Patterns formation during the drying of a colloidal suspension : influence of the contact line velocity.

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1 Introduction

Coating is usually achieved by the drying of a suspension or a solution. Evaporation flux formally diverges at the contact line where the diffusion layer vanishes. This effect, together with a pinning of the contact line, seems to play a great role in the famous "coffee-ring" effect that is usually observed when drying water suspensions or solutions [1]. The evaporation induces a flow that carries particles and thus leads to an accumulation of the particles. If they deposit onto the substrate, a defect is formed and can pin the contact line. At soon as it is pinned, the phenomenon holds and forms a macroscopic particle deposition.

Depending on the contact line velocity, the pinning of the contact line may or not occur. At small velocities, particules do have enough time to accumulate, but when getting to high velocity, one may expect that the pinning would not occur since particle deposition is not fast enough. This idea is supported by the observations of Rio *et al.* [2] on advancing contact lines of water suspension droplets. A stick-clip phenomenon is observed at low velocities, and disappear above a critical one. This authors proposed a model that accounts for the critical velocity that is observed, depending on the particle volume fraction. However, the pinning force that is responsible for the stick-slip is rather unknown and is an empirical data of their analysis. Deeper observations and analysis seems to be necessary to completely describe the transition from pinning to non-pinning of the contact line.

This transition is certainly of great importance concerning coating and pattering. Indeed, one may expect that it would be somewhat correlated to a uniform coating above the critical velocity and to a patterning of the surface in the stick-slip regime.

We present an experimental approach of these problems, using the capillary growth phenomenon. We focus on the characterization of the particle deposition and to its direct link to the movement of the contact line. Stick-slip or patterning that are observed allows an analysis of the pinning force that growths during the particle deposition.

2 Experimental method

A capillary growth is achieved between two parallel glass plates that are partially immersed in a reservoir filled with a water solution of colloidal silica sphere of radius 37 nm (±2 nm). The thickness of the cell is varied from 0.2 to 2 mm, and the particle volume fraction of the solution from 1 to 40%. The glass plates are cleaned in an hydrogen peroxyde and sulfuric acid fresh mixture (0.3/0.7) just before the experiment. A vertical air flow (1 m/s) is driven in between the plates in order to control evaporation flux.

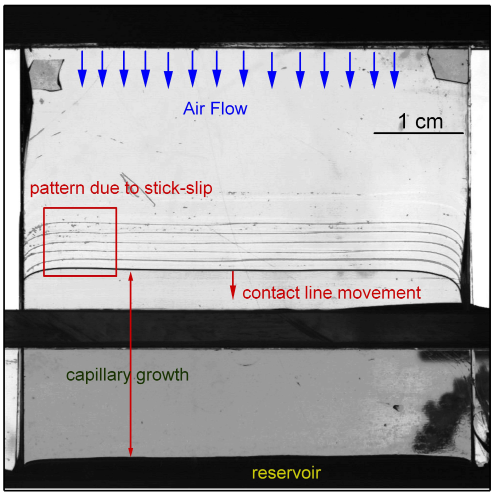

Fig. 1. Optical image of the capillary growth during a typical experiment. The cell thickness is 0.45 mm. On this image, horizontal patterns can be seen above the capillary growth. Contact line velocity is 500 nm/s, particle volume fraction is 3%.

A contact line velocity is imposed through a controlled evacuation of the reservoir. This set up allows to explore velocities ranging from 500 nm/s to 1 cm/s. We focus on retracting contact lines, for which particle deposition can be studied at posteriori, using to atomic force microscopy (AFM), optical or electronic microscopy (MEB). The movement of the contact line is followed by a standard camera, and then analyzed by image analysis. The figure 1 sum up the experimental set up.

Due to particle deposition, when pinning of the contact lines occurs, the height of the capillary growth deviate from its equilibrium position (see figure 2). It can be shown that this deviation Δh is proportional to the pinning force F that is applied on the contact line, $\Delta h = F/\rho g e$, where e is the distance between the two plates. Thus, the variations of the capillary growth height during the pinning and unpinning of the contact line give a measure of the pinning force.

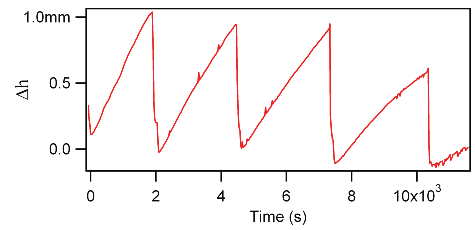

Fig. 2. Capillary growth height deviation Δh as a function of time (same conditions as Figure 1).

