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DYNAMICS OF A COMPLETE WETTING LIQUID UNDER EVAPORATION

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Wetting phenomena are extensively studied from a experimental to a theoretical point of view (see Refs. [1, 2] for reviews) and much attention has been drawn recently to the case of the dynamics of liquid droplet under evaporation [3–9]. In this paper, we propose a model of a contact line under evaporation and total wetting conditions taking into account van der Waals interactions and the divergent nature of evaporation near the border of the liquid evidenced by Deegan et al. [3]. We apply this result to study the dynamics of an evaporating droplet in complete wetting situation.

1. Low constant speed model

In this section, we study the shape of the free surface of an evaporating liquid corner moving at a *constant* velocity V along a totally wetting solid surface, both under the effect of a fluid motion $U(x, z)$ linked to pressure gradient, and of an evaporation flux $J(x)$. The edge of the liquid is set at $x = 0$ (see Fig. 1(a) for notations).

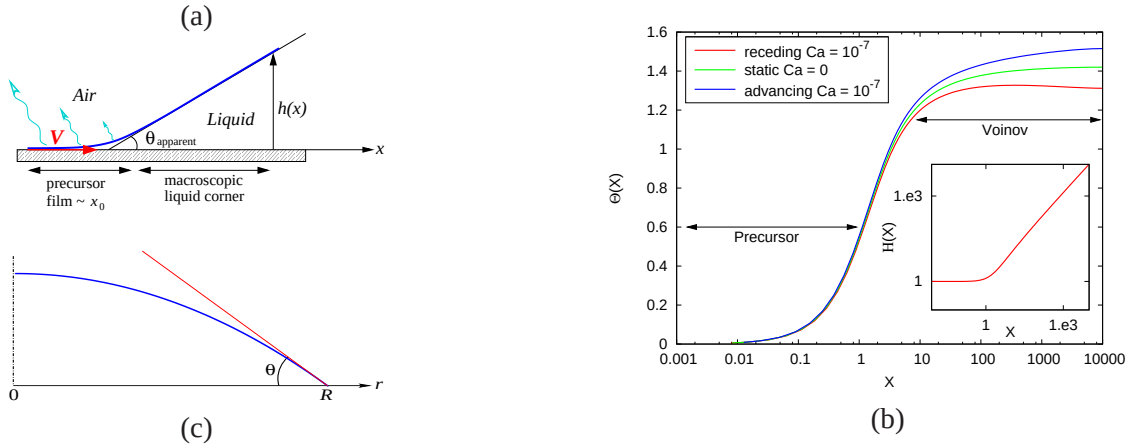

Figure 1: (a) Notations for the model studied in Section 1 of a liquid moving at constant speed V on a totally wetting substrate and undergoing evaporation. (b) Numerical calculation of the slope of the liquid interface $\theta(x) = h'(x)$ for different capillary numbers. Inset: profile of the liquid height. We used dimensionless units $X = x/x_0$, $H = h/h_0$ and $\Theta = (x_0/h_0)\theta$. (c) Notations used in Section 2: R is the droplet radius and θ the apparent contact angle of the spherical cap.

Standard lubrication theory in the limit of low Reynolds numbers and small interface slope leads to a mean local velocity of the liquid given by: $\langle U \rangle = \frac{1}{h}\int_0^h U(x,z)\,\mathrm{d}z = -\frac{h^2}{3\eta}\frac{\partial P}{\partial x}$ where $h(x)$ is the liquid thickness, η the liquid viscosity, and the pressure term reads $P = P_a + P_\mathrm{c} + P_\mathrm{d}$ with P_a, 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 $P_\mathrm{c} = -\gamma h_{xx}$ and $P_\mathrm{d} = +\frac{\mathcal{A}}{6\pi h^3}$; γ is the surface tension and $\mathcal{A} < 0$ the 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:

$$\frac{\partial}{\partial x}\left[h\left(\langle U\rangle - V\right)\right] + J(x) = 0 \tag{1}$$

to be combined with the previous expression of $\langle U \rangle$.

