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## Evaporation induced flow near a contact line: consequences on coating and contact angle

G. BERTELOOT<sup>1,2</sup>, C.-T. PHAM<sup>1</sup>, A. DAERR<sup>1</sup>, F. LEQUEUX<sup>2</sup> and L. LIMAT<sup>1</sup>

<sup>1</sup> *Laboratoire Matière et Systèmes Complexes (MSC), UMR 7057 CNRS & Université Paris Diderot, 10 rue Alice Domon et Léonie Duquet, 75013 Paris*

<sup>2</sup> *Laboratoire Physico-chimie des Polymères et Milieux Dispersés, UMR 7615 du CNRS, ESPCI, 10 rue Vauquelin, 75005 Paris*

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**Abstract.** - We propose a simple model of the dynamics of a contact line under evaporation and partial wetting conditions, taking into account the divergent nature of evaporation near the contact line, as evidenced by Deegan et al. [1]. We show that evaporation can induce a non negligible change of the contact angle together with modification of the flow near the contact line. We apply our results to dip-coating of a substrate with non volatile solutes. We show that at small velocities the coating thickness increases and scales like the inverse of the square of the velocity which implies a minimum of the coating thickness at the cross-over with the more familiar Landau-Levich regime.

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The deposition of homogeneous layers of colloidal particles behind a receding, evaporating contact line constitutes a challenge, important for many applications: control of optical properties of surfaces, realization of thick photonic crystals [2], etc. In practice things are very complicated as the physics at contact line mixes several effects [1]: complex dewetting hydrodynamics, non-trivial distribution of liquid evaporation very near contact line, particle migration with possible accumulation that can trap the contact line, etc. This often leads to a complex dynamics of the contact line, with possible occurrence of stick-slip effects [3, 4], that

increases the heterogeneity of the deposit. The complexity of the physics is such that there is presently no complete theory able to define the optimal conditions for deposition, conditions that are also very dependent upon the geometry of the problem. By itself, even the simpler problem of a contact line edging a pure fluid receding on a flat solid under the effect of evaporation remains poorly explored. Most of available works, experimental [5] as well as theoretical [6], deal with the case of perfect wetting. Also, most of available models neglect a very important feature, pointed into evidence by Deegan et al. [1], i.e. the fact that, ac-

According to an analogy with electrostatics, the evaporation flux of liquid towards ambient air should diverge very near contact line. To our knowledge, the implications of this statement on contact line dynamics with evaporation has poorly been explored.

In the present letter, we propose a simple model of the flow near a contact line, receding at constant speed under both the effects of capillary pressure gradients and evaporation. We write the lubrication equations governing the local liquid thickness, and investigate the effect of the evaporation singularity on the interface shape, focussing our discussion on the case of partial wetting. The problems of stick-slip phenomenon encountered in experimental works under partial wetting conditions or the consequences of evaporation under total wetting conditions are left for future work. We also investigate how the well known Tanner-like mobility law proposed long ago by Cox and Voinov [7,8] should be modified by the presence of evaporation. Compared to recent insight on dynamics of the contact line [9], our goal is not to refine the description that is still the subject of many discussions but rather to discuss in a simple model the effects of evaporation that we will show to be perturbative. We thus discuss the implication of the divergence of evaporation on the Cox and Voinov law in the first part of the article. In the second part, we focus specifically on dip-coating.

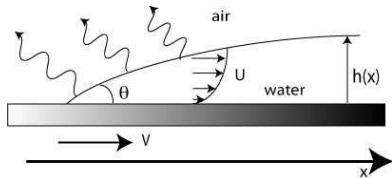


Figure 1: Notations of the problem

The situation under study is suggested in Fig. 1. A contact line recedes at a constant velocity  $V$  on a solid surface, both under the effect of a fluid motion linked to capillary pressure gradient  $U(x, z)$ , and of an evaporation flux  $J(x)$ . Standard lubrication theory in the limit of low Reynolds numbers and small slope of the interface leads to a mean local velocity

