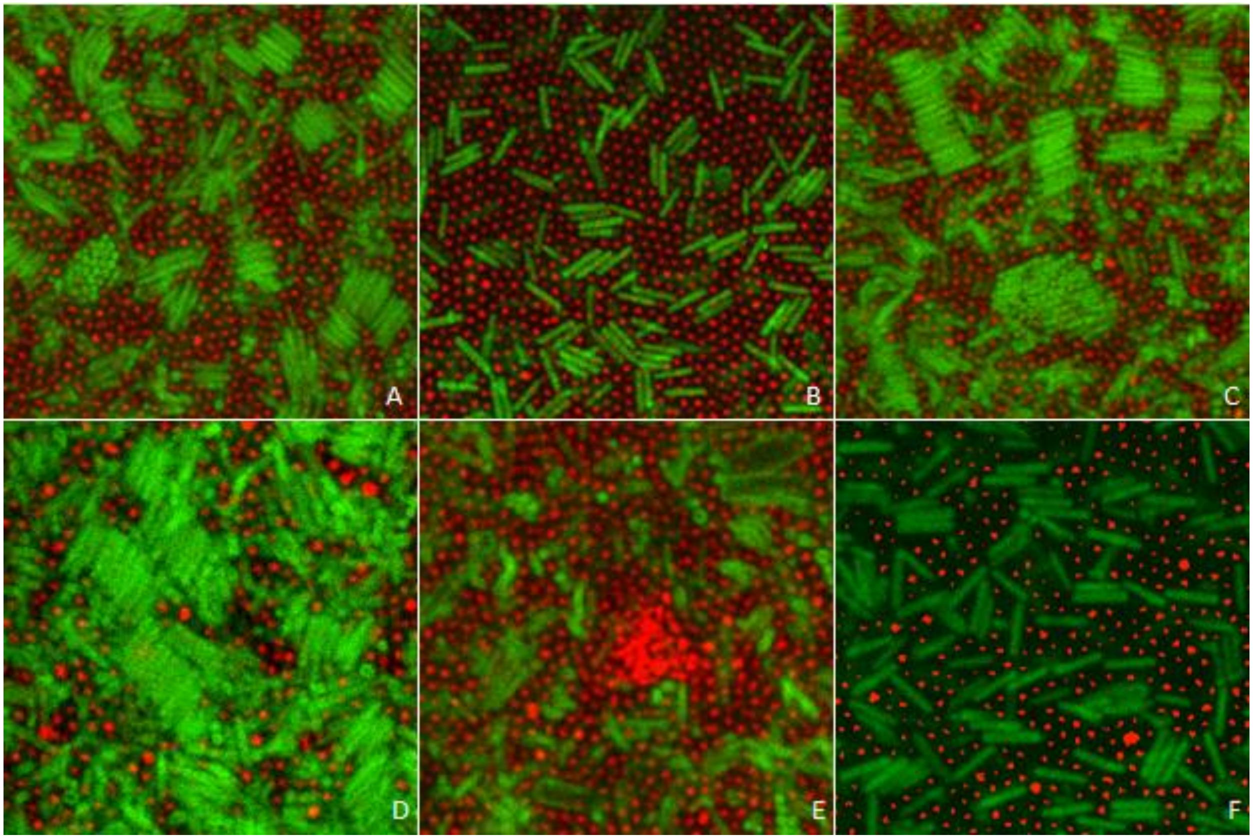


Figure 36. Sample 43 after respectively 1, 3, 3, 7, 7 and 15 days. A is taken at 25µm above the bottom, B is taken at the bottom, C is taken 25µm above the bottom, D is taken 26µm above the bottom, E is taken 8µm above the bottom and F is taken at the bottom.

From the previous results we already knew what to expect in this sample. Large discs, the chamber structure and demixing of rods and spheres are what were seen in either version of sample 12 (5% rods, 10% large spheres). The large discs returned, as can be seen in figures C and D. The discs started "building" right away as there were some small discs after one day (figure A) and became progressively larger. The bottom of this sample doesn't look too much like the bottom of sample 12; there are far less rods in this sample as can be seen on figures B and F. Note how the spheres follow the 'sphere rules' that I described earlier; there is sufficient space on the bottom so the spheres crystallize (figure B).

I have not found any of the chamber structure I found in sample 12, although I did find some hints that the chamber structure tends to form in this sample, but this could also be my imagination. Figure F shows that although the rods are not necessarily in contact with each other, they share their orientations over a large range. This behavior was also the case for the chambers in sample 12.

In one of the versions of sample 12 the rods and spheres demixed in large patches like a giraffe's skin. This demixing did not return at the same magnitude in this sample, but there was some small scale demixing in the form of clusters of spheres (figure E). Whether this demixing is a favoured state of the system or just random clustering I do not know. If I didn't know a similar sample demixed on large scales I would probably think this cluster was the result of a chemical side effect, as the spheres cannot be told apart.

The sedimentation layer was about 40µm thick at each time and discs were observed between 21 and 30µm above the bottom.

4.5.2.2 Sample 45

This sample contains 5% rods and 7.5% large spheres.

