

Colloidal Crystallization in Capillaries and on Fibers

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Abstract

A great deal of research has been devoted to studying the growth of colloidal crystals on substrates, especially for optical applications. This research explores the formation of colloidal crystals inside capillaries and on micron-sized fibers, substrates that have not, until now, been used in this area of research. The capillary coating experiments utilized an evaporative method to coat ethanol and water colloidal solutions inside capillaries of 400 μm in diameter. Interesting results of periodic band formation were observed for the ethanol solutions with particle sizes ranging from 0.1 – 1.1 μm and particle concentrations of 0.1 – 0.4 % solid. In this report, a model is suggested as an explanation for these observations. The fiber coating experiments were conducted using a method of slow withdrawal from a reservoir containing the colloidal solution. The continuous growth of crystals was observed for water solutions with particle sizes ranging from 0.53 – 2.2 μm and particle concentrations of 0.4% solid with withdrawal velocities up to 110 $\mu\text{m/s}$. Some of the crystals formed, however, contained defects such as voids and multilayers.

Introduction

Colloidal crystals are regular crystalline arrays of highly monodisperse spheres of dielectric materials such as silica and polymers.¹ The applications of textured surfaces with controlled periodicity are wide and varied, ranging from data storage to anti-reflective coating³. In addition, colloidal crystals have found prominence in the field of optics. More specifically, the use of colloidal crystals to form “photonic band gap” materials has urged researchers to develop novel robust methods for creating high quality, uniform, and mechanically stable colloidal crystals.¹ Photonic band gap crystals are spatially periodic structures fabricated from materials having different dielectric constants. These materials can influence the propagation of electromagnetic waves in such a way that there exists a bandgap that excludes the passage of photons of a chosen range of frequencies.⁴

Popular techniques for the formation of colloidal crystals include gravity sedimentation, spin coating, vertical deposition, and the flow cell method.^{1,2} All techniques have been performed on planar substrates only. Thus this research is unique with regards to the substrates chosen for investigation – glass cylindrical capillaries and stainless steel fibers. Both types of substrates have curved geometries. To coat the capillaries, the vertical deposition technique is used. The method relies on the balance between ethanol evaporation and particle sedimentation. For a certain particle size, sedimentation is faster than ethanol evaporation, and self-organization does not take place.² We see this taking place in our experiments.

The fiber coating experiments rely on the slow withdrawal technique during which capillary forces drive the colloidal particles to self assemble³. Research has been conducted on coating fibers with complex fluids such as surfactant solutions, mixed surfactant systems, and polymer solutions.^{5,6} There has not been a great deal of investigation into the behavior of colloidal solutions during the coating process. At sufficiently high concentration of particles, the behavior of colloidal solutions is non-Newtonian and more complex to understand.⁶

Most of the factors affecting the crystallization on the fiber and in the capillary are the same. These include concentration of the colloidal solution, size of the particles, and the capillary number. The capillary number is a dimensionless quantity given by $C = \mu U / \gamma$, where μ is the fluid viscosity, γ is the fluid surface tension, and U is the substrate speed for fiber coating experiments or it indicates the evaporation rate for the capillary coating experiments. These factors affect the dynamic contact angle, which is the angle that the fluid makes with the substrate. For the particular problem of crystallization in the capillary, the rate of evaporation is an extremely important factor to consider. The two coating processes are nonetheless separate and distinct, because whereas during capillary coating the evaporation is the dominant factor, during fiber coating, withdrawal velocities are more important.

For the sake of clarity, the fiber coating and capillary coating experiments will be treated separately. In section one, details of the capillary coating experiment, including the results are given, and in section two, the fiber coating experiment is described.

1. Capillary Coating

Experimental

We used charge stabilized surfactant-free polystyrene latex micro spheres (Interfacial Dynamics Corp.) for all of our experiments. For the experiments with water solutions the particles were used directly, and diluted to specific concentrations using distilled water. Some experiments were conducted with surfactants in the colloids. The surfactant used was Sodium Dodecyl Sulfate, SDS (ICN Biomedicals Inc.). The concentration of SDS in the colloid was 0.24 wt%, which is the critical micelle concentration for SDS. For ethanol solutions, the latex was centrifuged and the supernatant liquid was removed, equivalent portions of ethanol (95%, Pharmco Products Inc.) were added and diluted to specific concentrations (0.1 – 0.4% solid). Precision capillary tubes (Drummond Scientific Co.) were used directly and also used after soaking in a Sulfuric Acid/ Hydrogen peroxide cleaning solution. The internal diameter of the capillary was 400 μm and the height was 75 mm.