of the liquid given by:

$$\langle U \rangle = \frac{1}{h} \int_0^h U(x, z) dz = -\frac{h^2}{3\eta} \frac{\partial P}{\partial x} = \frac{\gamma}{3\eta} h^2 h_{xxx} \quad (1)$$

where  $h(x)$  is the liquid thickness,  $\eta$  the liquid viscosity, and the capillary pressure reads approximately  $P = P_a - \gamma h_{xx}$ ,  $P_a$  being the ambient pressure and  $\gamma$  the surface tension. For a contact line receding at velocity  $V$ , mass conservation imposes that the local thickness  $h(x - Vt)$  satisfies  $\partial_t h + \partial_x(h\langle U \rangle) + J(x) = 0$ , which leads to:

$$\frac{\partial}{\partial x} [h(\langle U \rangle - V)] + J(x) = 0 \quad (2)$$

to be combined with the relation  $\langle U \rangle = \frac{\gamma}{3\eta} h^2 h_{xxx}$  found above. To go further, one now would need an approximation of the local evaporation rate distribution  $J(x)$ . For a sessile axisymmetric drop, Deegan [1] assumed an analogy between the vapour diffusion in air and an electrostatic problem, the vapor concentration near the liquid surface being supposed to saturate at the value  $c_v^{\text{sat}}$ .

In analogy with this work, we will assume that very near contact line  $J(x)$  diverges as  $J(x) = J_0 x^{-(\pi/2-\theta)/(\pi-\theta)}$  which yields for very small values of angle  $\theta$ :

$$J(x) \approx \frac{J_0}{\sqrt{x}} \quad (3)$$

in which  $J_0$  is given by  $J_0 = \frac{D_g}{\sqrt{\lambda}} \frac{c_w^{\text{sat}}}{\rho_w}$  where  $D_g$  is the diffusion constant of evaporated solvent in air,  $c_w^{\text{sat}}$  its mass concentration in air at saturation, and  $\rho_w$  its mass density. The length scale  $\lambda$  can be either the thickness of a diffusive boundary layer, or the typical curvature of the contact line. For instance, for the sessile drops of in-plane radius  $R$  with low contact angle considered in Ref. [1] one has exactly  $\lambda = 2R$ . For a water drop of millimetric size evaporating in ambient air one has typically  $J_0 \approx 10^{-9} \text{ m}^{\frac{3}{2}} \cdot \text{s}^{-1}$ . After integrating once Eq. (2) upon  $x$ , one gets:

$$(\langle U \rangle - V)h = -2J_0\sqrt{x} \quad (4)$$

that can be written as:

$$V = \frac{2J_0}{h} \sqrt{x} + \frac{\gamma}{3\eta} h^2 h_{xxx} \quad (5)$$

The local thickness of liquid  $h(x)$ , is supposed to vanish or at least to reach microscopic values at contact line placed here for simplicity at the location  $x = 0$ . The physical meaning of this equation is that the recession of contact line at a given velocity  $V$  is in fact due to both migration of liquid under the capillary pressure gradient  $\gamma h_{xxx}$  and to evaporation itself. This evaporation term will add a new term to the ordinary differential equation governing  $h(x)$ , considered years ago by Voinov [8], that reads in this specific case:

$$h_{xxx} = \frac{3\text{Ca}}{h^2} - \frac{6\eta J_0 \sqrt{x}}{\gamma h^3} \quad (6)$$

where  $\text{Ca} = \eta V / \gamma$  designates the capillary number built upon the receding contact line velocity  $V$ . In this article, we will consider water so that we can neglect the temperature gradients (which do not change the form of the evaporation rate [10]) together with Marangoni effects [11]. Note that some aspects of the thermal effects on pinned evaporating drops have been reported [12] but are of no importance in the absence of Marangoni effect.