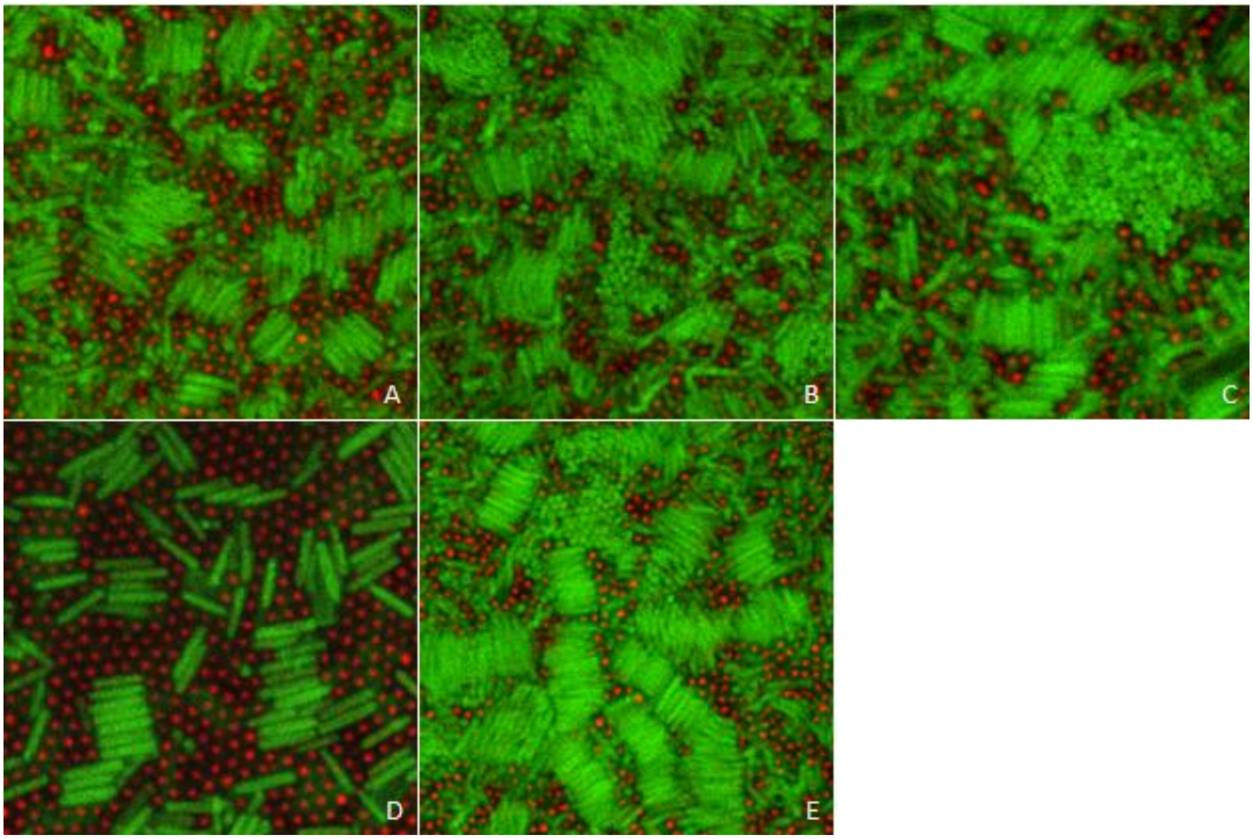


Figure 37. Sample 45 after respectively 1, 3, 7, 7 and 15 days. A was taken in a 40µm thick sedimentation layer at a height of 25µm above the bottom. B was taken in a 33µm thick sedimentation layer at a height of 20µm above the bottom. C and D were taken in a 22µm thick sedimentation layer and C taken at a height of 9µm above the bottom. E was taken in a 40µm thick sedimentation layer at a height of 27µm above the bottom.

Although these images look quite similar, they're all in a different situation. Other than each image being taken at a different time (apart from C and D, which are both taken 7 days after the sample was made) does the thickness of the sedimentation layer differ at each moment. At first this didn't seem too strange because I presume it's possible that the sedimentation layer might shrink a bit over the first week as it becomes denser (although an amount of 18µm over 1 week in a sample that used to be 40µm is questionable), but after 15 days the sedimentation layer was about 40µm again. This probably means the sample was slightly tilted and I took the images at different x-coordinates, this also seems a lot more reasonable as a 18µm difference over 2.5cm, the length of this sample, only requires an angle of about $1/25^{th}$ degree.

Although this difference in thicknesses is not intentional, it produced some interesting results. The images I took in thick sedimentation layers showed a discs region above an isotropic region. The discs layer at 1 day ranged from 23 to 29µm above the bottom, this ranged from 17 to 23µm at 3 days, at 7 days this was from 0 to 14µm. The discs reached the bottom at 7 days, which may explain the sudden structure on the bottom at this moment. At 1 and 3 days the bottom was fully isotropic, without clusters like the ones in figure D. At 15 days the discs layer was much higher again, from 18 to 30µm above the bottom.

The fact that there are such different height scales in the same sample could be very interesting. There doesn't seem to be any apparent demixing in the sample so the ratio rods/spheres is about constant everywhere in the sample. The behavior of the colloids also seems to be about constant everywhere in the sample; figures A, B and C look very similar even though the height scales are very different each time. The behavior of the colloids is therefore independent of the thickness of the sedimentation layer they're in. The sedimentation layer can be related to pressure if we can assume the pressure to be higher the more colloids are above the measuring site. With 'measuring site' I mean anywhere in the sample where one would want to know the pressure. If the behavior of the colloids (i.e. forming discs) is independent of the sedimentation layer thickness, it is independent of pressure and therefore more likely to be just dependent on concentration ratio. However, as beautiful this conclusion may seem, I know it is not true, as nucleation has also been observed in purely rod systems using simulations [7].