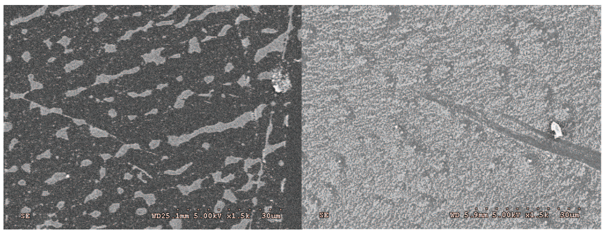

Fig. 3. MEB images (65.4μm$\times$87.3μm) of particles depositions at high velocities. In both case, no stick-slip occurs. They were obtain with contact-line velocities of 60μm/s (left) an 15μm/s (right), with a 3% solution.

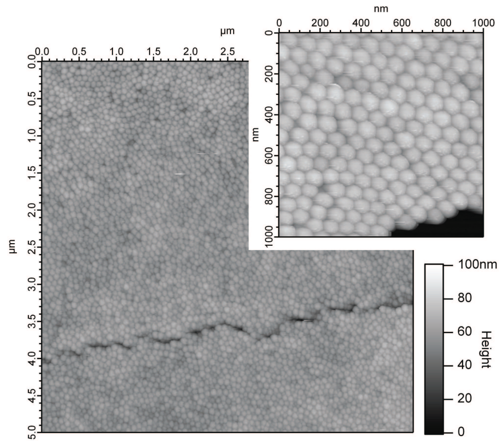

Fig. 4. AFM image of an almost uniform deposition of one particle monolayer. The contact-line velocity was 1.5μm/s.

3 Results

At high velocity, the contact line movements is continuous. We observe only a partial deposition of the particles onto the glass. When the velocity is decreased, the surface coverage increases (see figure 3) and reaches a uniform surface coverage of the surface (see figure 4). However, for similar or lower velocity we observe an horizontal pattering of the surface. This patterning is correlated with a pinning of the contact lines. The contact lines movement is in this case not continuous, but exhibit a stick-slip. The characteristic velocities that corresponds to the different regimes (partial coating, uniform coating, stick-slip) increase with the particle volume fraction.

When stick-slip occurs, it has been checked that the contact angle θ remains constant. This is consistent with the fact the cell thickness is small as compared to capillary length. The geometry thus remains constant, which simplify the interpretations. The pinning force that is responsible for this stick-slip is systemically measured as a function of velocity, particle volume fraction and cell thickness. It has been checked that, under similar drying condition, the pinning force is approximatively independent on the cell thickness (the stick-slip step increases when the thickness decreases). The pinning force decreases when the velocity increases. Detailed interpretations and full characterization are under development.

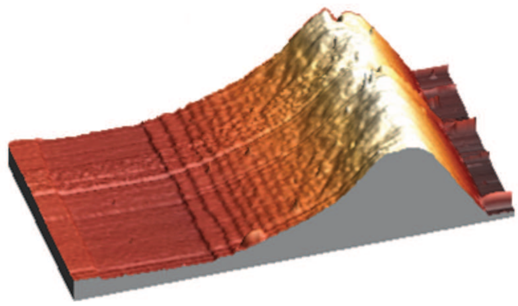

Fig. 5. AFM image of a typical particle deposition at a pinning point, obtained with a contact line velocity of 1 μm/s (from the left to the right). The height of the defect is 1.45μm at the top. The lateral dimensions are 100μm$\times$50 μm. The parallel lines that can be seen at the bottom of the defect corresponds to successive stairs of particles layers.

The characterization of the particle deposition is of great interest since it is possible to correlate the shape of this deposition (see Figure 5) to the maximum pinning force. Our results indicate that the characteristic slope of the defect is proportional to the pinning force measured. The effect of a small geometrical defect on the contact line can be accounted by a pinning force with is simply given by $\gamma p \sin\theta$ [3], where p is the slope of the defect and γ the surface tension. Such a pinning force is in numerical agreement with our measurements which shows that coupling between pinning and deposition is of geometric nature.

4 Conclusion

These preliminary results will be completed by systematic measurements of the pinning force that growth during the drying of a colloidal suspension as a function of the contact line velocity. Complete characterization of the particle depositions will be achieved and correlated to the pinning force measurements, in order to improve our understanding of patterns formation during the drying of colloidal suspensions.

References

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