



## Effect of the initial particle volume fraction on the structure of a drying colloidal deposit



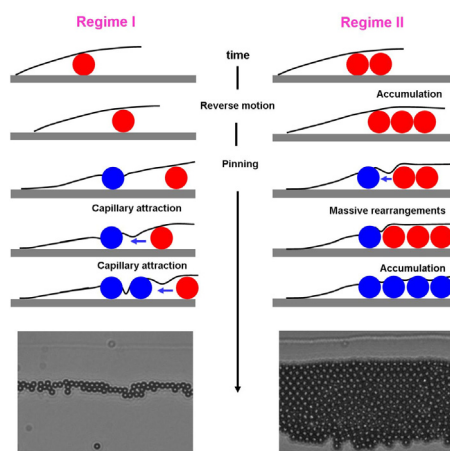
Janine Emile, Hervé Tabuteau\*

Institut de Physique de Rennes, CNRS UMR 6521, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes, France

### HIGHLIGHTS

- For low volume fractions, below  $10^{-4}$  (regime I), the capillary force breaks the colloidal structure.
- Above  $10^{-4}$  (regime II), the colloidal ring is rigid, pins the contact line and consequently keeps a hexagonal order.

### GRAPHICAL ABSTRACT



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### ABSTRACT

During the drying of a droplet on a substrate, dispersed colloidal particles are advected towards the contact line and then accumulate in its vicinity, forming in this way a ring-shaped deposit. Up to now, the structural properties at the particle scale of such pattern have been provided only by its final inspection at the end of the drying process. Here we follow all the stage of the ring formation, up to the complete drying, and for different particle volume fractions. We show that for low particle volume fractions, the final structure of the ring is always disordered, which results only from capillary attraction due to the deformation of the air-water interface. In contrast, for higher particle volume fractions, above  $10^{-4}$ , different consecutive rearrangements lead eventually to the formation of a ring with an ordered structure.

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### 1. Introduction

The drying of a colloidal suspension droplet on a substrate leads to the formation of various patterns [1] including the so called *coffee-ring* [2,3], extensively studied in a wide range of phenomena (see the review of Sefiane [4]). For particle volume fractions  $\phi \geq 10^{-2}$ , the scenario of the coffee ring formation is the following.

\* Corresponding author.

E-mail address: [herve.tabuteau@univ-rennes1.fr](mailto:herve.tabuteau@univ-rennes1.fr) (H. Tabuteau).

We first observe the spreading of the droplet on a solid surface, motion which stops when some particles draw near the contact line (CL), driven by the evaporative flux, and pin it [5]. There is a depletion distance between the CL and these particles, ruled by the contact angle and the particle size [6]. Thereafter, some particles start to accumulate near the CL slowly enough to form here a crystal. Even later on, the particle velocity near the CL increases rapidly and the rate of particle deposition is so high that the particles can pile up only in a disordered manner [7]. At the end of the drying process, we get a thick and multiple layers ring with a high particle concentration. The liquid drainage within this ring is supposed to not modify its final structure [7]. However, this scenario has not been confirmed since the overall dynamics of the ring formation has not been monitored so far. Studies have focused either on the early times [5,6,8] or on the latest stage of the drying process, when all the solvent is evaporated [6,7].

In the very dilute regime, for  $\phi$  between  $10^{-6}$  and  $10^{-2}$ , the morphology of the final deposit is quite different. Initially, the suspension droplet spreads on the solid surface until it reaches a maximum contact diameter and gets pinned. Then there are successive depinning and pinning events, which lead to the formation of multiple rings [9–12]. Kaplan and Mahadevan developed a theory that couples the liquid flow inside the deposit and the evolution of the shape of the air-water interface near the deposit [11]. They showed that all the different features of deposit can be explained by using only two parameters,  $\phi$  and the inverse capillary number. Their theory also describes the transition from multiple rings, at low  $\phi$ , to a single ring for higher  $\phi$ . However there is no experimental works that confirm their theory, especially the dynamics of such transition. In addition, the possible influence of the structural properties of the ring on such processes has also not been investigated. Finally no one has studied these phenomena at the particle scale so far, in order to make the link between the macroscopic flow and the particle ordering within the deposit.

Here, we study the influence of  $\phi$ , over an extended range ( $10^{-6}$  to  $5 \times 10^{-3}$ ), on the overall formation of the colloidal ring. Our aim is to determine the dynamics of the ring formation at the particle scale in order to define the influence of both the colloidal assembly and the air-water interface on such process. We also discussed the relevance of the so called *rush hour effect* on the structural transition observed inside the deposit.