Two experimental set-ups were used as shown in figure 1. In the first, we simply filled the capillary to about 60% of its length with the colloid and placed it vertically on a Petri dish to dry. The capillary was held almost perfectly vertical with a wire frame. In the second set-up, the capillary was placed in a bottle with diameter of approximately 27 mm, containing between 5-6 ml of colloid. The liquid was evaporated from both inside the capillary and in the bottle. Once drying was complete, the capillaries were viewed with an optical microscope, the Leica DM IRB.

Figure 1: Experimental set-up

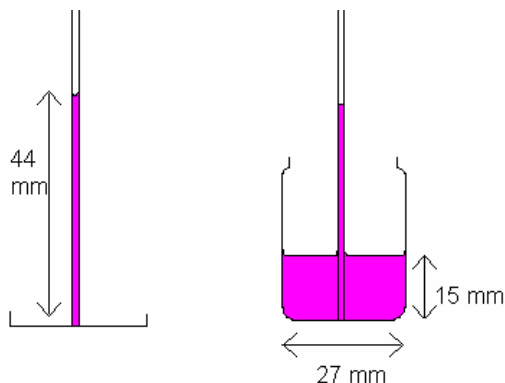
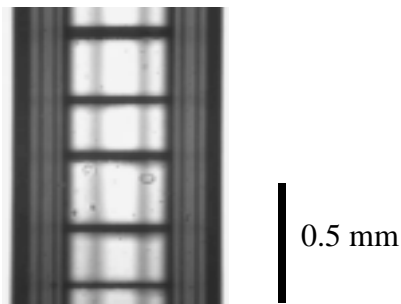


Figure 2: Magnified image of a region of the capillary showing the periodic bands of colloidal particles of diameter $1.1 \mu\text{m}$. (The bands are the horizontal black lines.)



Results

Table 1 summarizes the observations made during these experiments. Of all the systems studied, the one that showed the most promise for deposition of a colloidal crystal was the ethanol solution with a reservoir. Thus, further investigations were performed on this system. The ethanol solutions yielded some unexpected results – the formation of periodic bands of colloidal particles (Figure 2 above).

Repeated trials of the experiments were performed to determine the reproducibility of these observations. It was seen that some of the systems resulted in fairly reproducible patterns while others did not. For the conditions that led to band formation, bands were always observed regardless of how often the experiment was repeated. However, the band spacing and band widths sometimes varied from trial to trial. It is uncertain if the irregularities were experimental artifacts or the system was unstable and thus not reproducible. More trials are needed to make a more definitive statement concerning the reproducibility.

