

Self-assembly of Drying Colloidal Suspensions at Low Capillary Number

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Surface coating technologies used nowadays to fabricate nano-scale patterning is a main issue to investigate. To make structured patterns, people use different methods: from the top-down point of view, photolithography and electron-beam lithography are well-developed. However, the parallelization and 2-D limitations are challenges for the next generation. From the bottom-up point of view, self-assembly by evaporation is one of the promising ideas to fabricate nano-scale patterns [1-3]. Droplet drying has been widely investigated in fundamental studies [4-5] and for various applications, like biochemical ones [6]. Despite the simplicity of this geometry, its physical description remains quite complicated. Indeed the drying of a droplet is a non stationary phenomenon since its volume decreases and the non volatile solute concentration increases. In dip-coating configurations [7], also widely used in industrial coating processes, the concentration of the liquid bath remains constant so that a stationary phenomenon can be observed. Moreover, it offers a new experimental parameter that is the velocity at which the plate is withdrawn from the bath. This configuration can then help to better describe and control the different phenomena that are exhibited in patterning.

In our study, a dip-coating-liked setup was constructed. The benefits compare to spin coating and droplets drying are 1. to control several parameters “independently” (contact line velocity, evaporation rate, bulk concentration) 2. to get a steady regime. At high speed, the viscous force dominates; the coating forms a continuous layer and the thickness is proportional to the speed to the power 2/3 (Landau-Levich regime [7]). At low speed (low capillary number), stick-slip motion and stripe patterns are obtained. This is mainly due to evaporation and convective self-assembling process. In this paper, we focus on low capillary number [$<10^{-6}$]. We use silica suspension in water. Based on our previous results [8-9], we studied the pinning force and the pattern periodicity by systematically varying several parameters: the receding contact line velocity, particle concentration, and pH of the solution. Results show that there is a power law governing the pinning force; the electrical surface charge changes the deposition morphologies significantly, but not the pinning force.

Experimental setup:

Unlike in classical dip-coating method where a substrate is withdrawn from a reservoir which contains coating materials we do the opposite way —i.e. we pump out the solution from the reservoir and fix the position of the substrate. Figure 1 shows the main design of our experimental setup: a sandwich device made of two paralleled glass plates separated by 1mm spacer is vertically immersed into a reservoir which contains the colloidal suspensions. Due to the 1mm-thin gap, there is a spontaneous capillary rise. By pumping out the solution, the contact line velocity has been varied from 0.5 $\mu\text{m/s}$ to 20 $\mu\text{m/s}$. The planar dimensions of the reservoir are 3.06 cm x 8.52 cm. This is sufficient for the reservoir to be assumed infinite. An air flow (0.77m/s-1m/s) is controlled by a fan. The whole system is put into a closed box thermally insulated where the temperature and humidity are controlled by a PID system. Temperature can be varied from 5°C to 70°C, and humidity from 10% to 80%. By adjusting the temperature, humidity and the air flow speed, we can control the evaporation rate in the range 0.01—3.2 $\mu\text{m/s}$.

We used commercial suspensions of silica particles in water (Klebosol from AZmaterials). Particle size is 92nm (Std=9nm) measured by dynamic light scattering. To prepare the desired concentration we use pure water to dilute the initial solution. A pH 2 buffer was prepared by diluting Nitric Acid (sigma-aldrich 438073) in pure water; while Acetic Acid (sigma-aldrich 320099) was used for pH4.