## 2. Experimental methods

A droplet formed with a micro-syringe (volume  $0.60 \pm 0.05 \mu\text{l}$ ) is deposited on a glass microscope slide and viewed through a SCMOS camera (Hamamatsu Orca Flash 4.0) connected to an inverted microscope (LEICA DMI 3000). Such a low injected volume allows us to study the formation of a single ring during the droplet drying. We get sessile droplets with a diameter roughly equals to 1 mm at the base of the cap at the beginning of the experiments. Colloidal suspensions are made of sulfate latex spherical particles (diameter  $D = 1.6$  and  $2 \mu\text{m}$ , Life technologies, USA). They are diluted in pure water, with  $\phi$  in between  $3 \times 10^{-6}$  and  $5 \times 10^{-3}$ . Before each measurement the solution is sonicate for 30 min to break eventual aggregates. The evaporation process is performed under ambient air with controlled temperature ( $20.0 \pm 0.5^\circ\text{C}$ ) and high relative humidity RH ( $50 \pm 3\%$ ). The particle deposition in the vicinity of the CL is followed every 0.5–1 s and the images were analysed using ImageJ software. Glass slides are cleaned with Hellmanex (Sigma-Aldrich, diluted 10 times in pure water), acetone, ethanol, rinsed with pure water and dried with clean compressed air. The solvent we used, deionised water for HPLC (Chormanorm, VWR), wets the clean glass slide completely. The microparticles are partially wetted by the solvent since they are hydrophobic (polystyrene latex).

## 3. Results

In this work, we used suspension droplets with a fixed volume and various volume fractions  $\phi$ . The suspension droplet initially spreads on the solid surface at  $t = 0$  s and reaches eventually the same maximum contact diameter for the different  $\phi$  used and gets pinned here at  $t = 30$  s, before colloids arrive and start to pile up near the CL. We distinguish two regimes based on the width of ring obtained at the end of the drying process. For very dilute suspensions ( $10^{-6} < \phi < 10^{-4}$ , regime I), the final ring is a monolayer composed of 2–4 rows of particles, while for more concentrated solutions,  $10^{-4} < \phi < 5 \times 10^{-3}$  (regime II), it can be close to 32–34 rows. We get a monolayer of particles for both regimes except for  $\phi = 5 \times 10^{-3}$ . In the following, we mainly focus on the dynamics of the ring formation with a fixed evaporation rate while the influence of the evaporation rate on the ring formation, for a given  $\phi$ , is considered at the end.

### 3.1. Regime I

We present the overall dynamics of the ring formation for  $\phi = 6 \times 10^{-5}$ . At the beginning of the drying process, particles move towards the CL due to the evaporative flux and the first deposited particles lie in average at a depletion distance  $L_1$  from the CL (Fig. 1a) as observed previously [5,6,13].

It has been shown that  $L_1$  is roughly equal to  $D/\tan(\theta)$  (Fig. 2c–1), where  $D$  and  $\theta$  are the particle diameter and the contact angle respectively [6]. This expression is related to the capillary force between the particle and the air-water interface. This force prevents particles to go closer towards the CL, beyond  $L_1$ , since at shorter distance the air-water interface should be deformed by the particle [6,8,13]. Hereafter, chain-like aggregates grow parallel to the CL as new particles arrive (Fig. 1a–b) [6,13]. Since the arrival rate at  $L_1$  is slow (0.5 particle/s) we observe undulation and breakage of the chains between two successive depositions. The growth of the chains relies on two mechanisms. Either adjacent chains grow individually until they get connected to the neighbouring ones or they move along the CL until they come across other chains and merge (see Video V1 in the Supplementary material). The depletion distance  $L_1$  increases with time up to  $t = 200$  s (full circles in Fig. 2a and red dashed line in Fig. 1a–c). Therefore particles first come from the droplet centre towards the CL, stop at the line  $L_1$  and then move slowly in the opposite direction, towards the droplet centre, i.e., they undergo a reverse motion [8,13].  $L_1$  follows an inverse power law of the rescaled time ( $t_f - t$ ),  $L_1 = L_0(t_f - t)^{-1}$ , where  $L_0$  is the prefactor defined by the contact angle and the particle diameter at the beginning of the drying,  $L_0 = D/\theta_0$  (Fig. 2c–1), and  $t_f$  the time when the droplet is completely dried (Fig. 2a-inset). As shown by Weon and Je [8], the scaling of  $L_1$  is also directly related to the linear decrease of the contact angle with the rescaled time,  $\theta = \theta_0(1 - t/t_f)$ . Therefore, the reverse motion of the particles corresponds to a decrease of the contact angle near the CL and the subsequent downward motion of the meniscus, i.e., the thinning of the liquid film in between  $L_1$  and the CL (Fig. 2c–2). Before the reverse motion stops, around 160 s, some particles get out of the chains and move rapidly and over a short distance in the opposite direction, towards the CL. Those individuals form progressively a second row at a distance  $L_2$  of the CL (blue dotted line in Fig. 1c), which is close to the first one (Fig. 1d). It is worth noting that in the following, from  $t = 160$  s, all the particles coming from the droplet centre first flow towards the CL then stop at the line  $L_1$ , undergo the reverse motion for a while and then move again in the opposite direction, towards the CL, and stop at a distance  $L_2$  of the CL (insert Fig. 2b). We distinguish four consecutive steps:

For  $160 < t < 200$  s, both  $L_1$  and  $L_2$  increase, the distance between the two rows being constant, around  $1.3D$ ; value which is greater

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