From this result I now know how to regulate the height of a discs layer. The discs layer seemed to be always about 10µm below what I called the top of the sedimentation layer. Because the ability of a sample to form discs is likely highly influenced by the concentration ratio I would only have to change the total amount of colloids to change the height at which discs form. This could be useful if I would want to put large discs on the bottom, perhaps the influence of the bottom would make large discs more stable which could turn disc behavior into large scale smectic (or even lamellar) behavior.

4.5.2.3 Sample 47

This sample contains 5% rods and 1% large spheres.

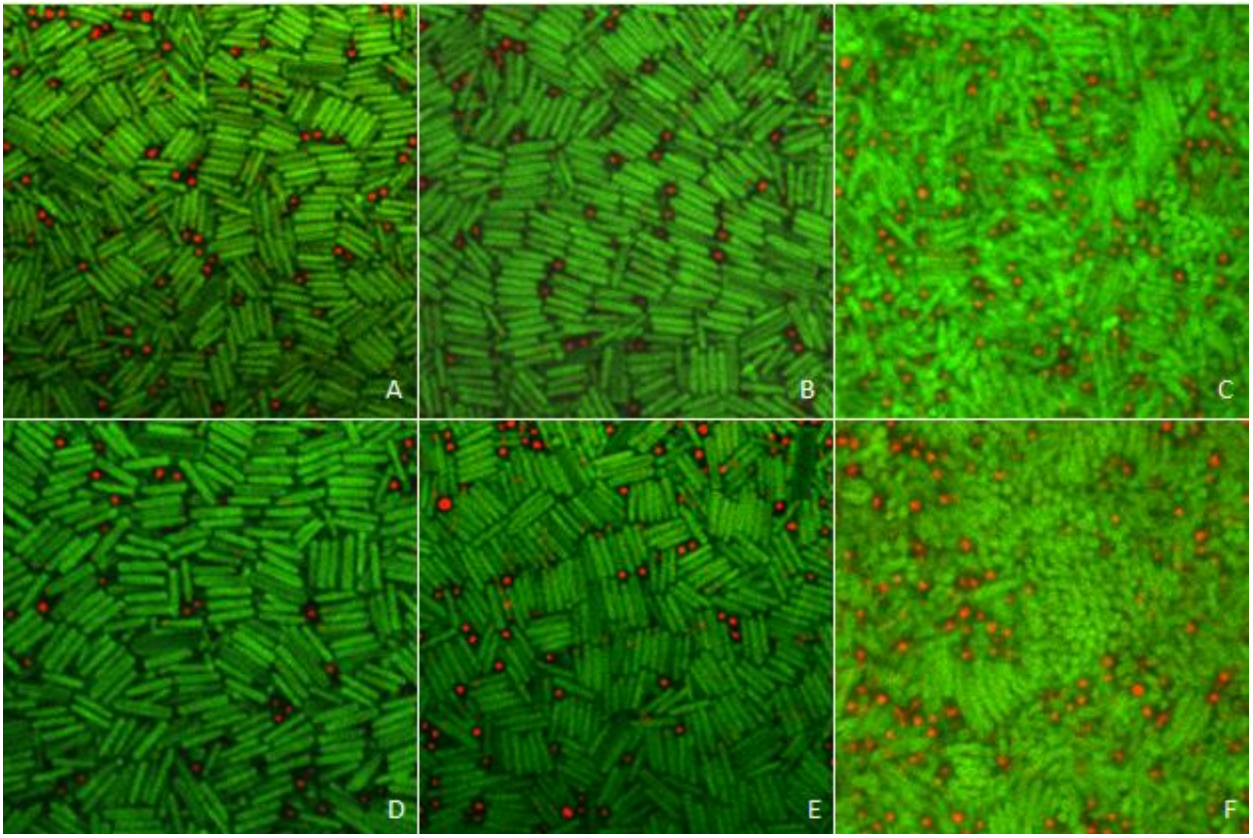


Figure 38. Sample 47 after respectively 1, 3, 7, 7, 15 and 15 days. C is taken at 7µm above the bottom and F is taken at 18µm above the bottom, the others are taken at the bottom.

This sample promised us a large scale smectic bottom. According to the images above this sample did not live up to its expectations. Some rows of aligned rods have formed at the bottom after one day and at later times the rows didn't seem to turn into larger scaled structures. Apart from a couple of rows here and there, the sample was mostly isotropic at each time. The structures in figures B and E are only very local, the rods that lie outside these images are mostly isotropic. At 7 days a small disc showed up (figure C, look for green dots; the normal of the disc lies in the z-direction) and at the 15 day mark some larger discs were visible (figure F).

The consistent disorder at the bottom is not reflected in the thickness of the sedimentation layer, which was very different each time. One day after the sample was made this layer was 19µm thick, at 3 days 15µm, at 7 days 25µm and 29µm thick at the 15 day mark. I'm not sure what to make of this, but the heights seem to be related to the amount of disc in the sample. The discs could also be affected by time, as the 15 day disc is much larger than the 7 day disc and the sedimentation layer thicknesses don't differ very much for these two moments.