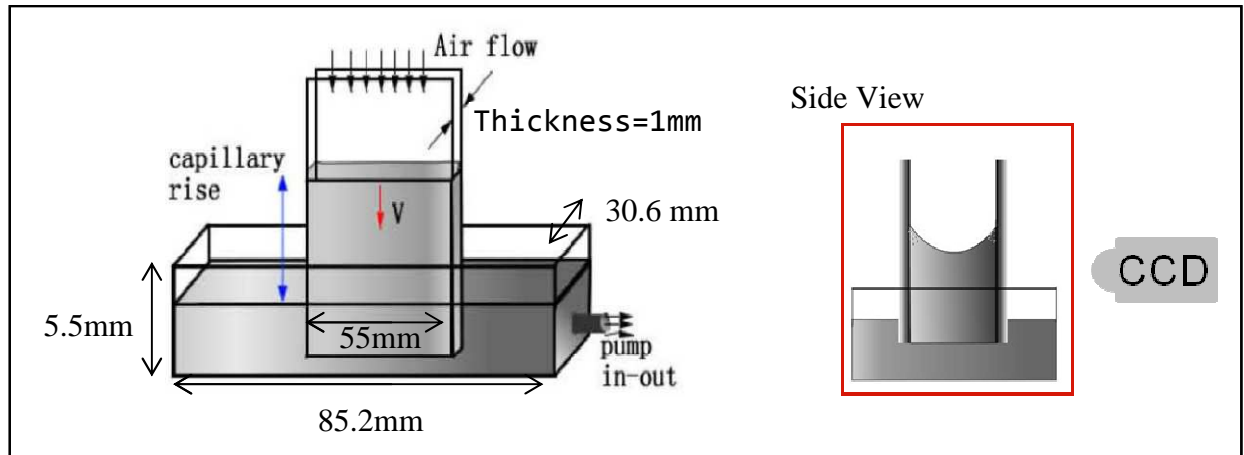


Fig. 1. Scheme of the experimental setup.

Glass plates are cleaned by “Piranha” solution for 20min then dried by nitrogen flow. At the beginning of the experiment, the receding contact angle is 10° - 15° degree due to contamination by the environment. We record the movement of the contact line during all the experiment by a CCD camera (AVT Marlin F131B) with resolution 1280 x 1024 pixel. Images are analyzed by Igor software. The dried deposits are characterized by optical profilometry.

Results and Discussion

1. Pinning force measurement

For very low velocities, a strong stick-slip motion of the contact line is observed. An example of the contact line displacement versus time is shown in Figure 2 (red line) where a periodic movement can be observed. What we define as the stick motion is the period during which the velocity is much smaller than the average velocity (blue arrows); the slip motion is the period during which the velocity is much larger than the average velocity (black arrows). The velocity shown by a green dash line is considered as the equilibrium position that would be obtained for pure water. We measure the maximum pinning force by using the deviation of the contact line from the equilibrium position, just before unpinning occurs: $F_p = \frac{1}{2} \rho g e \Delta h$, where ρ is the suspension density, g is gravity, e is the distance between the two glass plates. In previous studies performed at pH 9 with 76nm silica particles [8-9], the following empirical law has been obtained for the pinning force :

$$\frac{F_p}{\gamma} = 1.4 \frac{\Phi \times V_{ev}}{V} \quad (1)$$

where γ is the surface tension of water, Φ the solute volume fraction, V_{ev} the evaporation rate and V the contact line velocity.