One now needs an approximation of the local evaporation rate distribution $J(x)$. For a sessile axisymmetric drop, Deegan [4] assumed an analogy between 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 $c^{\rm sat}$. In analogy with this work, we 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. This yields for very small values of angle θ: $J(x) \approx J_0/\sqrt{x}$ in which J_0 is given by $J_0 = \frac{D_g}{\sqrt{\lambda}} \frac{c^{\rm sat}-c^\infty}{\rho}$ where D_g is the diffusion constant of evaporated liquid 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 contact line. For instance, for the sessile drops of in-plane radius R with low contact angle considered in Ref. [4] one has exactly $\lambda = 2R$. For volatile alkanes or silicon oil drops of millimetric size evaporating in ambient air one typically has $J_0 \approx 10^{-9}\ {\rm m}^{\frac{3}{2}} \cdot {\rm s}^{-1}$. Note that we are here treating the limit of a liquid evaporating in the presence of air. It is also important to note that the activity of a thin film of liquid is approximately that of the bulk up to the last molecular layer of liquid. Thus the divergence of the evaporative flux holds at the border of the precursor film. In our purely diffusive model, Marangoni and thermal gradients will be neglected.

After integrating once Eq. (1) with respect to x, one gets: $(< U > -V)h = -2J_0\sqrt{x}$ that can be written as:

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

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 displacement of a liquid at velocity V involves migration under capillary and disjunction pressure gradient together with evaporation itself. This adds new terms to the ordinary differential equation governing $h(x)$, considered years ago by Voinov [10], that reads in this specific case:

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

where ${\rm Ca} = \eta V/\gamma$ is the capillary number built upon the velocity V (${\rm Ca} > 0$ in the receding case and ${\rm Ca} < 0$ in the advancing case).

In the framework of this model, it is convenient to set a typical horizontal length scale x_0 and a typical height h_0 that respectively read

$$x_0 = \left(\frac{|\mathcal{A}|}{12\pi J_0 \eta}\right)^{\frac{2}{3}}, \qquad h_0 = x_0^{\frac{1}{2}} \times \left(\frac{|\mathcal{A}|}{2\pi\gamma}\right)^{\frac{1}{4}} = \frac{|\mathcal{A}|^{\frac{7}{12}}}{(2\pi)^{\frac{7}{12}}(6\eta J_0)^{\frac{1}{3}}\gamma^{\frac{1}{4}}} \tag{4}$$

Setting $J_0 = 10^{-9}\,{\rm m}^{3/2} \cdot {\rm s}^{-1}$, $\mathcal{A} = 10^{-19}\,{\rm kg} \cdot {\rm m}^2 \cdot {\rm s}^{-2}, \eta = 10^{-3}\,{\rm kg} \cdot {\rm m}^{-1} \cdot {\rm s}^{-1}$ yields typical lengths $x_0 \simeq 2\,\mu{\rm m}$ and $h_0 \simeq 30\,{\rm nm}$. These values have the same order of magnitude as those found experimentally by Kavehpour et al. [11] in the advancing regime *without* evaporation for ${\rm Ca} = 3 \times 10^{-4}$. The horizontal length x_0 corresponds in our model to the typical length of the precursor film at zero velocity.

We can analytically solve Eq. (3) and find the expression of profile of the liquid interface, confirmed by numerical simulations (See Fig. 1(b)) [8]. From the latter expression, one can deduce the following expression of the apparent contact angle θ

$$\theta^3 = \theta_{\rm m}^3 - 9{\rm Ca}\left(\log\frac{\mathcal{L}_{\rm macro}}{\ell_{\rm micro}} + 1\right) + \frac{24 J_0 \eta}{\gamma\theta_{\rm m}}\frac{1}{\sqrt{\ell_{\rm micro}}} \tag{5}$$

or in a more straightforward way

$$\theta^3 = (1 + \frac{4}{\sqrt{3.4}})\,\theta_{\rm m}^3 - 9{\rm Ca}\left(\log\frac{\mathcal{L}_{\rm macro}}{\ell_{\rm micro}} + 1\right). \tag{6}$$

where $\ell_{\rm micro} \simeq 3.4x_0$ is a microscopic length corresponding to the length of the precursor film, $\mathcal{L}_{\rm macro}$ a macroscopic length and

$$\theta_{\rm m}^3 = \left(\frac{h_0}{x_0}\right)^3 = \left(\frac{2\pi}{\gamma^3|\mathcal{A}|}\right)^{\frac{1}{4}} 6\eta J_0 \tag{7}$$

corresponding the apparent contact angle at zero velocity [9].

