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Dynamics of complete wetting liquid under evaporation

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Abstract. - The dynamics of a contact line under evaporation and total wetting conditions is studied taking into account the divergent nature of evaporation near the border of the liquid, as evidenced by Deegan et al. [Nature **389**, 827 (1997)]. Complete wetting is assumed to be due to Van der Waals interactions. The existence of a precursor film at the edge of the liquid is shown analytically and numerically. The length of the precursor film is controlled by Hamaker constant and evaporative flux. Past the precursor film, Tanner's law is generalized accounting for evaporative effects.

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Introduction. – Much work has been devoted to contact line dynamics (see [1–3] for reviews). One of the most difficult problem to address may be the case of total wetting, in which the affinity of the liquid for the solid is such that a "precursor film" develops and spreads ahead of the contact line. The properties of this film (length, thickness, profile) have been calculated in the eighties [4, 5] but the precursor film (in particular its thickness profile) has been observed and measured accurately only recently [6].

In the past decade, people showed a great interest in the dynamics of contact lines involving evaporation in addition to capillarity and

hydrodynamics. This interest is motivated on the one hand by specific applications (coating processes [7, 8], deposition of particles close to contact lines [9], heat exchangers (see [10] and references herein) and on the other hand by fundamental issues [11]. Most related experiments have been developed in the case of total wetting, where pinning/depinning on the substrate can be eliminated. By monitoring the evaporation of drops lying on a horizontal substrate [12], Poulard et al. evidenced remarkable power law behaviors with time of both apparent contact angle and drop radius whose exponents remain to be interpreted. In the latter paper, a model has been developed as well, which relates the macroscopic contact angle to the capillary

number by a generalized "Tanner's law" [13]. However this model neglects the divergence of viscous stresses at contact lines [14] and leads to a bit surprizingly very tiny precursor film whose length seems to be independent of the evaporation rate.

In the present work we reconsider the theoretical description of total wetting in the presence of evaporation. Using the same strategy as in a previous work of ours in partial wetting situation [7], we consider a divergent evaporation field at contact line similar to that evidenced by Deegan [15], and we solve the lubrication equations of the flow. The problem that we address here is of importance not only for understanding drop critical dynamics when the radius vanishes [12], but also for its potential applications to coating [8] in other flow geometries (dip coating, spin and roll coating [16]...).

The paper is organized as follows. We first present the problem and establish its governing equations. After discussing some orders of magnitude, we perform numerical resolutions of these equations. We then propose a small scale analytical solution governed both by evaporation and the disjoining pressure that matches a large scale logarithmic flow solution. We eventually find a generalized Tanner's law that links the apparent contact angle to the capillary number for both advancing and receding contact lines. For the first time to our knowledge, this analytical approach yields the calculation of the actual length of an evaporative precursor film together with the induced correction to the effective Tanner's law introduced previously by Poulard et al. [12].

Model and Equations. – The situation under study is suggested in Fig. 1. A liq-

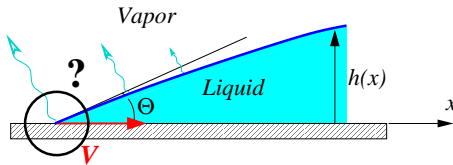


Figure 1: Notations of the problem

uid moves at a constant velocity V on a solid surface, both under the effect of a fluid mo-

tion linked to 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:

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

where $h(x)$ is the liquid thickness, η the liquid viscosity, and the pressure term reads

$$P = P_a + P_c + P_d = P_a - \gamma h_{xx} + \frac{\mathcal{A}}{2\pi h^3}, \quad (2)$$

P_a being the ambient pressure, P_c the capillary pressure and P_d the disjoining pressure (we assume van der Waals interactions) playing a role at the edge of the liquid. Both latter pressures read respectively

$$P_c = -\gamma h_{xx}, \quad P_d = +\frac{\mathcal{A}}{2\pi h^3}. \quad (3)$$

γ is the surface tension and $\mathcal{A} < 0$ the so-called Hamaker constant. For a liquid moving 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:

$$\frac{\partial}{\partial x} [h(\langle U \rangle - V)] + J(x) = 0 \quad (4)$$

to be combined with the relation $\langle U \rangle = \frac{\gamma}{3\eta} h^2 h_{xxx}$ found above. To go further, one now needs an approximation of the local evaporation rate distribution $J(x)$. For a sessile axisymmetric drop, Deegan [9, 15] assumed an analogy between the vapor diffusion in air and an electrostatic problem, the vapor concentration near the liquid surface being supposed to saturate at the mass concentration in air c^{sat} . In analogy with this work, we will assume that very near the edge of the liquid $J(x)$ diverges as $J(x) = J_0 x^{-(\pi/2-\theta)/(\pi-\theta)}$ where x is the distance to the edge of the liquid. This expression yields for very small values of angle θ : $J(x) \approx J_0/\sqrt{x}$ in which J_0 is given by $J_0 = \frac{D_g}{\sqrt{\lambda}} \frac{c^{\text{sat}}}{\rho}$ where D_g is the diffusion constant of evaporated solvent in air, and ρ its mass density. The length scale λ can be either the thickness of a diffusive boundary layer, or the typical

curvature of the liquid interface. For instance, for the sessile drops of in-plane radius R with low contact angle considered in Ref. [15] one has exactly $\lambda = 2R$. For a water drop of millimetric size evaporating in ambient air one has typically $J_0 \approx 10^{-9} \text{ m}^{\frac{3}{2}} \cdot \text{s}^{-1}$. Note that we are here treating the limit of a liquid evaporating in the presence of air, and not that of a liquid in the presence of its own vapour only, as in Ref. [10], in which the divergence of evaporation at contact line disappears.

After integrating once Eq. (4) upon x , one gets: $(\langle U \rangle - V)h = -2J_0\sqrt{x}$ that can be written as:

$$V = \frac{2J_0}{h}\sqrt{x} + \frac{\gamma}{3\eta}h^2h_{xxx} + \frac{\mathcal{A}}{6\pi\eta} \frac{h_x}{h^2} \quad (5)$$

The local thickness of liquid $h(x)$, is supposed to vanish or at least reach microscopic values at the tip of the liquid placed for simplicity at the location $x = 0$.

The physical meaning of this equation is that the recession of a liquid at a given velocity V is in fact due to both migration of liquid under the capillary and disjunction pressure gradient and to evaporation itself. This evaporation term will add new terms to the ordinary differential equation governing $h(x)$, considered years ago by Voinov [17], that reads in this specific case:

$$h_{xxx} = \frac{3\text{Ca}}{h^2} - \frac{6\eta J_0}{\gamma} \frac{\sqrt{x}}{h^3} - \frac{\mathcal{A}}{2\pi\gamma} \frac{h_x}{h^4} \quad (6)$$

where $\text{Ca} = \eta V/\gamma$ is the capillary number built upon the velocity V .

Setting the following nondimensional variables $X = x/x_0$ and $H = h(x)/h_0$ with

$$x_0 = \left(\frac{|\mathcal{A}|}{12\pi J_0 \eta} \right)^{2/3} \quad (7)$$

$$h_0 = x_0^{1/2} \times \left(\frac{|\mathcal{A}|}{2\pi\gamma} \right)^{1/4} \quad (8)$$

Eq. (6) reads

$$H_{XXX} = \text{Ca} \left(\frac{x_0}{h_0} \right)^3 \frac{1}{H^2} - \frac{X^{\frac{1}{2}}}{H^3} + \frac{H_X}{H^4}. \quad (9)$$

Setting $J_0 = 10^{-9} \text{ m}^{3/2} \cdot \text{s}^{-1}$, $\mathcal{A} = 10^{-21} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2}$, $\eta = 10^{-3} \text{ kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$ yields typical lengths $x_0 \simeq 100 \text{ nm}$ and $h_0 \simeq 2 \text{ nm}$. Note

that these values do not have the same order of magnitude as those recently found experimentally by Kahvehpour et al. [6]. We are in a totally different situation where the system undergoes evaporation. Moreover, changing \mathcal{A} and J_0 leads to substantial changes in the values.

