Drying of colloidal suspensions and polymer solutions near the contact line: deposit thickness at low capillary number

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Abstract

Drying experiments with a receding contact line have been performed with silica colloidal suspensions and polyacrylamide (PAAm) polymer solutions. The experimental set-up allows to control the receding movement of the contact line and the evaporation flux separately. Deposit thickness as a function of these two control parameters have been investigated. The different systems exhibit a similar behavior: in the regime of very low capillary numbers the deposit thickness scaled by the solute volume concentration and the evaporation rate is proportional to the inverse of the contact line velocity. Both the scaling exponent and the constant (which has the dimension of a length) do not depend on the system understudy. The observation of this evaporative regime confirms some recent results obtained by Le Berre et al. on a very different system (phospholipidic molecules), and fully supports their interpretation. Following their approach, a simple model based on mass balance accounts for these results. This implies that this regime is dominated by the evaporation, and that the deformation of the meniscus induced by viscous forces does not play any significant role. When increasing the velocity, another regime is observed where the thickness does not depend significantly on the velocity.

1 Introduction

The drying of a suspension or a solution is a common technique to realize the coating or covering of a solid surface. Though many studies have been devoted to the design of controlled patterned deposits, ^{1–4} a full understanding of the dominant phenomena is still lacking, as the process is governed by the coupling between hydrodynamics, heat and mass transfer, and physicochemical properties of the solution and the substrate.

A lot of studies reported so far were realized with droplets^{5–8} for which the receding motion of the contact line is set by the evaporation. If one considers the evaporation of a suspension droplet, it is known⁹ that the hydrodynamic flow coupled with the pinning of the contact line result in an accumulation of solute.^{10,11} This is however a complex geometry in the sense that the movement of the contact line is governed by the evaporation and by the competition between pinning and receding forces, and that the droplet mean concentration changes during the drying. In order to better understand the influence of the different parameters that affect the final deposit, we have developed an experimental set-up where the contact line movement and the evaporation flux can be controlled independently and where a steady state can exist. This is achieved by using the capillary rise phenomenon in a Hele-Shaw cell partially immersed in a large reservoir whose level can be precisely varied with a push-pull syringe, allowing to change the contact line velocity on four orders of magnitude. The evaporation flux is controlled thanks to an external air flow with known humidity and temperature.

This configuration is quite similar to the standard dip coating experiments where plates are withdrawn out of a bath. These experiments usually take advantage of dynamical wetting to produce films of varying thicknesses at the micron scale. Hydrodynamics behavior as a function of the plate velocity has been widely characterized in particular by Landau, Levich and Derjaguin^{12,13} who have calculated the thickness of the dragged film for different regimes, for non volatile fluid. Cox¹⁴ and Voinov¹⁵ have studied the variation of the effective contact angle for a moving contact line. A review of these approaches can be found in^{16,17} (and references herein). Extension to volatile fluids and changes induced by the evaporation on the meniscus geometry have also been studied for example by Berteloot at al.¹⁸ who have extended the well known Cox and Voinov approach to take into account the evaporation.

Other drying experiments using a controlled moving contact line were also developed. For instance Rio et al.¹⁹ studied the pinning/unpinning of an evaporative colloidal solution, Ghosh et al.²⁰ studied the pattern for different plate velocities in dip-coating experiment, Abkarian et al investigated evaporation of a suspension of polystyrene beads inside a tube.²¹ Le Berre et al.²² recently reported results on coating by phospholipid films. These last authors studied the influence of the velocity of a receding meniscus on the thickness of the deposit film, in presence of evaporation. They showed that the thickness is a non-monotonic function of the velocity, which indicates a crossover between two regimes. The observed scaling - though only observed in a narrow range of velocity, i.e. one decade - support the interpretation of an evaporative regime at low velocities and a Landau-Levich regime at higher ones. If the latter has been well described for years, the observation of an evaporative regime where the thickness is inversely proportional to the velocity asks for deeper investigations, and is in contradiction with the theoretical prediction of Bertheloot et al.¹⁸ We should indeed address the question of the universality of this evaporative regime and of its extent to very small capillary numbers. Then, the proposed model which is based on a simple mass conservation asks for complementary quantitative checks, concerning in particular the evaporation rate.