4.5.3 Small spheres

4.5.3.1 Sample 49

This sample contains 5% rods and 10% small spheres.

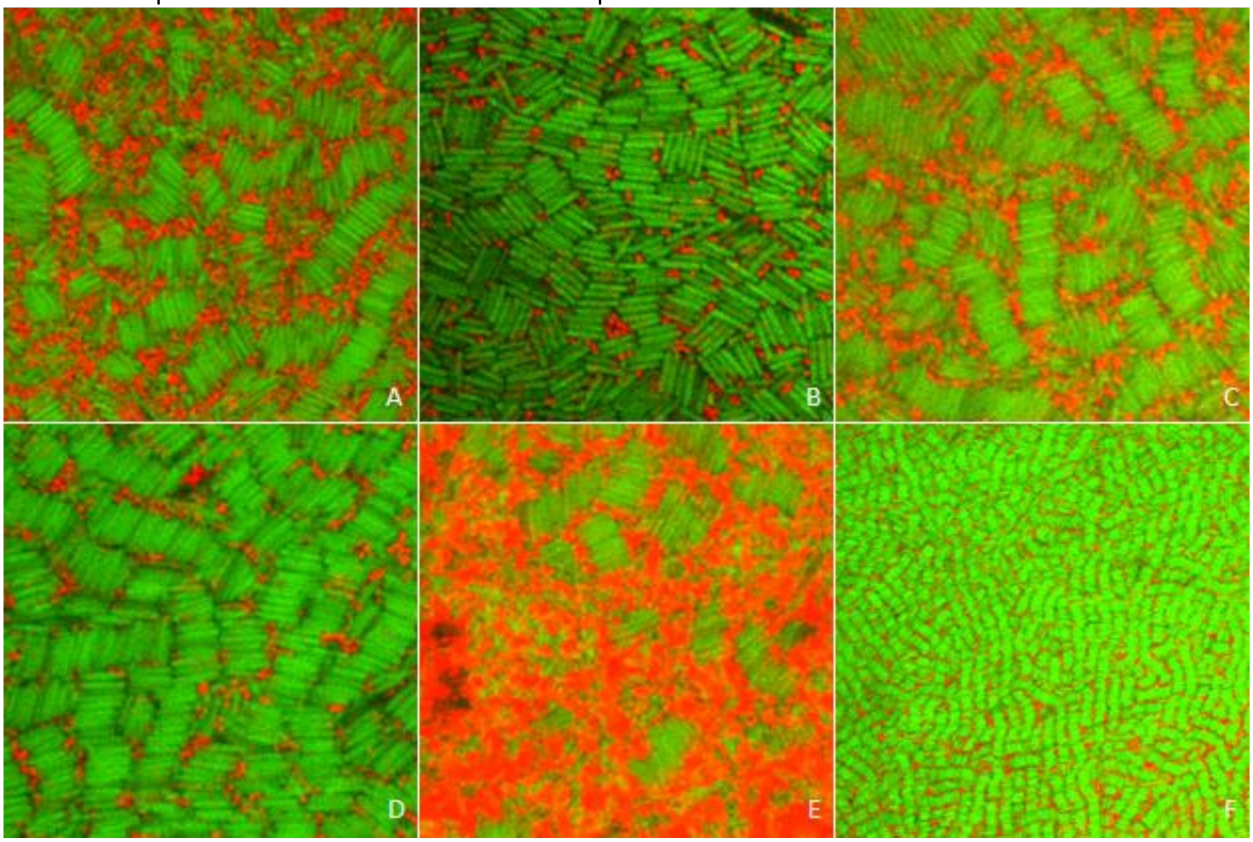


Figure 39. Sample 49 after respectively 1, 3, 3, 7, 15 and 15 days. A is taken at a height of 7µm above the bottom, B is taken at the bottom, C is taken at 11µm above the bottom, D is taken at 3µm above the bottom, E is taken 14µm above the bottom and F is taken at 3µm above the bottom.

As expected there will be discs in this sample. The discs at the 1 day mark lie at heights between the bottom and 11µm above. The top of the discs region (a few micrometers under 11µm) contains the largest discs and are most numerous here (figure A). It seems like the discs region that is usually separated from the bottom by an isotropic region is now very close to the bottom, so the isotropic region is replaced by a region containing small discs. This behavior is generally the same at the 3 day mark but now the bottom itself is also more structured (see figure B). Seven days after the sample was made the discs region was between 0 and 8µm above the bottom and the difference in size of the discs in the top and bottom part of this region is no longer there. The discs region consists mostly of discs that lie on the bottom with one side and therefore most discs are oriented with their normals in the x,y-plane (figure D). At the 15 days mark the discs were found a little higher again, up to 14µm above the bottom; figure E shows the top part of the discs region. Zooming out on the structures shows the real beauty of this sample, as is done in figure F. The structures after 15 days looks quite smectic, or even lamellar as there are spheres between the smectic layers. However, taking a closer look at the structure, as is done in figure D, it is apparent that spheres are not consistently between the smectic layers but in small groups here and there.

The sedimentation layer of samples with small spheres is usually not very easily determined, but the thickness of the rods layer can be determined. The rods layer is about 15μm thick at each time and the sample also becomes increasingly dilute of spheres at about 60μm at each time.

4.5.3.2 Sample 51

This sample contains 5% rods and 7.5% small spheres.