**Evaporation and contact angle.** – As in the case of the original Voinov limit ( $J_0 = 0$ ), Eq. (6) must be completed by boundary conditions either at the vicinity of the contact line or far from it. Physically, at small scales, in the case of partial wetting, we have to look for solutions with vanishing height at a cut-off microscopic distance  $a$ . At large distance  $L$ , we will suppose that the interface has zero curvature.

As Eq. (6) cannot be integrated analytically, we propose here an ansatz of the solution in the limit of slowly variable interface slope that we will compare with a direct numerical simulation of the equation. Setting the following nondimensional variables  $X = x/x_0$  and  $H = h(x)/h_0$  with

$$x_0 = \left(\frac{2J_0}{V}\right)^2 (3\text{Ca})^{-\frac{2}{3}} \quad (7)$$

$$h_0 = \left(\frac{2J_0}{V}\right)^2 (3\text{Ca})^{-\frac{1}{3}} \quad (8)$$

Eq. (6) reads

$$H_{XXX} = \frac{1}{H^2} - \frac{X^{\frac{1}{2}}}{H^3}. \quad (9)$$

Considering that the slope of the interface  $\Theta = H_X$  is slowly variable and writing  $H(X) \approx X\Theta(X)$ , we can rewrite Eq. (9) as

$$\Theta_{XX} \approx \frac{1}{X^2\Theta^2} - \frac{1}{X^{\frac{3}{2}}\Theta^3} \quad (10)$$

Assuming that  $\Theta$  is equal to  $\Theta_e$  at given small  $X = A$  and does not deviate much from a mean value, we can get from Eq. (10) the following expression for  $\Theta(X)$

$$\Theta^3 = \Theta_e^3 - 3 \ln \frac{X}{A} + \frac{4}{\Theta_e} \left( \frac{1}{A^{\frac{1}{2}}} - \frac{1}{X^{\frac{1}{2}}} \right) + \alpha(X - A) \quad (11)$$

with constant  $\alpha$  ensuring the adequate boundary conditions  $\Theta_X(\Lambda) = 0$  (vanishing curvature of the interface at a given renormalized large distance  $\Lambda$ ). The details of the calculation are given in appendix together with a calculation of the errors due to the approximation.

In order to validate this ansatz, we performed direct numerical simulation of Eq. (9) (see Fig. 2). The agreement between the numerical simulation and the ansatz is very good. As a comparison, we also performed the numerical calculation of the Voinov case (that is with no evaporation:  $H_{XXX} = 1/H^2$ ) starting with the same *macroscopic* angle  $\Theta(\Lambda)$  as that found in the evaporative case and no curvature at  $X = \Lambda$ . For  $X > 1$ , both curves are very similar.

Note that in the limit  $\Lambda \rightarrow \infty$ , the constant  $\alpha$  vanishes and we can rewrite our ansatz, in dimensional quantities,

$$\theta^3(x) = \theta_e^3 - 9\text{Ca} \ln\left(\frac{x}{a}\right) + \frac{24\eta J_0}{\gamma \theta_e} \left( \frac{1}{a^{\frac{1}{2}}} - \frac{1}{x^{\frac{1}{2}}} \right) \quad (12)$$

In practical situations, let us first remark that for water, using  $J_0 = 10^{-9} \text{m}^{\frac{3}{2}} \cdot \text{s}^{-1}$ ,  $\eta = 10^{-3} \text{Pa} \cdot \text{s}$ ,  $\gamma = 7 \times 10^{-2} \text{N} \cdot \text{m}^{-1}$ , for a velocity  $V$  equal to  $1 \mu\text{m} \cdot \text{s}^{-1}$ ,  $x_0$  is of the order of  $3 \times 10^{-1} \text{m}$ , and  $h_0$  of the order of  $1 \times 10^{-3} \text{m}$ .