Numerical results. – We now turn to the numerical study of our model. The equation describing our model is third order in derivative. We study this equation in the domain ϵ, L_{max} . The full resolution of this equation involves a set of three boundary conditions which are usually the values of H, H' and H'' at one given boundary point (ϵ or L_{max}). The main difficulty lies in choosing consistent boundary conditions. At macroscopic scale L_{max} , one can choose the curvature to vanish ($H_{XX}(L_{\text{max}}) = 0$) and the slope of the interface to be equal to a given value ($H_X(L_{\text{max}})$). We have no apriori indication on the exact value of $H(L_{\text{max}})$ to fulfill the set of boundary conditions. Conversely at microscopic scale ϵ , one can naturally choose the value of $H(\epsilon) = 1$ (starting at the minimal height given by Joanny and de Gennes [4] or that given by Kavehpour experiments [6]) and consider that we start with a flat precursor film which yields $H'(\epsilon) = 0$ but no indication on the value of $H''(\epsilon)$ can be inferred. Whatever the boundary we start from, one boundary condition is missing. In order to solve properly the equation, we have to resort to a shooting method.

In order to complete the set of two boundary conditions at one boundary, we have to choose one condition at the opposite side of the domain. Starting from ϵ , it is natural to assume that at L_{max} we will have $H''(L_{\text{max}}) = 0$. Conversely, starting from L_{max} , we will look for solutions with minimum height at ϵ .

The timestepping of our shooting method is based on adaptive Runge-Kutta method (see for instance Ref. [18]).

When starting from large distance L_{max} , no precursor film is found and at the tip of the liquid, one numerically recovers a parabolic power law profile (see Fig. 2) that can be found analytically (see below Eq. (10)).

Starting from a microscopic length. The cri-

terion at large distance is that the curvature vanishes. We obtain a profile with a precursor film connected to a slowly varying slope interface as can be seen in Fig. 2 in which we have calculated solutions with three different capillary numbers ($Ca = 10^{-7}, 0, = 10^{-7}$) respectively, receding, static and advancing situations.

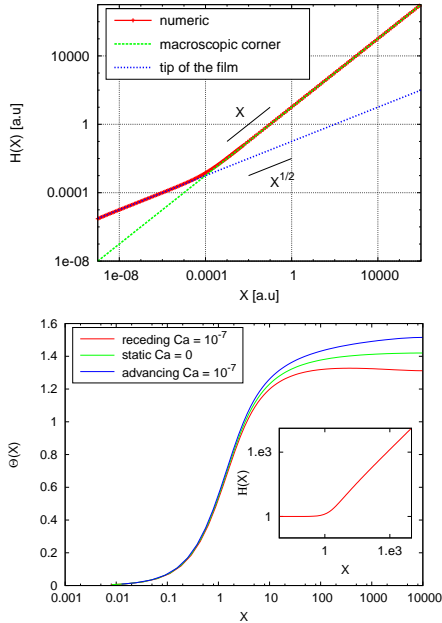


Figure 2: Top — Shooting starting from large distance A in arbitrary unit and assuming vanishing height at origin: plot of $H(X)$. Two distinct regimes are observed: linear and parabolic (see straight lines). Bottom — Shooting starting from microscopic distance and assuming vanishing curvature at large distance (here $X_{\max} = 10^4$): plot of angle Θ versus X (non dimensional unit). Inset: Corresponding $H(X)$ profile (receding case, same parameter): a macroscopic wedge is connected to a flat precursor film.

One can look for the values of $\Theta(L_{\max})$ at L_{\max} both in the advancing and receding cases. We show the results in Fig. 3. The macroscopic angle strongly depends on the capillary number and eventually vanishes in the receding case.

Analytical results. — From the observation of the numerical results, we can search for analytical results.

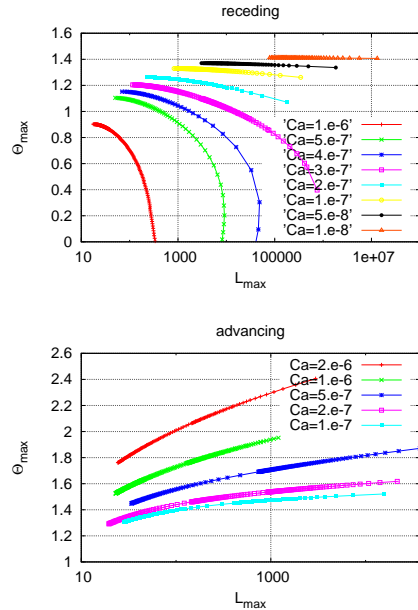


Figure 3: Given a capillary number Ca , we plot the values of Θ_{\max} at L_{\max} in the receding and advancing case.