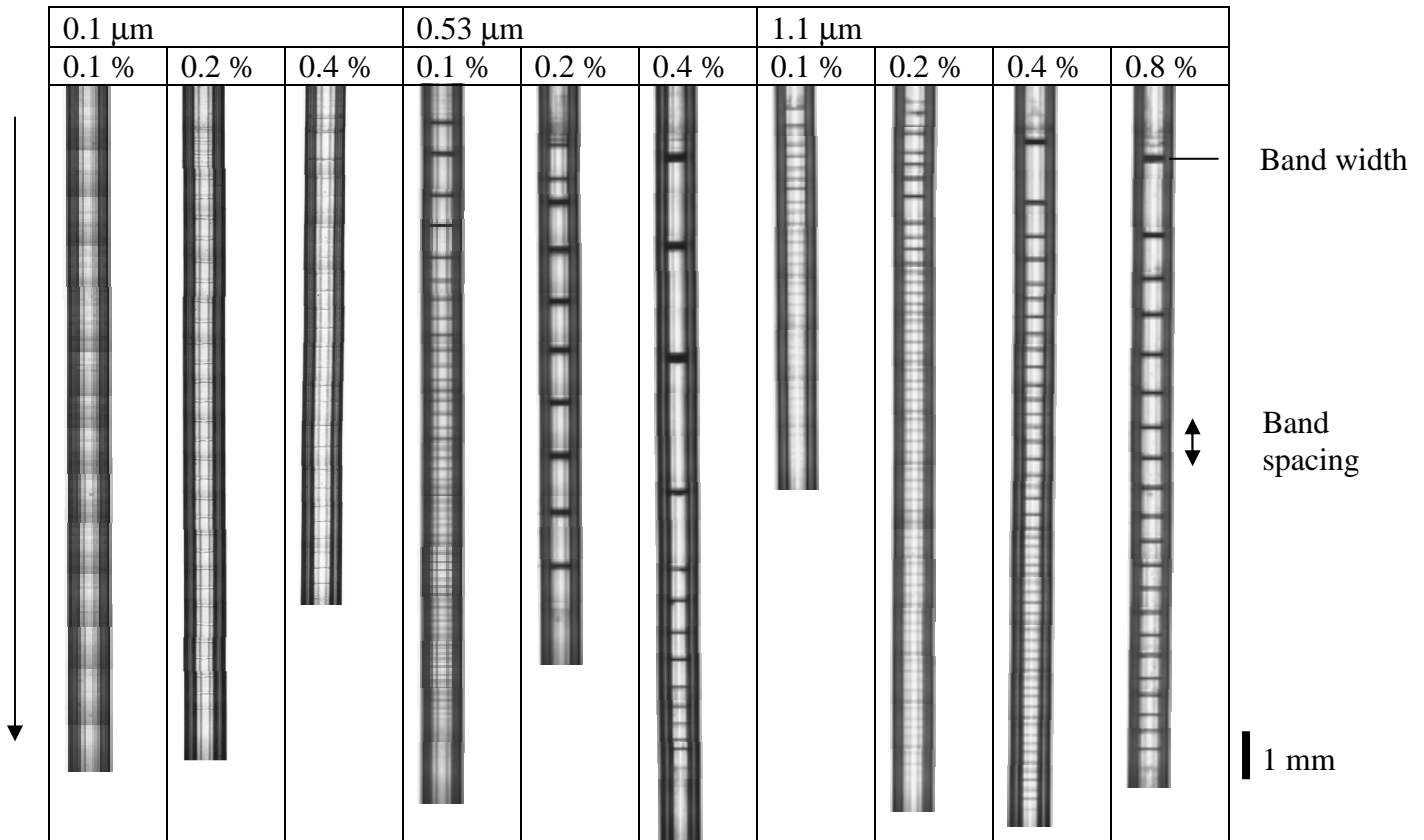
Three concentrations were investigated, 0.1%, 0.2%, 0.4% solid for the four particle sizes under study – $0.1 \mu\text{m}$, $0.53 \mu\text{m}$, $1.1 \mu\text{m}$, and $2.2 \mu\text{m}$ (Figure 3). The temperature was maintained at $65 \text{ }^\circ\text{C}$ by placing the system in a standard convection oven. For these parameters, bands were observed for all particle sizes except for the $2.2 \mu\text{m}$ sized particles. This may be because in the time frame for the bands to form, sedimentation is faster than evaporation. Only one system was investigated at room temperature but no bands or crystallization of any kind was observed. Furthermore, since the drying process required approximately one week to complete, no further experiments with a reservoir were conducted at room temperature. One system was also studied in real time, meaning that the conditions in the oven were simulated in a makeshift oven so a movie could be made of the band formation. The average temperature was $70 \text{ }^\circ\text{C}$.

To determine the effect of capillary radius on the band formation, a second capillary was used with an internal diameter of $150 \mu\text{m}$. Particles of diameter $0.53 \mu\text{m}$ were used and the concentrations ranged from 0.025 % - 0.4 % solid. The temperature was maintained at $65 \text{ }^\circ\text{C}$, though one trial was performed at $85 \text{ }^\circ\text{C}$. None of these capillaries showed band patterns upon drying.

Table 1: Summary of results

Colloid	Crystallization inside capillary?
Without reservoir	
Water	None
SDS	Sparse random particle deposition
Ethanol	Sparse random particle deposition
With reservoir	
Water	None
SDS	Sparse random particle deposition
Ethanol	Periodic bands of densely deposited particles