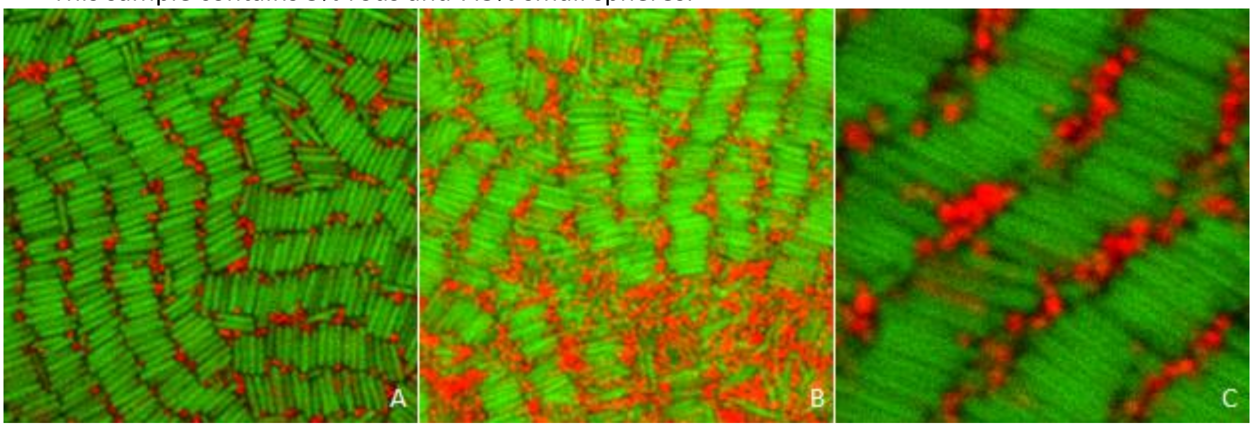


Figure 40. Sample 51 after one day. A is taken at the bottom, B is taken 5μm above the bottom, C is taken about 2μm above the bottom.

The smectic/lamellar structure in this sample ranges over every x-coordinate of the 2.5cm long sample and over about half the possible y-coordinates. There is demixing of rods and spheres near one wall –likely the cause of a small tilt that gives the usual demixing along the z-axis a y-component –and the colloids are isotropic near the other. In the center region the colloids are arranged as can be seen in figure 1. The structure in this sample at this particular moment is what comes closest to a fully lamellar phase that I have found in my research. The structure is present on the bottom (figure A) and is built up to about 5μm (figure B) with relatively very little defects –relative to other samples like sample 49 (p. 51). The structure is most smectic at the bottom, where there are a couple of places without spheres between the smectic layers. Going up to about 2μm we will find the best lamellar structures without too many defects. The structure here consists of smectic layers with 1 or 2 spheres between each layer as can be seen in figure C. Going up even more the structure becomes more defective as can be seen in figure B which is taken near the top of the structured region –at about 6μm and up the colloids are isotropic. The rods layer is about 11μm, which is possibly the thinnest rods layer among all my samples; structured rods take up less space than isotropic rods so a lot of structure leads to a thin rods layer. The spheres layer disappears around 60μm above the bottom.