Tip of the liquid. Searching for solutions to Eq. (6) vanishing at $x = 0$ by considering asymptotic expansion in power of x , one finds that the solution is at leading order $h(x) = \alpha\sqrt{x}$ with

$$\alpha^4 = \frac{2}{3\pi} \frac{|\mathcal{A}|}{\gamma} \quad (10)$$

Connecting this parabolic solution to a macroscopic corner $h_{\text{macro}}(x) = \theta x$ leads to the crossover length

$$\ell_{\text{cross}} \sim \frac{1}{\theta^2} \left(\frac{2}{3\pi} \frac{|\mathcal{A}|}{\gamma} \right)^{\frac{1}{2}} \quad (11)$$

Note that Poulard et al. [12] found the same scaling law. By inspection of the latter expressions, one can note that the evaporation term is absent while one expects a dependance on J_0 of the cross-over length ℓ_{cross} expected to be related to the existence of a precursor film. This solution, validated with numerical simulations presented previously, excludes the existence of a precursor film and is in contradiction with

the small angle assumption yielding the evaporation term we use in the framework of our model. Nevertheless, one can still consider this crossover length as being the parabolic tip of the precursor film as stated by Joanny and de Gennes [4].

Inside the precursor film (heuristic). At the tip, normally, one should expect zero height. However, as mentioned by Joanny and de Gennes [4], the minimum thickness of the precursor film is bounded from below by the static thickness $e = a(3\gamma/2S)^{1/2}$ with $a = (\mathcal{A}/6\pi\gamma)^{1/2}$ and $S = \gamma - (\gamma_{SL} + \gamma_{LV})$ being the spreading coefficient.

Following the idea that capillary forces can be neglected near the contact line where disjunction pressure effects are dominant, we can turn Eq. (5) into $V = \frac{2J_0}{h}\sqrt{x} + \frac{\mathcal{A}}{6\pi\eta}\frac{h_x}{h^2}$. This Bernoulli equation has the general solution

$$h(x) = \frac{\beta h_0 \exp\left[\frac{2}{3}\left(\frac{x}{x_0}\right)^{\frac{3}{2}}\right]}{1 + \beta \text{Ca} \frac{x_0^2}{h_0^3} \int_0^x \exp\left[\frac{2}{3}\left(\frac{y}{x_0}\right)^{\frac{3}{2}}\right] dy} \quad (12)$$

with constant β insuring the adequate liquid height at $x = 0$ ($\beta = 1$ corresponds to $h(0) = h_0$). The typical length of the tip of the film is x_0 . Note that at $\text{Ca} = 0$, one gets an elementary expression of the precursor film. There is no singularity for $\text{Ca} > 0$ (receding case) where as for $\text{Ca} < 0$ (advancing case), the denominator vanishes at a given value of x for given capillary number Ca . The bigger $|\text{Ca}|$, the closer to $x = 0$ the singularity occurs, which is reminiscent of a shortening of precursor film length while the liquid advances faster.

However, yet instructive, this solution does not satisfy the assumption that the capillary term (third order derivative of function f) can be neglected close to $x = 0$.

Inside the precursor film (rigorous approach). If we now consider that we start at $x = 0$ at height h_0 , assuming that the film starts flat, one can look for solutions to our model in term of a power series. As stated in the previous numerical section, in order to solve our model, we need the prescription of the boundary conditions at $x = 0$ and we will take advantage of the degree of freedom yielded

by the value of the second order derivative at $x = 0$.

In these conditions, one can calculate the solution to Eq. (9) that can be written as a power series which first terms read

$$H(X) = 1 + \lambda_1 X^2 + \frac{c}{2} X^3 - \frac{8}{105} X^{\frac{7}{2}} + \frac{1}{12} \lambda_1 X^4 + o(X^4) \quad (13)$$

with $c = \text{Ca}(x_0/h_0)^3$ and $\lambda_1/2$ the free curvature parameter (depending on c). We can see that this solution is in excellent agreement with the numerical simulations (see Fig. 4) and that the c -dependance of coefficient λ_1 scales numerically as (data not shown)

$$\lambda_1 = \lambda_1^0 \left(1 - \frac{11}{3}c\right) \quad (14)$$

λ_1^0 being the value at zero capillary number.