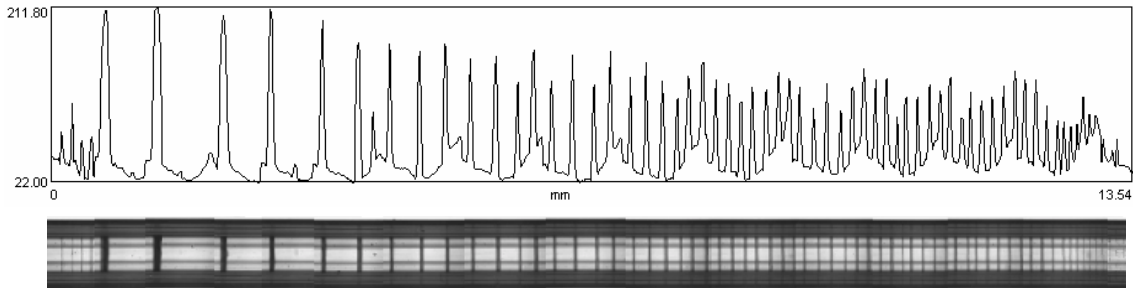
Figure 3: Microscope images of the regions of the capillaries with band patterns for the particle sizes and concentrations shown. The arrow to the left of the figure shows the direction of the meniscus during drying (the bands are the horizontal black lines).



For all the systems that resulted in the band patterns (Table 2), the one fairly consistent characteristic is that as you move down the capillary in the direction of the meniscus during evaporation, the band spacing appears to decrease. With changes in concentration or particle size, the trends are difficult to rationalize or explain. More investigations are needed to understand why the spacing and band widths differ.

In an effort to obtain as much information about the patterns that we have been observing in the capillaries, we used software (Scion Image) to plot the intensity of the pixel of the capillary image versus the distance along the length of the capillary. Thus we obtained a graph from which we will be able to extract information like the band spacing and the change in intensity of each individual band (Figure 4). The peaks in the plot indicate the presence of the band, where the darker, thicker bands are more intense.

Figure 4: Plot of intensity of the pixel versus the distance in mm along the capillary (the capillary used to obtain this plot is shown below the plot).



Proposed model

Movies made on the band formation were analyzed and it was observed that the motion of the contact line can be decomposed into a few major (and periodic) steps. It appears from current observations that the contact line first sticks at a certain height along the length of the capillary, and then the contact line brightens leading us to assume that particles are being deposited on the glass at this point. During this time, the contact angle appears to decrease in magnitude, and finally the contact line slips to a new height along the capillary length.

An explanation of this phenomenon can be split into two major parts, the sticking of the contact line and the slipping of the contact line to a new height. Let us first examine the sticking of the contact line (Figure 5). We assume that the contact line is pinned during this part of the motion. Contact line pinning is not new behavior, as others have observed it especially during the drying of water droplets.^{7,8} The reasons for the pinning of the contact line are not known for certain. It can be conjectured that the particles near the contact line get stuck on the glass in the part of the meniscus where the thickness of the film is close to the diameter of the particle. All this time there is the evaporation taking place at the meniscus. As evaporation occurs there is a movement of solution towards the contact line, this movement brings particles to this region of the meniscus. The particles self-assemble due to capillary pressure. This is because the fluid film near the particles is deformed and curves in the small regions near the particles. The pressure in the fluid (P_{liquid}) is less than the atmospheric pressure (P_{gas}). The two pressures are related by the Laplace equation

$$P_{gas} = P_{liquid} + 2\gamma/a,$$

where γ is the surface tension of the fluid and a is the radius of curvature of the interface. The term a is of the order of the radius of the particles meaning that there is a huge “negative pressure” in the fluid and the particles are forced together.

The second part of this phenomenon is the slipping motion of the contact line. To understand why this may be occurring we need to look at the entire system (Figure 6). There is evaporation occurring inside the capillary as mentioned above, but we also have evaporation occurring in the reservoir. As the fluid evaporates, the height of solution in the reservoir decreases. The height of fluid in the reservoir determines the height of fluid in the capillary. So it should be expected that if the height of fluid in the reservoir decreases the height of fluid in the capillary should also decrease. However, as we mentioned above, the contact line is pinned so the height cannot decrease. On the contrary, it increases relative to the height in the reservoir. What we observe is the decrease in magnitude of the contact angle. This angle appears to decrease until some value when contact line slips. This behavior is confirmed by the Jurin law

$$h_{eq} = \frac{2\gamma \cos \theta(t)}{\rho g a}$$

where h_{eq} is the height of fluid in the capillary above the height of fluid in the reservoir, γ is the surface tension, $\theta(t)$ is the contact angle which varies as a function of time, ρ is the fluid density, g is the acceleration due to gravity, and a is the capillary diameter. According to the equation, as the height of fluid increases, the angle decreases; this is consistent with our observations. We do not yet have a consistent explanation for why the contact line slips or why the wavelength of the bands seems to decrease with time