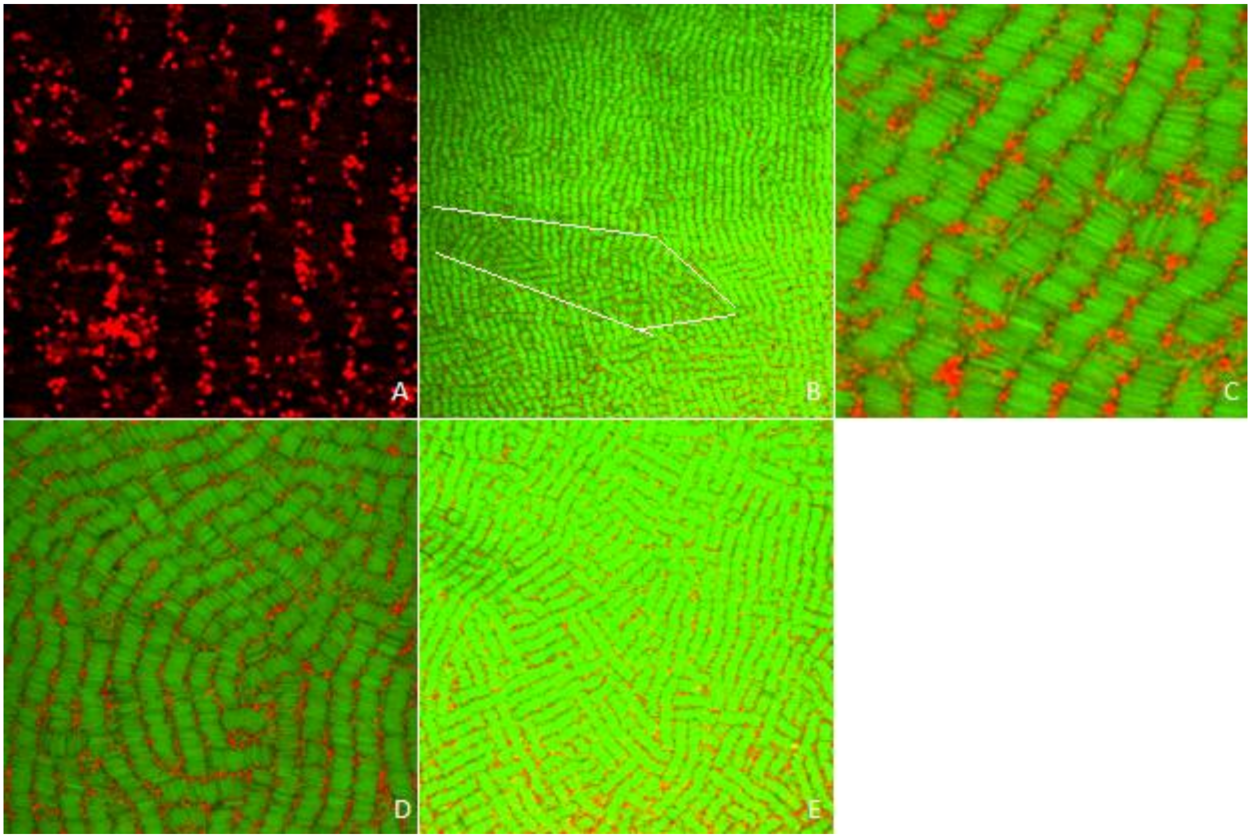


Figure 41. Sample 51 after respectively 3, 3, 7, 15, and 15 days, all are taken a few micrometers above the bottom.

I also looked at the sample 3, 7 and 15 days after it was made, but not much has changed after the first day I looked at it. How little the sample has actually changed can be seen in figure B; each time the confocal microscope scans the sample the dye on the colloids decays a little. This decay lets the colloids appear a little darker on the image as they emit less light. In previous samples I've never found the rods with decayed dye from a different day, possibly because the colloids move around and mix with the nondecayed colloids so they don't stand out anymore. In this sample I did find such patches of decayed dye, as I've accentuated in figure B. This may imply that the structures in this sample are stable –or at least relatively stable in comparison to structures in other samples.

The other images show some other interesting feats: From image 2A one can see how neat a lamellar structure is by just looking at the spheres. The consistency of the rows of spheres show that there are spheres between each of the smectic layers at most places. Figures D and E show that the structure doesn't tend towards a more global orientation; most samples with smectic structures prefer the x-orientation which is probably an influence of the walls. The structure in this sample is not directly connected to a wall as there is demixing of rods and spheres on one side and isotropy on the other side. Figure C shows the consistency of the structure at greater heights (5µm here).

The reason that this sample shows such great structures as soon as 1 day after the sample was made, is probably the same as the prediction I made when discussing sample 45 (pp. 48-49); large discs on the bottom may turn into large smectic or lamellar structures. In fact, I made this prediction in hindsight as I had already seen this sample before discussing sample 45. The definite reason for why this sample shows such beautiful structures I do not know, and could be a possible future research option.

4.5.3.3 Sample 53

This sample contains 5% rods and 0.1% small spheres.