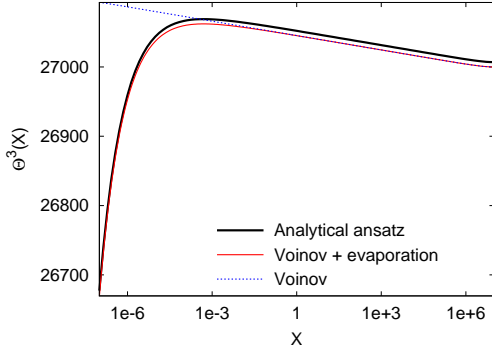


Figure 2: Plot of  $\Theta^3(X)$ . Comparison between the analytical ansatz (bold solid line) given by Eq. (11) and the numerical integration of Eq. (9) (normal line). The nondimensional microscopic length was chosen as  $A = 10^{-7}$ . As a comparison, we show the results of the numerical simulation of the Voinov case for the same *macroscopic* apparent angle (dotted line, see text). The agreement between the ansatz and the numerical simulation is very good. The effect of evaporation are significant for values of  $X$  lower than  $10^{-3}$ .

This means that in Fig. 2, the effects of evaporation are significant at distances from the contact line  $X < 10^{-3}$  that is actual values lower than  $10^{-4}$  m, for a velocity of  $1 \mu\text{m}\cdot\text{s}^{-1}$ . We can see that the modification of the shape of the interface is small provided that one defines properly the macroscopic apparent angle.

To be more specific, at large scale  $L$ , one can deduce the macroscopic angle  $\theta_M$  from the microscopic angle  $\theta_e$  using Eq. (12)

$$\theta_M^3 = \theta_e^3 - 9\text{Ca} \ln\left(\frac{L}{a}\right) + \frac{24\eta J_0}{\gamma\theta_e a^{\frac{1}{2}}} \quad (13)$$

The evaporation term appears to increase the macroscopic angle  $\theta_M$  compared to the Voinov situation ( $J_0 = 0$ ) in a proportion of  $\Delta\theta/\theta \simeq 8\eta J_0/(\gamma a^{\frac{1}{2}}\theta_e^4)$ . For a cut-off length  $a = 1$  nm, we have  $\Delta\theta/\theta \simeq 3 \times 10^{+3} J_0/\theta_e^4$ . For angle  $\theta_e = 10^{-1}$  rad and  $J_0 = 5 \cdot 10^{-9} \text{m}^{\frac{3}{2}} \cdot \text{s}^{-1}$  one obtains an increase in the macroscopic angle of 15% which is small but non negligible. In contrast, for high value angle, the evaporative effects are negligible and one can expect dramatic effects in the case of total wetting which will be the object of a further article.

Although the evaporative effects on the contact line are small but non negligible, they will have strong consequences on the deposit of colloidal particles as we will show in the following part of this article.

**Evaporation and Coating.** – Let us focus now on the effect of evaporation on the coating with a solute. Let us consider a droplet of a solution with a solute that is not volatile (a colloid or a polymer for instance). If the droplet is receding, because of evaporation, a solute can be deposited on the surface. Let us assume that the contact angle, while receding in the presence of evaporation, is not vanishing. In that case one can consider the respective effect of evaporation and motion of the droplet on the water flow. Eq. (4) shows that in the framework of the substrate, when  $V.h = J_0 \cdot x^{\frac{1}{2}}$ , the flux due to evaporation is exactly opposite to the flux due to the motion of the contact line. In this condition the flux of solution is vanishing. This occurs at a distance  $\ell_d$  (see Fig. 3) from the contact line given by:

$$\ell_d = \left(\frac{J_0}{V\theta}\right)^2 \quad (14)$$

A similar statement about the existence of a stagnation point near the tip of a pinned droplet under evaporation has evidenced by Deegan et al. [13] while measuring transport of solute.