In this paper, we use our above-described experimental set-up to get some deeper insights on this evaporative coating regime and to answer the main questions that remain, the most important being probably to know whether this regime exists for different type of solutes. We thus systematically measure the mean thickness of the deposit as a function of the contact line velocity and the evaporation flux for different systems (colloidal suspension and polymer solutions with different viscosities) and for low capillary numbers. It is observed that the thickness is predicted by the same scaling law for all these systems. Moreover, we propose an extension of the model proposed by Le Berre et al. that throws some light on the solute transport mechanism at low capillary numbers, below the dynamical wetting threshold.

2 Experimental

2.1 Systems

Two different systems have been compared. The first one is a colloidal suspension of silica spheres of radius 37 nm (± 2 nm) (KLEBOSOL, AZ Electronic Materials). Density of silica spheres is 2150 g/l (from picnometer measurement). The solution pH is about 10. The second system is a polymer solution of polyacrylamide (PAAm). Two different molecular weight have been tested, Mw $\simeq 22$ kg/mol (Sigma-Aldrich) and Mw $\simeq 5000$ -6000 kg/mol (Biovalley). For the small molecular weight, the polydispersity estimated from gel permeation chromatography performed in Laboratory PPMD (ESPCI, France) is 3.5. The polymer density is 1470 kg/m³. Conversion from mass fraction to volume fraction is made with the assumption of volume additivity.

The solvent is water for the two systems. The polymer concentration at glass transition has been determined by preliminary gravimetry experiments in a pressure and temperature controlled chamber: $\Phi_g \simeq 0.74$ at $T = 25^{\circ}$ C (a description of the method can be found in²³). The viscosity of the silica suspension and of the PAAm solutions has been measured for different solute concentration with a Low Shear 30 rheometer, cf. figure 1. As it is well known for such systems, the viscosity depends on solute volume fraction. The viscosity of the colloidal suspension and of the low molar mass polymer solution remains close to the pure water viscosity for solute volume fraction less than about 5% and 1% respectively. Rheological behavior is very different for the high mass polymer solution, since the viscosity increases as soon as the solute volume fraction exceeds 0.01%.

Crossing the results obtained with those three different samples allows to characterize a possible influence of the viscosity on one hand and of the nature of the solute (hard spheres versus macromolecules) on the other hand.

2.2 Set-up

A capillary rise is achieved between two glass plates separated by a gap of thickness d = 1mm. The plates are partially immersed in a reservoir filled with the colloidal suspension or polymer solution. The schematic setup is represented in figure 2. Prior to each experiment, the glass plates undergo the following protocol: a hot mixture of



Figure 1: Dynamic viscosity at 25°C as a function of the solute volume fraction for the colloidal suspension and polymer solutions - dashed line: water viscosity.

hydrogen peroxide (Prolabo) and sulfuric acid 95-98% (Sigma-Aldrich), with volume ratio of 0.3/0.7, is used to clean the glass plates for 20 min. Then they are rinsed four times into pure water and dried with nitrogen gas. Just after this cleaning procedure, the glass slides exhibit a total wetting by water. Then the glass plates are transferred into the setup and the experiment begins about 15 minutes after. After this delay, the contact angle for pure water is of order of 10 degrees, probably due to uncontrolled contamination of the surface.



Figure 2: Scheme of the experimental setup.

Three control parameters can be imposed during the experiments. The first one concerns the choice of the system (colloidal suspension or polymer solution) and the solute volume fraction Φ (0.14% to 4.9% in our experiments). The second one is the average velocity of the contact line V that can be precisely controlled by pumping out the liquid from the reservoir thanks to a push-pull syringe (Pumping system: Kd Scientific ; Syringe: 60ml Maximum). The velocity V can be varied from 0.2 μ m/s to 2 mm/s. The third control parameter is the evaporation rate. The set up is put in a large box (not drawn in figure 2) whose temperature and humidity are carefully controlled by a standard PID system. A channel and a fan above the two plates allow to blow a vertical air flow between the two plates. The air flow velocity is chosen to get a uniform evaporation close to the meniscus but a negligible interface deformation due to the pressure increase above the meniscus. To get the evaporation flux corresponding to the different experimental conditions (air flow, temperature, humidity), previous experiments were performed with pure water, by cutting the connection between the plates and the reservoir and measuring the decrease of the water level between the two plates. Changing the air temperature and humidity, the evaporation rate v_{ev} can be varied from 0.28μ m/s to 3μ m/s (the mass evaporation flux being $Q_{ev} = v_{ev}S\rho$ with S the rectangular cross section between the plates and ρ the water density).

