# Scaling properties of deposition induced by evaporation

## at a moving contact line

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## Introduction

Many coating processes involve the drying of a suspension or a solution. Though many studies have been devoted to the design of controlled patterned deposits [1,2], a full understanding of the dominant phenomena is lacking so far, as the process is governed by the coupling between hydrodynamics, heat and mass transfer, and physicochemical properties of the solution and substrate. Using an experimental set-up where contact line velocity and evaporation rate can be independently controlled, we analysed the different regimes obtained for low Capillary numbers.

## **Experimental**

Two different fluids have been compared. The first one is a colloidal suspension of silica spheres of radius 37 nm ( $\pm 2$  nm) (KLEBOSOL, AZ Electronic Materials). The second system is a polymer solution of polyacrylamide (PAAm). For the polymer solution, two different molar masses have been used, Mw ~ 22 kg/mol (Sigma-Aldrich) and Mw ~ 5000-6000 kg/mol (Biovalley). The solvent is water for the two systems, and experiments were performed with a solute volume fraction  $\Phi$  varying from 0.14% to 4.9%.

A capillary rise is achieved between two glass plates separated by a 1mm gap. The plates are partially immersed in a reservoir filled with the colloidal suspension or polymer solution. The schematic setup is represented in Figure 1. The average velocity of the contact line V can be precisely controlled by pumping out the liquid from the reservoir thanks to a push-pull syringe. The velocity V can be varied from 0.2  $\mu$ m/s to 2 mm/s. The evaporation flow rate is imposed thanks to a fan and a channel blowing a vertical air flow between the two plates. All the set up is embedded in a large box (not drawn in Figure 1) whose temperature and humidity are carefully controlled. The evaporation rate v<sub>ev</sub> is about 0.3  $\mu$ m/s in the results presented here. The influence of the evaporation flux is studied in a forthcoming paper [4].

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The position of the contact line is measured during the experiment by a CCD camera. After complete drying, the deposit is analyzed by scanning electron microscopy (SEM, JEOL JSM-5200) or by an optical profilometer (Fogale Microsurf 3D).



Figure 1: Scheme of the experimental setup



Figure 2: Optical profile image, V=30µm/s Colloidal suspension, mass fraction=10%. (the line in the middle of the plate has been made with a steel needle, to get the substrate basic line)

### Stick/slip regime

For colloidal suspension, when the reservoir pumping rate is very low, a periodic deposition is achieved with typical wavelength ranging from 50µm to 1 mm depending on the experimental conditions. An illustration of this periodic regime is given in Figure 2. In this regime the contact line position as a function of time roughly follows the position of the reservoir, but exhibits small periodic deviations around the linear imposed variation, due to an interaction between the contact line and the deposit that is formed on the glass substrate. The pinning force can be estimated from the deviation of the contact line compared to the case of pure water [3]. In a previous communication, we report a correlation of the maximum pinning force f<sub>max</sub>, measured in situ by image analysis, with the tilt of the deposit, measured a posteriori by AFM [3]. This allowed us to conclude that the pinning force is due to the geometry of the patterns. In this paper, the experimental conditions are varied systematically and we focus on the amplitude f<sub>max</sub> of the pinning force. This amplitude is defined as the value of the pinning force just before the unpinning occurs. Figure 3 shows the results obtained with different particles concentration. The pinning force decreases when increasing the velocity and it increases when increasing the concentration. An empirical scaling is found, shown in insert in Figure 3. The amplitude of the pinning force  $f_{max}$  in the studied regime is found to be proportional to  $\Phi/V$ , where V is the imposed velocity.

#### **Deposit mean thickness**

When the contact line velocity increases, the stick slip phenomenon fades away and a continuous deposit is obtained; its mean thickness can be determined with the optical profilometer. At higher velocities, a non continuous coverage with random dispersed particles or small aggregates is observed. The mean thickness corresponds to the mean coverage of the substrate by particles. For polymer solution, a continuous film is obtained whatever the velocity is, in the range covered in the experiments. The results obtained for the three samples (colloids, low mass and high mass PAAm) and for different concentrations are summarized in Figure 4. As can be seen, all the results gather together on the same master curve after scaling up the dried thickness h<sub>d</sub> by the concentration. Moreover two regimes can be distinguished: in the regime of low velocities (typically smaller than 100 µm/s), the following scaling applies:  $h_d / \Phi$  is proportional to 1/V. Then a plateau regime appears where the thickness does no depend much on the contact line velocity, with  $h_d/\Phi \approx 1 \mu m$ . It is interesting to note that similar results have been recently reported on a very different system, i.e. phospholipid molecules [5]. Further analysis [4] shows that the first regime corresponding to low Capillary numbers is dominated by evaporation while the plateau regime can be viewed as a transition between the regime dominated by evaporation and the dynamical wetting regime (Landau-Levich regime) where the thickness is expected to increase with the substrate velocity.



Figure 3: Pinning force (colloidal suspension)

Figure 4: Deposit thickness

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