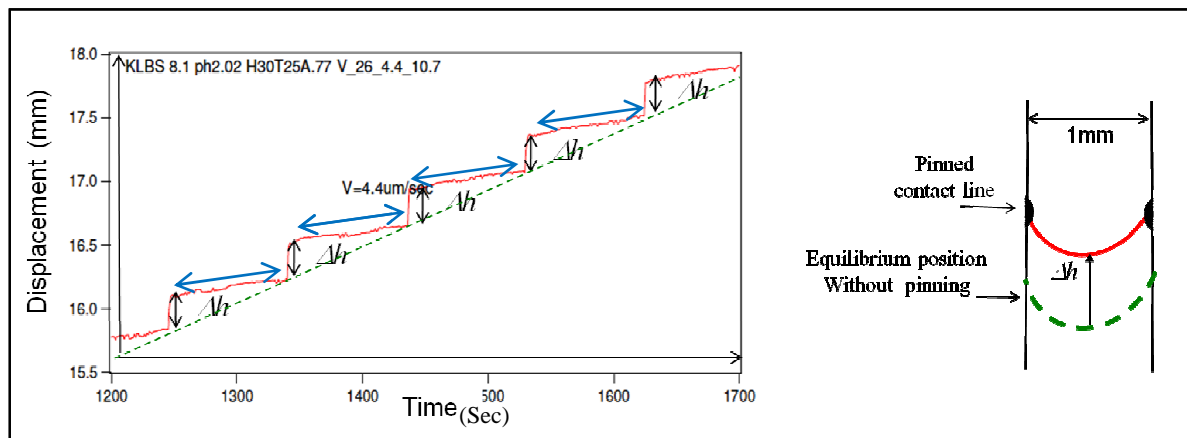


Fig. 2. Definition of stick-slip and pinning force

2. pH effect on pinning force

To study the influence of the pH value, we change it from pH1 to pH9. The electrophoresis versus the pH value is shown in the inset in figure 3. Despite the clear effect of pH on electrophoresis mobility, the pinning force does not depend on the pH and all the points gather around the same master curve shown by the solid black line, which represents parameters relation in Eq.(1).

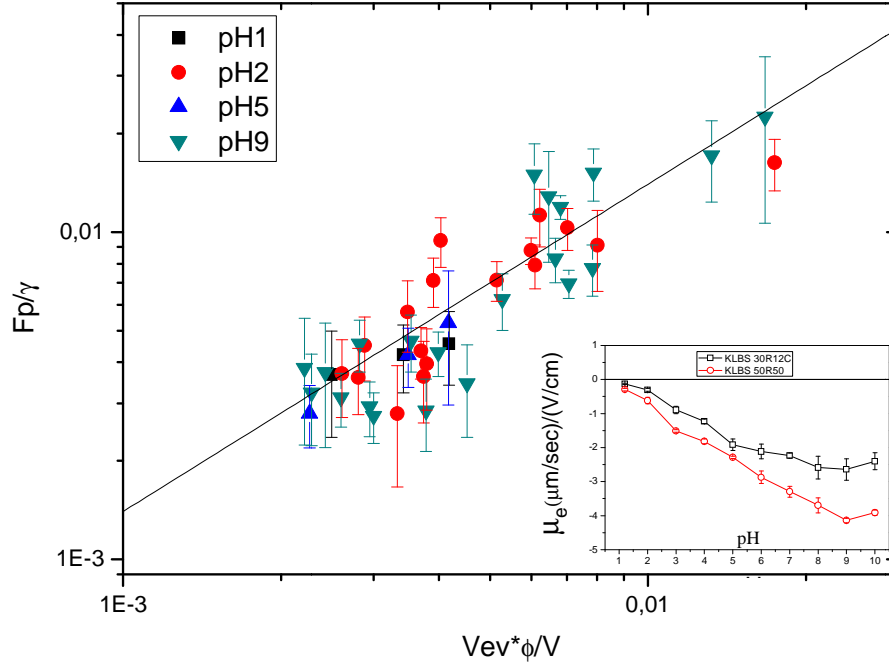


Fig. 3. Scaled pinning force as a function of the velocity normalized by evaporation rate and volume fraction. Inset figure is the electrophoresis mobility of the colloidal suspension versus the pH value.

3. pH effect on morphologies

To control the coating morphology is one of our purposes. While the pH does not modify the pinning force, it can affect the deposit morphology significantly. The two following images of the deposition of silica colloidal suspensions have been obtained with the same receding velocity, evaporation rate and particle size [Fig.4.]. The left image is at pH9 and the right one is at pH2. As can be seen, for pH9 the cross section of the deposit shown below the 3D image has smoother contour, longer wave length, and quite symmetric shape. For pH2, the deposit is much sharper at one side; which may suggest an important influence of the pH on the formation of the deposit.

