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Dip coating with colloids and evaporation.

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There is a growing interest in coating hard and soft substrates with colloids, with numerous applications to optics and microelectronics [1]. A possibility to realize these substrates is to use dip coating with evaporation [2], i.e. to remove at constant speed a plate from a bath of colloids while drying occurs. This leads to several undesired effects: defects, heterogeneous deposition, fracture and de-lamination [1,3]. The problem is also difficult to model as three divergences may coexist at the contact line (CL) receding on the substrate [4-5] (and even in a advancing case [6]) : (1) divergence of viscous stresses, (2) divergence of evaporation as in the well known "coffee stain" effect [7-9], (3) and divergence of colloid concentration.

In a recent paper we modeled the hydrodynamics in the vicinity of a moving, evaporating, contact line [4], and we found that in the dip coating case there should exist two different regimes at respectively low and high plate velocity, in which the deposed mean thickness should respectively decrease and increase with the plate velocity. This should lead to a minimum of the deposited thickness for a critical intermediate velocity. Up to a recent thesis in our group [5], this effect has never been evidenced in a dip coating experiment, though similar behaviors were found for deposition of phospholipids [10], and for colloids in a rather specific two-plate geometry (meniscus receding in a Hele-Shaw cell) [11-12].

We present here evidences in favour of this effect, revealed by this work, and we correct the model of ref.[4] which contained a mistake. A sketch of the experimental set up is suggested on Fig.1. A clean glass plate is plunged inside a colloidal suspension and removed from this bath at constant speed (V ranging between *50 μm/s* and *5 cm/s*), while deposition and evaporation takes place on the glass. We used silica suspensions (Klebosol silica sluries 50R50, 30R25 and 30R12) with three different particle diameters (*12 nm*, *25 nm* and *50 nm*), and two different volume concentrations (ϕ_0=*5%* and *10%*). The glass plate is cleaned and prepared before each experiment by the following protocole. First the glass surface is rub with a abrasive cerium oxid suspension (concentration 20%), cleaned with pure water, ethanol, and again pure water, and then let to dry. A plasma treatment is then imposed to the glass.
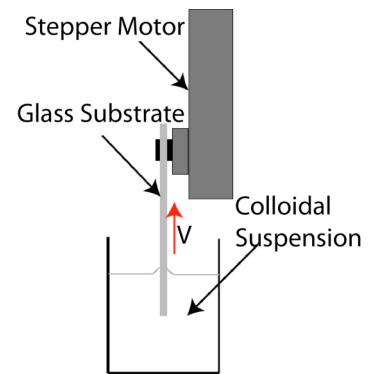

Fig. 1. Experimental set up.

Typical deposits obtained with this method, observed by optical profilometry, are reproduced on Fig. 2 for increasing plate velocities.
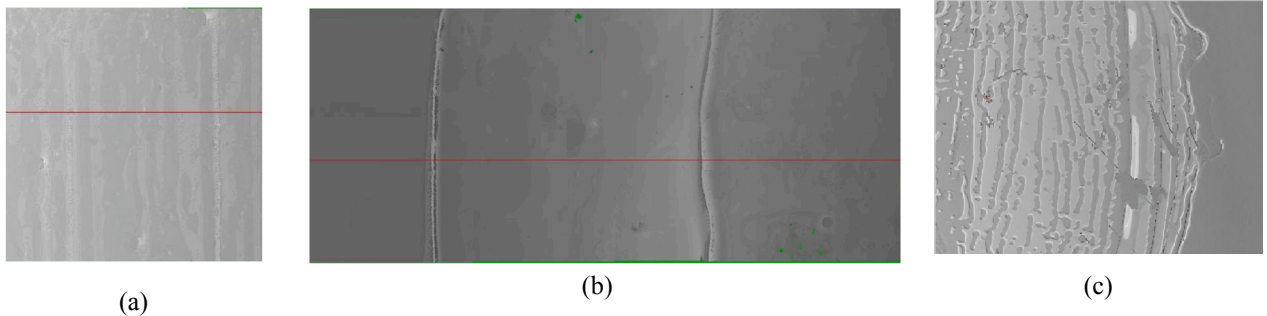