The present experimental set-up has several advantages: first the evaporation rate and the contact line velocity can be imposed separately, second they can be varied on a wide range. At last, the steady state corresponding to a given evaporation rate and contact line velocity can be observed.

Observations are made on line during the experiments and a posteriori on the dried deposit. The position of the contact line is measured during the experiment by a CCD camera (Marlin AVT F201B, Allied Vision Technologies) with an objective AF Micro Nikkor 60 mm f/2.8D. The camera resolution is 1280*1024 pixels. The position of the meniscus is then determined with a subpixel analysis of the images which leads to a precision of 2 μ m. This enables us to measure directly the velocity of the contact line. It is referred thereafter as "mean velocity".

2.3 Deposit mean thickness measurement

In the following we are interested in the mean thickness of the dried deposit, h_d , as a function of the experimental control parameters. The deposits are analyzed by an optical profilometer (Fogale Microsurf 3D), after having made a scratch with a steel needle to strip the substrate (this scratch can be seen on Figure 3(a)). The mean thickness of the deposit is given by step height measurements, repeated several times at different places and averaged. Another technique is used for colloidal suspensions at high velocities. In that case, the deposit is usually a non-continuous monolayer, as shown in Figure3(b). The mean coverage is determined by image processing of several scanning electron microscopy (SEM, JEOL JSM-5200) images performed at various places of the same sample. The mean thickness is computed from the covered surface ratio multiplied by the particle diameter (the mean thickness is then less than the diameter of one particle).

It should be noticed that for the colloidal suspensions at low velocities, a stick-slip motion of the contact line is observed, leading to a patterned deposit, as described in



Figure 3: Left. Optical profile image of a deposition pattern obtained from a colloidal suspension with $V = 0.3 \mu \text{m/s}$, $\Phi = 1.4\%$, $v_{ev} = 0.42 \mu \text{m/s}$. Right. Scanning electron microscopy image of the deposition, $V = 30 \mu \text{m/s}$, $\Phi = 0.14\%$, $v_{ev} = 0.28 \mu \text{m/s}$

a previous communication.²⁴ When measurement is possible, a mean thickness is still determined thanks to optical profilometry.

3 Drying of colloidal suspension

The mean thicknesses obtained with different volume fractions as a function of the contact line velocity are given in figure 4(a), for small evaporation rates v_{ev} . As expected the deposit thickness increases with the solute volume fraction. In the same way, h_d increases with the evaporation flux for a given solute volume fraction Φ (figure 4(b)).



 $v_{ev} = 0.42 \mu \text{m/s}$

Figure 4: Mean thickness as a function of the contact line velocity.

To go further, it can be seen that scaling the thickness h_d by the volume fraction and the evaporation rate gathers all the points on a master curve, as illustrated in figure 5. Moreover, if we consider the figure 5(a) two regimes can be distinguished: in the regime (I) corresponding to low velocities (typically smaller than 100μ m/s for $v_{ev} \sim$ 0.3μ m/s), the following relation applies: $h_d/(\Phi v_{ev}) \propto 1/V$. Then a plateau regime appears (regime (II)), where the scaled thickness does not depend significantly on the contact line velocity. The same master curve is obtained in figure 5(b) for the regime (I). The plateau regime is less obvious for high evaporation rate, but only few experiments have been performed in this configuration. Moreover, the velocity corresponding to the change of regime may depend on the evaporation flux (cf. the analysis section).



Figure 5: scaled thickness $h_d/(\Phi v_{ev})$ as a function of the contact line velocity - same symbols as in figure 4. Dotted line in figure (a) : $h_d/(\Phi v_{ev}) \simeq 3.6$ s.

As a first conclusion, experimental results on the colloidal suspension can be described in regime (I) by the following empirical law:

$$\frac{h_d V}{\Phi v_{ev}} \simeq L_{exp},\tag{1}$$

where the constant L_{exp} fitted from experimental data has the dimension of a length and is about 330 μ m.