Figure 5: Drawing of the contact line during “sticking”, when the line is pinned and evaporation occurs

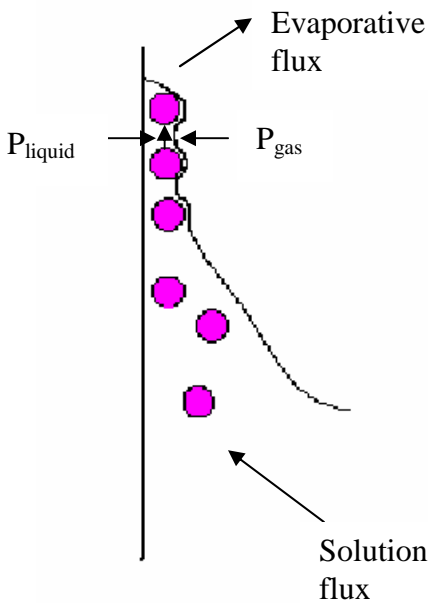
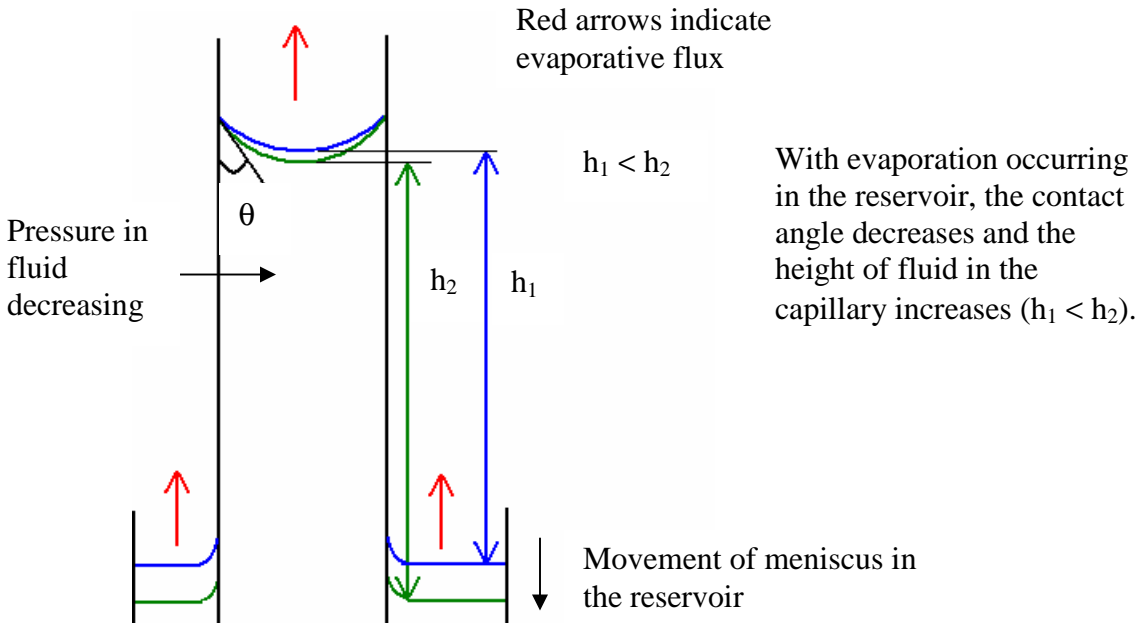


Figure 6: Drawing of the capillary in a reservoir containing the colloidal solution