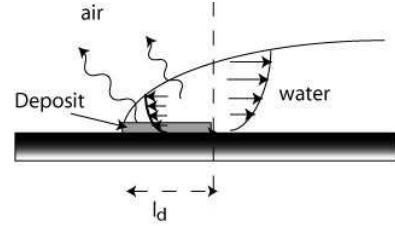


Figure 3: Influence of evaporation on the solute deposit

This distance is of the order of  $100 \mu\text{m}$  for a velocity of recession of the order of  $10 \mu\text{m}\cdot\text{s}^{-1}$ . Using this drying length  $\ell_d$ , it is straightforward to deduce the coating thickness. The solution trapped between the contact line and  $\ell_d$

will dry, and thus all the solute trapped in this domain will deposit on the substrate. Let  $\Phi$  be the volume fraction of non-volatile solute. The flux of solution in the frame of the contact line at  $\ell_d$  is  $V\Phi\theta\ell_d$ . The flux of solute in this frame after evaporation (or once the contact line has receded) is  $eV$  where  $e$  is the thickness of the coating supposed to be at a volume fraction of 1. These two fluxes are equal, leading to the relation between the thickness of the coating and the concentration of the solute:

$$e = \Phi\theta\ell_d = \frac{\Phi}{\theta} \left( \frac{J_0}{V} \right)^2 \quad (15)$$

It is interesting to remark that the thickness of the coating increases with the inverse of the square of the velocity, which is not intuitive. In fact for faster dip-coating, a different phenomenon occurs. If the solution does not have the time to dry just after the film formation, the Landau-Levich-Derjaguin theory has to be used or slightly modified when accounting for evaporation effects [14]. In that case the thickness of the film before drying is given by  $\text{Ca}^{\frac{2}{3}}\ell_{\text{cap}}$  where  $\ell_{\text{cap}}$  is the capillary length. Thus the thickness of the film after drying, neglecting flow in the film due to gravity, is thus given by :

$$e = \Phi \left( \frac{\eta V}{\gamma} \right)^{\frac{2}{3}} \ell_{\text{cap}} \quad (16)$$

In this more familiar regime, the coating thickness increases with the velocity. We can thus estimate the cross-over velocity for these two regimes, which corresponds to the situation where the velocity  $V_c$  is just small enough for the film to dry near the meniscus in a situation of dip coating. Using the two previous equations, one deduces that :

$$V_c = \left( \frac{\gamma^{\frac{2}{3}} J_0^2}{\eta^{\frac{2}{3}} \ell_{\text{cap}} \theta} \right)^{\frac{3}{8}} = \frac{\gamma^{\frac{1}{4}} J_0^{\frac{3}{4}}}{\ell_{\text{cap}}^{\frac{3}{8}} \eta^{\frac{1}{4}} \theta^{\frac{3}{8}}} \quad (17)$$

This velocity corresponds both to the appearance of a receding angle because drying is fast enough, but also to the minimum of the thickness of the coating that can be estimated as

$$e_{\text{min}} = \Phi \left( \frac{\eta J_0}{\gamma} \right)^{\frac{1}{2}} \frac{\ell_{\text{cap}}^{\frac{3}{4}}}{\theta^{\frac{1}{4}}} \quad (18)$$

which yields a thickness of about  $100\Phi$  nm, and a cross-over velocity of about  $10 \mu\text{m}\cdot\text{s}^{-1}$  for water solution (see Fig. 4) which corresponds to a capillary number  $\text{Ca} \simeq 10^{-6}$ . The existence of this minimum seems to be supported by preliminary experimental results [15].

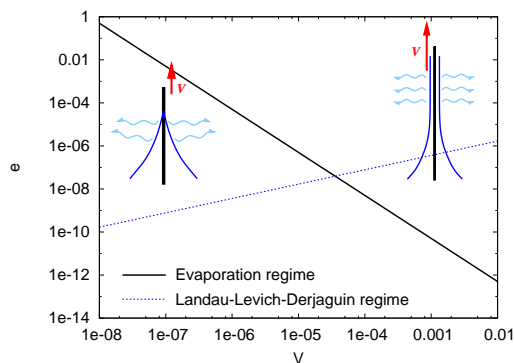


Figure 4: Coating thickness against contact line velocity for a water solution containing  $\Phi = 5\%$  of colloids in our evaporative regime and in Landau-Levich-Derjaguin regime.