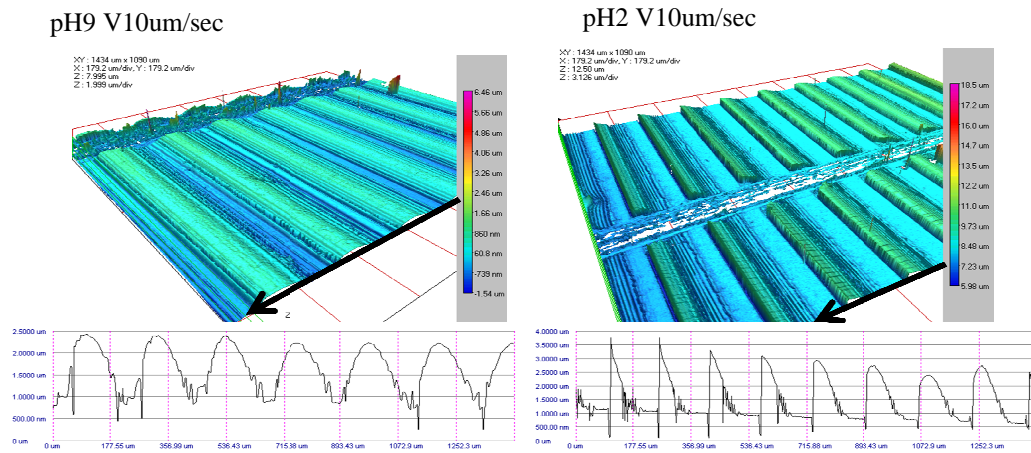


Fig.4. 3D images obtained from profilometer measurement of the colloidal depositions under different pH values. The lower images are the cross section contour line of the morphologies.

In figure 5 we plot the wavelength versus the normalized velocity. The wavelengths obtained with high pH are always larger than the ones obtained with small pH.

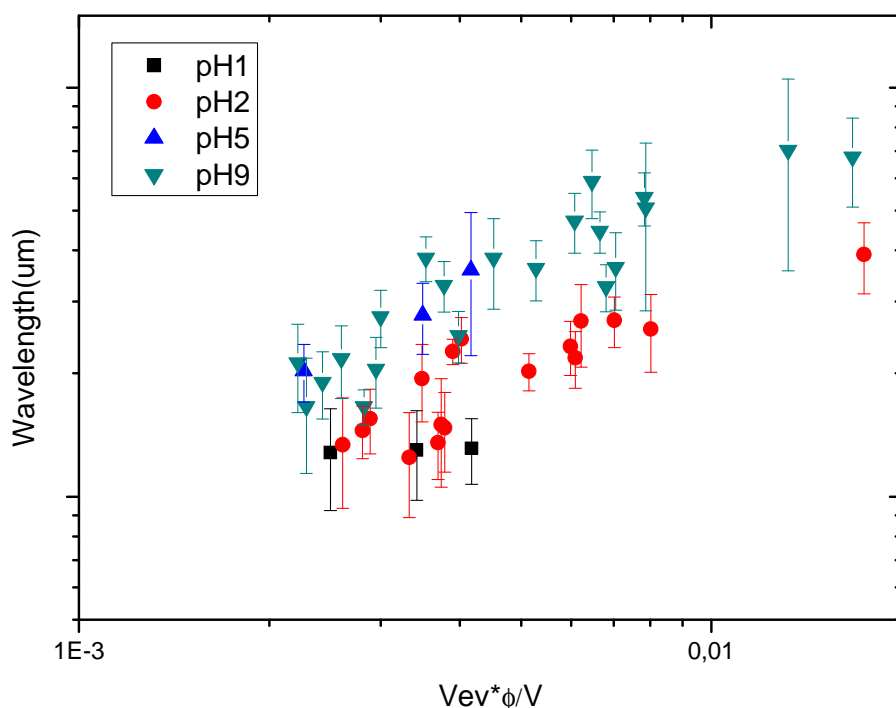


Fig. 5. Wave length of colloidal deposit under different pH values. Particle diameter is 92nm.

Conclusions

For low capillary numbers, we have studied the stick-slip motion of nano colloidal systems when drying drives convective self-assembly. The results show that with different pH values, we get the same pinning force but different wavelength and morphologies. These preliminary results ask for deeper investigation of the formation of the deposit.

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