(a)   (b)   (c)

Fig. 2. Deposit left on the plate after drying, observed by optical profilometry, for increasing plate velocity: (a) V=50 μm/s, (b) V=1 mm/s, (c) V=5 cm/s. The motion of the plate took place along the horizontal direction of these samples. The suspension concentration was equal to 10%, and the particle size (not visible here) was equal to 50 nm. The horizontal scale of these pictures are respectively equal to 1.5 mm, 8 mm and 1.5 mm (total extent of the pictures).
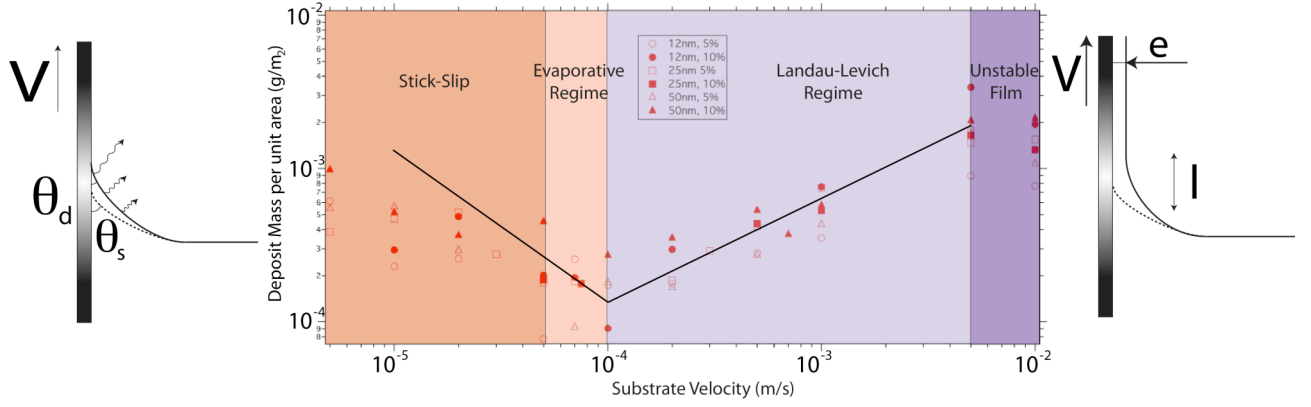
Fig. 3: Mean thickness of silica colloids deposed on a glass plate by dip coating. Roughly, two regimes of deposition appear, the one on the right being linked to the entrainment of a landau-Levich film at high plate velocity, the other on the left with deposition and evaporation directly at the contact line (the continuous lines, of respective slope -1 and 2/3 are guides for the eyes).

At low velocity (Fig. 2-a), the deposit is perturbed by a stick-slip effect, similar to the one observed by Rio et al [6] for advancing contact lines of colloidal suspensions, or to the one identified between two plates by Bodiguel et al. [11]. At intermediate velocities (Fig. 2-b), the deposit is reasonably uniform, before to be again perturbed by film flow instabilities at high plate velocity (Fig. 2-c). We have measured the mean thickness of the deposit, using these profilometry records, versus plate velocity for the different particle sizes and concentrations. The results are displayed on Fig. 3, where two distinct regims separated by a minimum of the thickness are clearly visible, in good agreeement with our theory [4-5]. We now remind the physical origin of these two very different behaviors, suggested by the two sketches on the same figure, and provide the reader with a qualitative modeling of the two regimes.