Finally we see that the divergence of evaporation, if it does not strongly modify the shape of the interface in practical situations, is responsible for a minimum for the coating thickness as a function of velocity. This is probably one of the reasons why small thickness coating are never prepared with dip-coating but requires other techniques like spray or spin coating.

**Appendix.** – In this appendix, we show how to obtain the expression of the analytical ansatz given by Eq. (11). We start from Eq. (10) and integrate it once, keeping  $\Theta$  constant (full numerical simulations show that  $H(X) \simeq X\Theta(X)$  is an excellent approximation and that  $\Theta(X)$  varies slowly), so that we get

$$\Theta^2 \Theta_X = -\frac{1}{X} - \frac{2}{3} \frac{1}{\Theta X^{\frac{3}{2}}} + \alpha \quad (19)$$

with constant  $\beta$  insuring  $\Theta_X = 0$  at large given  $X = L$ . For boundary condition  $\Theta(A) = \Theta_e$ ,

one gets after integration of Eq. (19)

$$\frac{1}{3}(\Theta^3 - \Theta_e^3) = -\ln \frac{X}{A} - \frac{2}{3} \int_A^X \frac{1}{\Theta(Y)Y^{\frac{3}{2}}} dY + \alpha(X - A) \quad (20)$$

Once more, under the assumption that  $\Theta(Y)$  is slowly variable, we can substitute in the integral  $\Theta(Y)$  with  $\Theta_e$  which yields Eq. (11).

In order to obtain our ansatz, we resorted to the assumption that  $\Theta$  is a slowly variable. In the following, we now turn to the calculation of the main errors made through this approximation in the limit of infinite domain. The actual solution  $\theta_*$  of Eq. (10) in the dimensional form satisfies

$$(\theta_*)_{xx} = \frac{3Ca}{\theta_*^2} \frac{1}{x^2} - 6 \frac{\eta J_0}{\gamma} \frac{1}{\theta_*^3 x^{\frac{5}{2}}} \equiv F(\theta_*, x) \quad (21)$$

From Eq. (12), we can write  $\theta_{\text{ansatz}}^{-1} = \theta_e^{-1} g(x)$  with  $g(x) \simeq 1 + \frac{3Ca}{\theta_e^3} \ln \frac{x}{a} + 8 \frac{\eta J_0}{\gamma \theta_e^4} (x^{-\frac{1}{2}} - a^{-\frac{1}{2}})$  yielding at first order of the different contributions

$$\begin{aligned} F(\theta_{\text{ansatz}}, x) &\simeq \frac{3Ca}{\theta_e^2} \frac{1}{x^2} g^2 - 6 \frac{\eta J_0}{\gamma \theta_e^3} \frac{1}{x^{\frac{5}{2}}} g^3 \\ &\simeq (\theta_{\text{ansatz}})_{xx} \\ &+ \frac{3Ca}{\theta_e^2} \frac{1}{x^2} \left[ \frac{6Ca}{\theta_e^3} \ln \frac{x}{a} + 16 \frac{\eta J_0}{\gamma \theta_e^4} \left( \frac{1}{x^{\frac{1}{2}}} - \frac{1}{a^{\frac{1}{2}}} \right) \right] \\ &- 6 \frac{\eta J_0}{\gamma \theta_e^3} \frac{1}{x^{\frac{5}{2}}} \left[ \frac{9Ca}{\theta_e^3} \ln \frac{x}{a} + 24 \frac{\eta J_0}{\gamma \theta_e^4} \left( \frac{1}{x^{\frac{1}{2}}} - \frac{1}{a^{\frac{1}{2}}} \right) \right] \end{aligned} \quad (22)$$

All the constants present in the right-hand side of this expression are of order at least lower than  $10^{-7}$  which implies that the errors caused by our approximation are really small, which was confirmed by our numerical calculations (see Fig. 2).

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