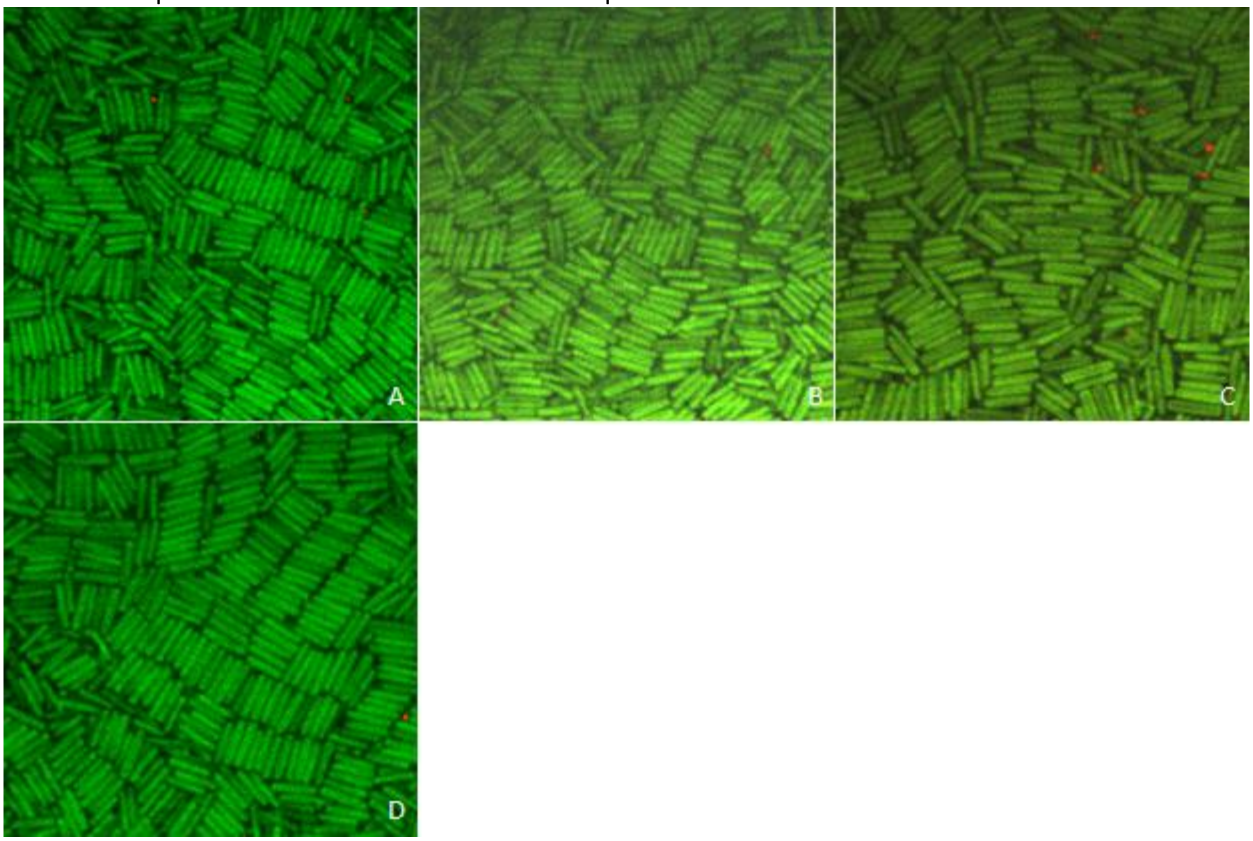


Figure 42. Sample 53 after respectively 1, 3, 7 and 15 days.

After one day the sample was mostly isotropic with some patches of rows like the ones in figure A. The sediment became progressively more structured over the following 2 weeks but a large scale smectic structure was never observed. Although the figures all look similar, the sample was clearly more structured after 15 days than after 1 day –I just don't want to present an image of isotropic rods when there are structures right next to it. The structure on the bottom after 15 days is still recognizable about 3µm above the bottom, at which point the sample becomes isotropic. The sediment is about 16µm thick at each time.

To convince you that there are really spheres present in this sample I tried to include at least one sphere in each image. The spheres are mostly located in the slightly more isotropic parts of the sample which is somewhat visible from figure C. Note that I'm not talking about full isotropy as the rods are almost always part of some kind of (small) cluster. I cannot say whether the spheres get pushed out of the structure formed by the rods, or if the rods are less likely to form structures when there are spheres near. If the spheres were pushed out I would have to find an increased amount of spheres near the edges of the structure and in the latter case I would find more spheres in isotropic parts. Because the edges of the structures are by definition adjacent to isotropic parts I cannot distinguish between the two. In general the amount of spheres is so low that I think either case is of moderate interest.

4.6 Discussion of the second samples

4.6.1 Only-rods samples

The sole purpose of these samples was for comparison with my other samples. Phase behavior of rods, or the kind of structures they form, is already known in theory. Still, rods might behave differently in the kind of samples I make and comparing my samples to the theory without reference samples is difficult.

That my samples don't seem to follow the theory may be stated from the results from the only-rods samples I made. The phase diagram I presented earlier (figure 4) suggests that if I would increase the number of rods in the sample –the density –I would expect to see the crystalline phase. However, the samples with the highest total densities (samples 31, 33 and 35) were mostly isotropic. The sample I found had most structure was sample 37 (p. 44) which contained 7.5% rods. The 2 samples containing 5% rods (pp. 45-46) had less structure than sample 37 but more still than the higher concentrated samples. This result is somewhat disappointing; I cannot control the density in the sediment by just varying the total density. Varying the total density just varies the pressure in the sediment. Apparently the density in the sediment is not a monotonic function of pressure as the density in the sediment decreases for increasing pressure. Obviously the density in the sediment also decreases at sufficiently low total densities so there exists a maximum in the function $\rho_{sed}(p(\rho_{tot}))$, the density in the sediment, for a value of ρ_{tot}, the total density, that lies somewhere between 5 and 7.5%. This function, or the function of pressure, also depends on z, but for simplicity I'll keep this out of consideration and just talk about the bottom for now. It may seem important to determine the pressure for $\rho_{sed}(p)$ but this is not necessary. Constructing a function of density in the sediment can be done experimentally as a function of the total density, leaving the pressure out.

Using my samples for their original purpose (i.e. for comparison) can be done perfectly fine without worrying about theoretical difficulties. Solving this problem, however, may be necessary when constructing phase diagrams and doing theoretical studies of phase behavior of rods and spheres.

4.6.2 Comparison; mutual structure

With the reference samples I can test whether the structures I found in samples containing both rods and spheres are really mutual structures, or just structures of the separate species. The structures that I particularly wanted to test are the discs structures and the smectic bottoms. As I've said before, the other structures I listed are generally just lesser versions of these 2 structures, and what forms them (the small discs for example) assumedly also forms either of these 2 structures (the large discs, in this example). An exception to this is the chamber structure, but this structure doesn't require testing as there is no imaginable way in which this structure can be formed by a single species of colloid.

It may sound strange to test if structures that have already been observed in systems with only one species of colloid are mutual structures. Obviously the smectic bottom and discs are not necessarily mutual structures, but these structures may be influenced by the spheres in the way they form (e.g. spheres can turn smectic into lamellar) and how likely they are to form. This influence of spheres on the structure of rods I will also call mutual structure.