4 Drying of polymer solutions

The same experimental protocol was used with the polymer solutions, for the two molar masses. The thickness dependance on the velocity is still described by Equation (1) as shown in figure 6. That means that regime (I) exhibits a characteristic length L_{exp} independent on the system under study and especially on the system viscosity, and independent of the control parameters V, Φ , and v_{ev} . Let us note that this length is of same order than half the gap between the two plates. Then the meniscus size should

fix the characteristic length of the system in this regime. This point is developed in the next section.

It is interesting to note that Le Berre et al²² obtain a close scaling exponent (-1.14) in the regime (I) on a very different system, that is phospholipid molecules .



Figure 6: Mean thickness (a) and scaled thickness (b) as a function of the contact line velocity for polymer solutions - $v_{ev} = 0.28 \mu$ m/s. Dotted line in figure (b): same plateau value than in figure 5a.

5 Analysis

5.1 Regime (I): evaporative regime

Le Berre *et al* recently proposed a mass balance model to account for the -1 exponent of the deposit thickness in the regime of low velocities.²² We revisit their model by introducing an extra length scale corresponding to the typical size on which concentration gradients are significant. The model is written in the meniscus frame, in which the plates move with a velocity V in the direction shown in figure 7. The following assumptions are used: the solute concentration is assumed uniform on the film thickness, and equations are written in the steady regime. The position "z = 0" corresponds to the glass transition Φ_g : beyond this point the deposit is solid-like. $\Phi_g \simeq 0.74$ for the polymer solutions (cf. the experimental section) and we assume that $\Phi_g \simeq 0.64$ for the colloidal suspension (volume fraction of a random stack of rigid spheres). The other boundary is located at the length L for which the solute concentration is equal to the bulk concentration Φ_b : $\Phi(z = L) = \Phi_b$. This length L is supposed to be of same order of the meniscus size, i.e. $L \sim d/2$. Mass balances are written in the domain $0 \le z \le L$ and we assume that this domain is liquid.



Figure 7: Scheme of the model assumptions

Given these assumptions, the total volume flux Q(z) and the solute volume flux $Q_P(z)$ (by unit length of the y axis) are respectively:

$$Q(z) = \int_0^{h(z)} u(x, z) dx$$
 and $Q_P(z) = \Phi(z) Q(z)$ (2)

where u(x, z) is the velocity component in the z direction.

The global mass balance reads:

$$\frac{\partial Q}{\partial z} = -J(z)$$
 with $Q(z=0) = -h(z=0) V$ (3)

where J(z) is the local evaporation rate. The volume fraction for z = 0 being the glass transition volume fraction Φ_g , the deposit thickness is given by: $h_d = \Phi_g h(0)$. As the solute does not evaporate, the solute mass balance is given by

$$\frac{\partial Q_P(z)}{\partial z} = 0. \tag{4}$$

In addition, we assume

$$\int_{0}^{L} J(z)dz \simeq v_{ev}L \tag{5}$$

Indeed the evaporation flux in the glassy zone (z < 0) is negligible. Then, integration of the global and solute mass balances between 0 and L gives:

$$\frac{h_d V}{\Phi_b v_{ev}} = \frac{\Phi_g}{\Phi_g - \Phi_b} L, \quad \text{that is} \quad \frac{h_d V}{\Phi_b v_{ev}} \simeq L \tag{6}$$

since in our case $\Phi_b \ll \Phi_q$.

Comparison between relations (6) and (1) shows that this simple model is consistent with experimental results. The regime (I) can be understood as a regime dominated by evaporation and the length L, independent on V, v_{ev} and Φ_b , is the geometrical size of the problem, i.e. the meniscus size. This model is similar to the one proposed by Le Berre et al,²² but it differs from the model by Berteloot and coauthors¹⁸ where this length depends on the velocity V (cf.¹⁸ for more details), which leads to a thickness scaling in V^{-2} not in agreement with the experimental scaling in V^{-1} . This constant characteristic length L suggests that the solute transport through the meniscus is mainly due to advection, and that diffusion is of second order.