Inside the liquid corner. The region we focus on is now the liquid bulk. Following the same procedure as in our previous work [7], we consider that the slope of the interface $\Theta = H_X$ is slowly variable and writing $H(X) \approx X\Theta(X)$, we can rewrite the non-dimensional Eq. (9) as

$$\Theta_{XX} \approx 3\text{Ca} \left(\frac{x_0}{h_0}\right)^3 \frac{1}{X^2\Theta^2} - \frac{1}{X^{\frac{5}{2}}\Theta^3} + \frac{1}{\Theta^3 X^4} \quad (15)$$

Assuming that the contributions due to disjunction pressure are negligible and that Θ is equal to Θ_m at given microscopic $X = \lambda$ and does not deviate much from a mean value, we can get from Eq. (15) the following expression for $\Theta(X)$

$$\Theta^3 = \Theta_m^3 - 9\text{Ca} \left(\frac{x_0}{h_0}\right)^3 \ln \frac{X}{\lambda} + \frac{4}{\Theta_m} \left(\frac{1}{\lambda^{\frac{1}{2}}} - \frac{1}{X^{\frac{1}{2}}}\right) + \alpha(X - \lambda) \quad (16)$$

with constant α ensuring the adequate boundary conditions $\Theta_X(L_{\max}) = 0$.

In Fig. 4, we can see the plot of numerical shooting simulations together with our analytical results (13) and (16). The agreement is excellent in both cases (precursor and macroscopic parts).

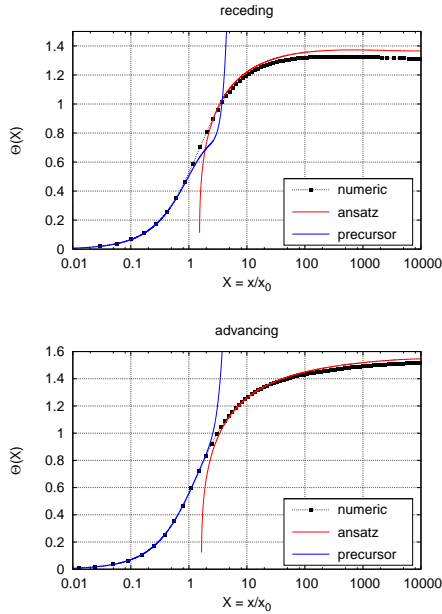


Figure 4: Matching of numerical simulations with analytical precursor solution (see Eq. (13)) and far from zero where we recover the ansatz of partial wetting (see Eq. (16)). The agreement is excellent for both receding and advancing cases.

Provided these results one can propose a Cox-Voinov-like wetting law that reads

$$\Theta^3 = \Theta_m^3 - 9Ca \left(\frac{x_0}{h_0} \right)^3 \ln \frac{L_{\max}}{\lambda} + \frac{4}{\Theta_m} \frac{1}{\lambda^{\frac{1}{2}}} \quad (17)$$

Fig. 5 shows the numerical calculations together with the analytical prediction. The agreement is very good. The errors are less than 5%, except at high Ca in the receding case.

Conclusion. – We have proposed a detailed analysis of contact line dynamics in the presence of both evaporation and total wetting. We recovered the solution found by Poulard *et al.*, but clearly evidenced another solution that seems better adapted to the description of the precursor film, and gives a more realistic expression of the modified Tanner’s law. We stressed the fact that our description combines two divergences at contact line: that of viscous stresses [14] and that of evaporation [9], which make this problem really non trivial and

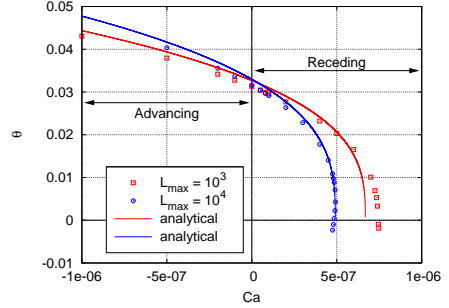


Figure 5: Wetting laws for $L_{\max} = 10^3$ and $L_{\max} = 10^4$. Analytical results from our ansatz together with numerical calculations. We can see by inspection of the figures that the agreement is really good.

difficult to address. It would be now interesting to examine how this modified Tanner’s law would affect the dynamics of their evaporating drops on a solid, and to see if it explains the remaining discrepancy between their first model and experimental data. Experiments are also underway in our group with liquid evaporating on another more viscous liquid [Hoang and Berteloot, unpublished].

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