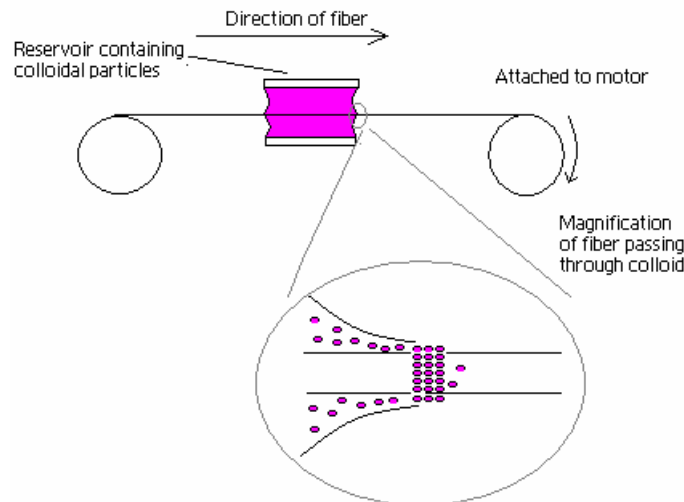


Section 2: Fiber coating

Experimental

In this experiment, we used a stainless-steel fiber (MWS Wire Industries) with a diameter of $80 \mu\text{m}$. The fiber was not treated except by blowing filtered air on it to remove any dust particles. A small glass reservoir with an internal diameter 4 mm and length of 13 mm was used. The reservoir contained water colloidal solutions prepared as described in section one. The experiment was set-up on the optical microscope so that the formation of the crystals as the fiber moves out of the reservoir was visible. Fluorescence microscopy was used to image the formation of the crystals. The fiber was withdrawn using a motor controlled by the computer. Note that the fiber was withdrawn horizontally so no effects of gravity were expected (Figure 7).

Figure 7: Drawing of the apparatus used in fiber withdrawal



Results

Initial results show that for a small range of velocities, given the conditions studied, it is possible to obtain crystallization on the fiber. Figure 8A shows that crystallization is possible for small size particles such as $0.53\ \mu\text{m}$ in diameter. $111\ \mu\text{m/s}$ is the upper limit for the withdrawal velocity; above this speed, crystallization is not possible as shown in Figure 8B. Above a certain critical speed, in this case $111\ \mu\text{m/s}$, the fiber is moving faster than the particles could align themselves at the contact line. In Figure 8B, the bright region is a large aggregation of particles that occasionally breaks apart onto the fiber.

Figure 8: Images of fiber coating using fluorescence microscopy. Particle size = $0.53\ \mu\text{m}$, concentration = 0.4% solid

A: speed = $111\ \mu\text{m/s}$

B: speed = $332\ \mu\text{m/s}$

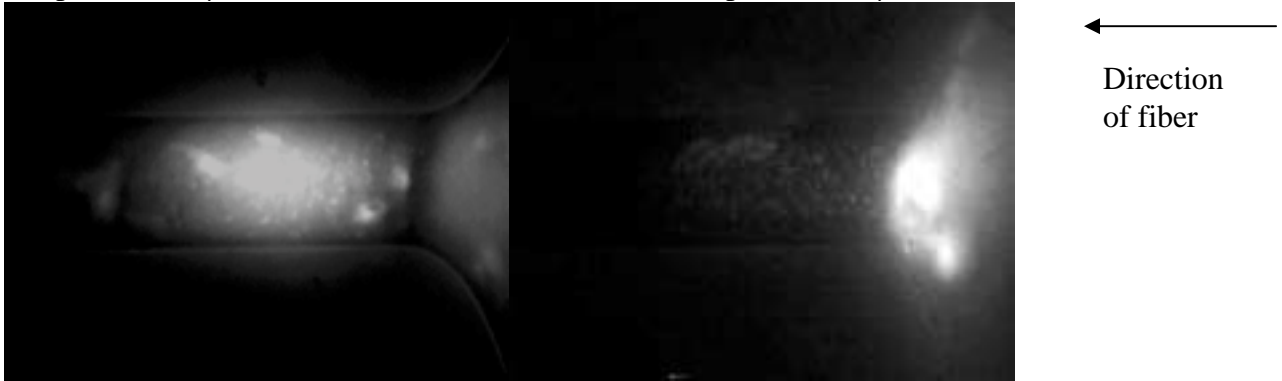
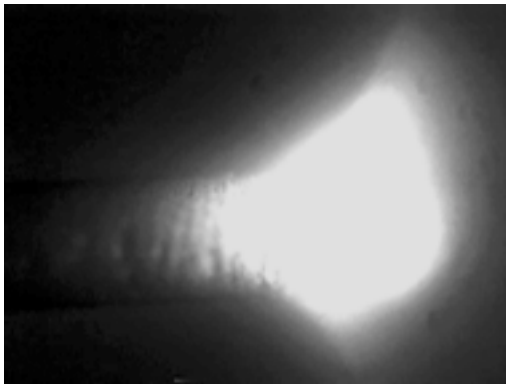


Figure 9: Images of fiber coating using fluorescence microscopy. Particle size = $1.1\ \mu\text{m}$, concentration = 0.4% solid, speed = $111\ \mu\text{m/s}$