4.6.2.1 Smectic bottoms

Comparing what should have happened in the only-rods samples with the rods/spheres samples that formed smectic bottoms, one would say that the spheres have a clear effect on forming this structure. None of the samples containing just rods formed smectic bottoms while some of the rods/spheres samples did. However, drawing such a conclusion would not be justified, as there are still many variables that were not taken into account. Some rods/spheres samples contained a different total amount of colloids than the only-rods samples because an amount of spheres was added to the 5% of rods in these samples. Another variable would be time; some versions of samples take longer to form structures than others, as was seen in, for example, sample 13 (p. 20). I gave my only-rods samples just 2 weeks to sediment, where I gave my previous samples at least 3 weeks. Similar to the time argument, the sedimentation is likely subject to chance. Dependent on the type of structure –I felt that the disc structure was more consistent in its forming than the smectic bottom structure –structures sometimes just don't form. If the samples would not be subject to chance this would mean the colloids have, at every moment, the ability to completely rearrange themselves throughout the sample. When they find a structure in which their free energy is minimal, the colloids wouldn't want to rearrange themselves as this would cause them to increase their free energy. This means the colloids in a sample will always end up in the structure with the lowest free energy, and this structure is always the same in samples that have the same starting conditions. The fact that I didn't find the smectic bottom structure in samples 47 and 53, whereas their duplicates –samples 13 and 21 –did form this structure, implies the structures in the samples are subject to chance. Another possibility is that the ability of the colloids to rearrange themselves happens on a timescale longer than 2 weeks, meaning that the expected structures may exist, but I just didn't observe them.

4.6.2.2 Discs

The difference between the behavior regarding discs in the only-rods samples and the rods/spheres samples is enormous. Samples 31 and 33, containing 15% rods and 12.5% rods, were especially aimed at being compared to the rods/spheres samples with high amounts of spheres. Because the sedimentation layers in samples with high amounts of colloids are so thick, there is a wide range of pressures and densities present in this layer. This could be the reason the large discs were highly reproducible; the required conditions for forming discs is very likely to be present if the range of conditions is large. The ability to form discs may also be enhanced by the fact that discs don't form at the bottom; the movement of the colloids is less impaired, increasing their ability to rearrange. All of this would make one expect to see large discs form in the only-rods samples with high concentration. The fact that these samples didn't form any structures that are remotely disc-like implies that the spheres have a major effect on the formation of discs in my samples.

I explicitly say 'my samples' because I cannot exclude the possibility that a large disc structure can form in a sample containing an amount of rods that I didn't include in my samples. In fact I'm convinced that this can happen as the nucleation of rods has been observed in simulations [7], which is the same as forming discs.

4.7 Conclusion

Having not one but two species of colloids in a colloidal system enhances the richness of the systems structural behavior, or phase behavior, in multiple ways. Completely new structures can be formed, like the lamellar structure, and the traditional single-species structures are influenced by the other species to alter the conditions under which they form.

Two traditional structures of only-rods systems were observed to have been influenced by spheres. In samples where structures form by the effect of sedimentation on a flat bottom, the smectic phase was observed at the bottom, only when both rods and spheres were present. Samples of only rods have not been observed to form the smectic phase to the same extent. Spheres could therefore be presumed to influence rods in the way that they form smectic structures in conditions in which rods alone cannot. The full magnitude of this influence is not known, as there are other possible reasons the smectic phase did not form in only-rod samples.

Another traditional structure in only-rods systems is the smectic phase formed by nucleation without influence of the bottom, that I called discs throughout this thesis. The formation of such discs was observed in great numbers in samples containing rods together with high amounts of spheres, while there were little to no discs in samples containing only rods. Because of the high reproducibility of the discs in samples with high amounts of spheres and the possibility to exclude variables that were not excludable for structures at the bottom, I can conclude that the spheres have a major influence on the formation of the discs structure.

A completely new structure –a structure that cannot be formed by rods or spheres alone –has also been observed; the lamellar structure. Discs were observed at various heights dependent on the concentration of each colloid. The bottom of the sample provides stability to adjacent colloids; at least some degree of structure was observed in all of the samples at the bottom. If the discs were to form at the bottom, the result might be a very stable disc structure; similar to the smectic bottom structure but with spheres around each disc. Discs, or smectic layers, surrounded by spheres is called a lamellar structure. This combination of events is likely the cause of the lamellar structure to form, as this structure has only been observed at the bottom of samples that were known to form discs.

4.8 Future research

Six months is a short time for doing research, hence many questions have to remain unanswered. The second set of samples I made were aimed at reproducing two types of structures I found from the first set, and to make reference samples so I could be more conclusive about which structures are mutual structures and which aren't. There are a couple of other goals I could have set at that point, or that I can set right now if I had the time:

Finding ways to control the height of the discs: I found discs at different heights in different samples. Usually the discs were higher in samples with a higher total amount of colloids so the height of discs may be related to the total amount of colloids. Being able to control the heights may be useful when trying to put the discs on the bottom, which will then hopefully form the lamellar phase. Having a reliable way to build the lamellar phase would make it easier to study the lamellar phase.

Investigating the lamellar phase; this is probably easier after a way is found to put discs on the bottom. The lamellar phase that formed in sample 51 (pp. 51-52) was quite neat, but still had many defects. Although there were spheres between smectic layers in most places, there were plenty of other places where the rods from smectic layers touched. The spheres didn't seem to fit in too perfectly in the structure so trying spheres of different diameters might result in a neater lamellar structure.

Finding the dependence of pressure and density on the concentration ratios: Everything in the samples I made came down to 2 numbers; the amount of rods and the amount of spheres. If I would be interested in the theory of the phase behavior of rods and spheres it would be useful to be able to determine parameters such as pressure and density.

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