In the high velocity range, the plate entrains a continuous film of liquid out of the bath, that dries later on the whole extent of the plate. As well known from available litterature [2], the thickness of the liquid film e is equal to that calculated long ago by Landau, Levich and Derjaguin, and should scale as $e \propto l_c C_a^{2/3}$ where $Ca = \eta V / \gamma$ designates the Capillary Number built upon liquid viscosity η, plate velocity V, surface tension γ, and where $l_c = \sqrt{\gamma/(\rho g)}$ is the capillary length (g acceleration of gravity, ρ mass density of the liquid). During drying, the volume fraction occupied by the particle in the liquid increases from the initial volume fraction ϕ_0 to a critical value close to the maximal packing concentration ϕ_c, which implies that the deposit thickness should scale as

$$ e_{HV} \propto \frac{\phi_0}{\phi_c} l_c \left(\frac{\eta V}{\gamma} \right)^{2/3} \tag{1} $$

in the limit of high velocities. A line of slope 2/3 has been indicated on the Log-Log plot of Fig. 3. As one can check, this slope is consistent with the obtained data. At low velocity (see the sketch on the left of Fig.3), the situation is very different. There is now a contact line, from which the deposit directly emerges, evaporation being now mainly localized at the contact line itself. Following Deegan et al. [7-8], the evaporating flux diverges there, following a law of the kind (see Fig. 4):

$$ J = J_0 / x^{1/2} \tag{2} $$

where J_0 can be estimated here by noting that at the scale of the meniscus size x_∞, the mean evaporating velocity should be given by:

$$ \frac{J_0}{\sqrt{x_\infty}} \propto \frac{D}{x_\infty} \frac{c_{sat}}{\rho_w} \tag{3} $$
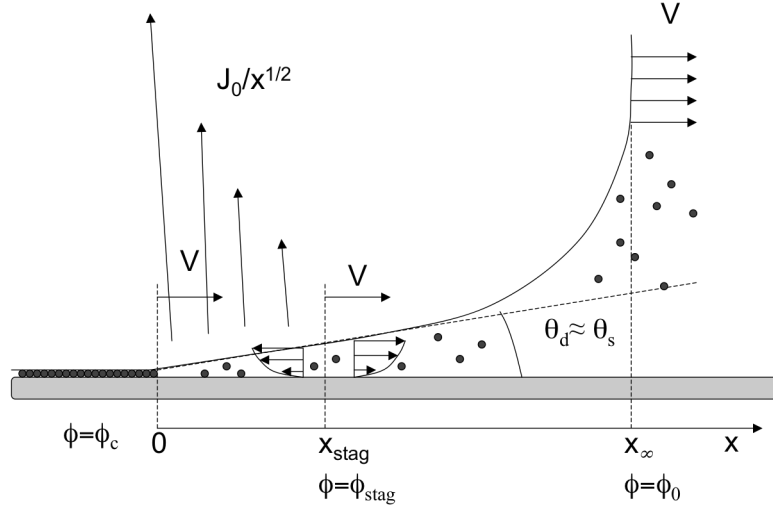
Fig. 4: Sketch of the low velocity problem in the framework of the plate, treated here as static, the liquid receding to the right.

where D is the diffusivity of water in air, c_{sat} the saturation mass concentration of water vapour in air, supposed to be reached at the free surface of the liquid (and to vanish at infinity), and ρ_w the mass density of water. In the framework attached to the plate, the liquid motion should obey the following mass conservation equation:

$$-V\frac{\partial h}{\partial x} + \frac{\partial}{\partial x}\left[h < u_x >\right] = -\frac{J_0}{\sqrt{x}} \tag{4}$$

where $<u_x>$ designates the mean velocity averaged on the liquid thickness h(x), given in the lubrication approximation by: $< u_x > = -(h^2/3\eta)(\partial P/\partial x)$, with $P = P_{atm} - \gamma\left(\partial^2 h/\partial x^2\right)$, P_{atm} being the reference atmospheric pressure. Integrating one time this equation leads to a mean velocity

$$< u_x > = V - \frac{J_0}{2h(x)}\sqrt{x} \tag{5}$$

that exhibits a stagnation surface located at a distance of the contact line equal to:

$$x_{stag} = \left(\frac{J_0}{2\theta_d V}\right)^2 \tag{6}$$

where θ_d is the dynamic contact angle, supposed to be rather close to the static angle θ_S in this low velocity limit. The structure of the flow is suggested on Fig. 4. For scales x<x$_{stag}$ evaporation drives everything to the contact line, and in particular all the colloids trapped in this region. We thus guess that x_{stag} will play the role of a capture length ruling the thickness deposited on the plate in the low velocity limit e_{LV}. To estimate it, a balance of solute can be written as follows: the plate is withdrawing from the liquid a volume per unit of length and unit of time of solute equal to $Ve_{LV}\phi_c$, while the stagnation surface crosses a volume of solute equal to $V\theta_S x_{stag}\phi_{stag}$ where ϕ_{stag} is the colloid concentration that holds at the stagnation line. If, as in ref. [4] one identifies ϕ_{stag} to the colloid concentration ϕ that holds in the bulk of the liquid, this balance leads finally to a deposit thickness that reads [4]:

$$e_{LV} \propto \frac{\phi}{\phi_c}\frac{J_0^{2}}{4\theta_S V^2} \tag{7}$$

As anounced at the begining of the present paper, unlike e_{HV} this thickness *decreases* with the plate velocity, which, combined to (1) leeds indead to a minimum of the deposed thickness. This description is enough to explain our results, but if one looks more carefully to the data at low velocity on Fig.3, the V-exponent predicted by this model (equal here to 2) overestimates the observed decrease of e_{LV} upon V, an exponent close to 1 (suggested by the line added to the graph) would be more reasonable. This observation is consistent with results obtained by Le Berre [10] in the deposition of phospholipids, and by Jing et al. [12] in

the deposition of colloids by a meniscus receding between two plates, both groups reporting an exponent close to 1. This results from the too rough nature of the approximate $\phi_{stag} \approx \phi$ used above. Obviously, the concentration of solute increases as the liquid becomes closer and closer to the contact line. A simple scaling argument built on a slide of liquid moving inside a wedge of angle θ_S, leads to

$$\phi(x) = \phi_0 \sqrt{\frac{x_\infty}{x}} \qquad (8)$$

when the concentration ϕ_0 holds at the scale of the meniscus (matching with the bulk of the reservoir). Using this expression in the estimate of $\phi_{stag} \approx \phi_0(x_\infty/x_{stag})^{1/2}$ leads finally to the following law ruling the "true" e_{LV}:

$$e_{LV} \propto \frac{\phi_0}{\phi_c} \frac{J_0}{\sqrt{x_\infty}} \frac{x_\infty}{V} \qquad (9)$$

in which the new exponent -1 , smaller than the previous value -2 is in better agreement with all available experiments [5, 10,12]. Note that this expression, as noticed by Doumenc [12], can be reached independently by a balance of solute at the level of the whole meniscus. While the meniscus deposits on the plate of volume of the coated film equal to $V e_{LV} \phi_c dt$, there is, at the scale of the whole meniscus, a volume of solvent that evaporates equal to $x_\infty \left(J_0 / \sqrt{x_\infty} \right) dt$, and which creates an excess of solute of quantity $\phi_0 x_\infty \left(J_0 / \sqrt{x_\infty} \right) dt$. Balancing this excess of particles with the quantity deposited on the plate leads directly to (9).

In summary, we have proved experimentaly that our prediction proposed in [4] of the existence of a minimal thickness of colloids deposited on a plate by dip coating, and corrected our model by including the increase of colloid concentration when the liquid reaches the vicinity of the contact line in the low velocity limit. We insist on the fact that this simple approach avoids any use of complicated partial differential equations, and allows one to get a simple understanding of the mechanisms at play here. The behavior that we found, experimentally as well as by a simple modeling, is in agreement with the observations of other groups on different systems [10,12], and with the interpretations proposed by one of them [12]. It would be interesting to explore experimentally in more details the spatial distribution of colloid concentration, to see to what extent a scaling law of the kind (8) could hold and to establish some possible connection with the fading out behaviour of the concentration, investigated recently by Witten in the case of the "coffee stain" experiment [13].

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