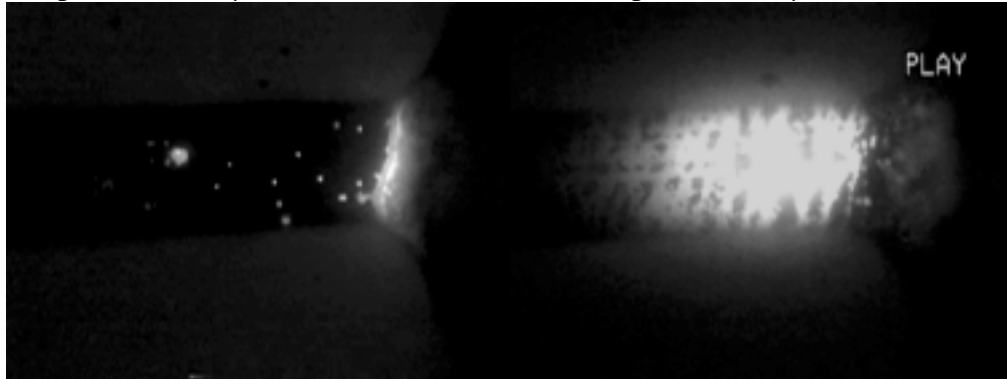


In this figure there are some bands visible but this is most likely due to slight vibrations during the movement of the fiber. This shows us clearly that a controlled environment is necessary for the formation of a uniform crystal.

Figure 10: Images of fiber coating using fluorescence microscopy. Particle size = $2.2\ \mu\text{m}$, concentration = 0.4% solid, speed = $111\ \mu\text{m/s}$

A: speed = $0.553\ \mu\text{m/s}$

B: speed = $1.11\ \mu\text{m/s}$



←
Direction
of fiber

C: concentration = 0.1%, speed = $0.553\ \mu\text{m/s}$



In figure 10A, particles begin to line up at the contact line; this nucleation process appears to be necessary before crystallization occurs. Figure 10B shows that sometimes the crystal formed contains many defects. Figure 10C shows that at lower concentrations, crystallization requires slower speeds; in this case only partial crystallization is possible.

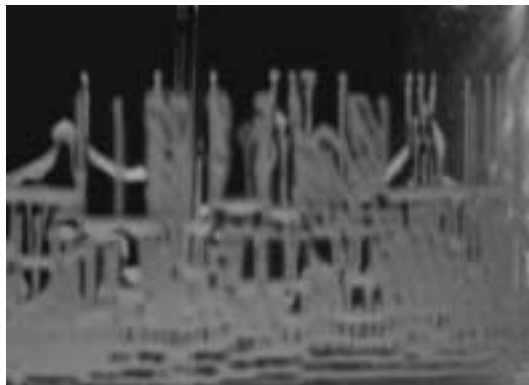
Conclusions

During this summer I worked on two related topics: capillary coating and fiber coating with colloidal crystals. In the introduction I mentioned that all current techniques used to coat with colloidal crystals have been performed on planar substrates, these experiments are unique in the substrates chosen. Both types of substrates have curved geometries: glass cylindrical capillaries and stainless steel fibers. The objective of this research was to monitor the conditions necessary to continuously coat with colloidal crystals the inside of the glass capillary and the outside of the fiber.

The conditions that were manipulated did not result in the continuous coating of the capillary. However, ethanol solutions did result in bands of deposited particles. We proposed a model that can account for these observations. Essentially we think the bands form due to a pinning of the contact line and capillary pressure forcing the particles to pack in a crystalline formation, and the movement of the meniscus of the reservoir controlling the slipping of the line. There is still a great deal of work to do in understanding the band formation, and thus the continuous coating by colloidal crystals. One interesting aspect of the capillary coating experiments that was not discussed in this report is the reservoir. It was not mentioned but the bottles used were also coated and revealed some very interesting patterns – there were the horizontal bands, as well as some

vertical bands. In particular for the colloidal solutions containing SDS, there were also some interesting designs combining vertical and horizontal patterns.

Figure 11: Image of the patterns formed on a bottle during the drying of a SDS solution containing 0.2% 1.1 μm particles



At this point in the fiber coating research, we have only looked at changes in velocity, concentration and particle size. The length scales and structures of the crystals have not yet been investigated. For the concentrations and particle sizes investigated, crystallization was observed by manipulating the withdrawal velocity. The experiments also revealed that for this system evaporation is not as important a factor as the withdrawal velocity. It will be interesting in future studies to determine the relative importance of these two factors.

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