5.2 Regime (II)

Let us first consider the well known problem of dip coating of a non volatile fluid, in the limit of small velocities for which inertial effects can be neglected. The pertinent dimensionless parameter to analyze the different regimes is the capillary number that compares capillary to viscous forces, with $Ca = \eta V/\gamma$, η being the dynamic viscosity and γ the surface tension.

For very low capillary number the "dry" regime is observed, i.e. there is a small deformation of the meniscus due to viscous stress but no film is pulled out from the bath. The change in contact angle can be estimated for instance by Cox¹⁴ and Voinov.¹⁵ Berteloot and coauthors¹⁸ have extended this model to take into account evaporation and get the following expression for the deviation of the contact angle:

$$\theta^{3}(z) = \theta_{e}^{3} - 9 \ Ca \ \ln(\frac{z}{a}) + \frac{24\eta J_{0}}{\gamma \theta_{e}} (\frac{1}{\sqrt{a}} - \frac{1}{\sqrt{z}})$$
(7)

where θ_e is the contact angle at thermodynamic equilibrium, *a* is a cut-off microscopic distance, and the flux near the contact line is given by $J(z) = J_0/\sqrt{z}$.

An estimation of the threshold from the "dry" regime to the dynamical wetting regime can be obtained from equation 7, assuming that dynamical wetting occurs when θ vanishes to zero. Then viscous forces are large enough to drag a film from the bath. This regime is known as the Landau-Levich regime. The thickness of the dragged film can be estimated by adapting the Landau law to our confined geometry:

$$h = 0.67 \ d \ C a^{2/3},\tag{8}$$

where d is the distance between the two glass plates.

For capillary numbers much larger than the critical value, one can assume that the final deposit corresponds to the drying of the dragged film $(h_d = \Phi_b h)$ and then the thickness of the deposit is expected to increase with the velocity, as confirmed by various experimental results in the literature (cf. for instance^{22,25}).

This is obviously not the case for the results presented in this paper. An estimation of the critical capillary number and then of the critical velocity in our experimental configuration can be deduced from equation 7, taking $z \sim d$ and $a \sim 10^{-9}$ m. For instance

for the colloidal suspension and $v_{ev} = 0.3 \mu$ m/s, we obtain a critical capillary number of about 5×10^{-5} and a critical velocity of about 3.6 mm/s close to the maximal velocity of our experiments. Moreover the film thickness at this velocity, deduced from equation 8, is about 1 μ m, that is close to the plateau experimental value $(h_d/(\Phi v_{evap}) \simeq 3$ s, that is $h_d/\Phi \simeq 0.9 \mu$ m). Then the Landau-Levich regime is never reached in our experiments that are performed in the domain of low capillary numbers. The domain (I) corresponding to very low capillary numbers ($3 \times 10^{-9} \lesssim Ca \lesssim 10^{-6}$) is dominated by evaporation, which leads to a thickness proportional to 1/V as developed in the previous section. The plateau regime ($10^{-6} \lesssim Ca \lesssim 3 \times 10^{-5}$) may correspond to a transition between this regime and the Landau-Levich regime dominated by viscous forces, as already observed by Le Berre *et al.*²²

6 Conclusion

Thanks to an experimental set-up allowing to control the receding movement of the contact line on one hand and the evaporation flux on the other hand, deposit thicknesses as a function of these two control parameters have been investigated on three different samples: a colloidal suspension and two polymer solutions with different molar masses and then different viscosities. These three samples exhibit a similar behavior: in the regime of very low capillary numbers the deposit thickness scaled by the solute volume concentration and evaporation rate is proportional to the inverse of the contact line velocity. The thickness deposit does not depend on the system understudy. A simple model based on global mass balances show that in this regime, the flow is driven by evaporation, and the viscous forces does not play any significant role. In addition, the distance between the point where glass transition occurs and the point where the solute concentration meets the bulk value is a constant, of order of the meniscus size. This suggests that solute diffusion should be negligible compared to advection. When increasing the velocity, another regime is observed where the thickness does not depend much on the velocity. This regime may correspond to a transition between the regime dominated by evaporation and the Landau-Levich regime where the thickness is expected to increase with the plate velocity, due to viscous forces. Indeed, an estimation of the critical capillary number characterizing the beginning of the Landau-Levich regime shows that the transition regime observed in our experiment is just below the velocity threshold.

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