2. Case of an evaporating sessile droplet

We will now apply the previous model to the study of an evaporating sessile droplet in total wetting condition. As already stated, the expression of the evaporative flux of a spherical cap of liquid of radius R, in the limit of small contact angle θ (see Fig. 1(c)), reads $J(r) = j_0/\sqrt{R^2 - r^2}$ with the following correspondence with previous section: $x = R - r$, $J_0 = j_0/\sqrt{2R}$ and $\mathrm{Ca} = -\eta\dot{R}/\gamma$. Substituting directly these expressions into Eqs. (6) and (7) yields the following wetting law without any adjustable parameters (but a logarithmic contribution)

$$\theta^3 = \frac{A}{\sqrt{R}} + B\dot{R} \tag{8}$$

with

$$A = 6\,(\frac{\pi}{2})^{\frac{1}{4}} \left(1 + \frac{4}{\sqrt{3.4}}\right) \frac{\eta j_0}{\gamma^{\frac{3}{4}}|\mathcal{A}|^{\frac{1}{4}}} \qquad \text{and} \qquad B = 9\frac{\eta}{\gamma}\left(\log\frac{\mathcal{L}_{\rm macro}}{\ell_{\rm micro}} + 1\right). \tag{9}$$

This is the same kind of expression as that found by Poulard et al. in a previous work using other arguments [5].

The volume of a spherical cap at small contact angle θ reads $V = \frac{\pi}{4}R^3\theta$. Moreover mass conservation reads $\frac{\mathrm{d}V}{\mathrm{d}t} = -\int_0^{2\pi}\int_0^R J(r) r\,\mathrm{d}r\,\mathrm{d}\varphi = -2\pi j_0 R$. Combining these two results yields the following relation

$$3R\theta\dot{R} + R^2\dot{\theta} = -8j_0. \tag{10}$$

With Eqs. (8) and (10) we then obtain a closed set of ordinary differential equations of variables R and θ that we will now study.

Given the initial conditions $R_{\rm i} = R_{|t=0}$ and $\theta_{\rm i} = \theta_{|t=0}$, we can see using Eq. (8) that, whether $(\theta_{\rm i})^3\sqrt{R_{\rm i}}$ is larger or smaller than constant A, the droplet starts spreading then retracts, or directly starts with retraction. Experiments show that, if $t_{\rm f}$ is the time at which the droplet vanishes, the radius of a droplet of completely wetting alkane on mica follows the scaling $R(t) \sim (t_{\rm f} - t)^\alpha$ with exponent α close to $1/2$ [5, 6]. During the retraction sequence, the contact angle θ has little variations up to late times before total evaporation [5]. Suppose that $R(t)$ scales like $(t_{\rm f} - t)^\beta$, Eq. (8) implies that $\beta = 2/3$ if θ is to remain bounded, which is not the case as we will see in the following.

We have performed numerical simulations of Eqs. (8) and (10). Results are shown in Fig. 2. The dynamics of spreading followed by the retraction sequence of the droplet is recovered with correct orders of magnitude compared with experiments. As in the experiments [5], we recover the steep decrease of the contact angle during the spreading and the beginning of the retraction. Radius vanishes at a given final time $t_{\rm f}$. In contrast, contact angle θ vanishes at time $t'_{\rm f} < t_{\rm f}$ (the spherical cap then becomes flat) and eventually becomes negative which is physically incorrect. This vanishing angle singularity is intrinsic to our wetting law model but experiments by Cazabat at al. also show sharp decrease of the contact angle at late times.

If we look carefully at the decay of the radius $R(\tau)$ with time $\tau = t_{\rm f} - t$ (see Fig. 2 (Right)), one can see that the radius follows two regimes with distinct exponents. At the beginning of the retraction, $R(\tau) \sim \tau^\alpha$ with $\alpha \simeq 0.33$, then, once the values of θ becomes negative, we have $R(\tau) \sim \tau^\beta$ with $\beta \simeq 0.11$. These scalings are in disagreement with the experiments where exponents are close to $1/2$. Nevertheless, by choosing a shifted reference final time $T_{\rm f}$ (see inset of Fig. 2 (Right)), one can recover an exponent $\alpha' \simeq 0.45$ in agreement with experiments, as did Poulard et al. in their numerical simulations as well [5].

Note that our wetting law (8) contains a logarithmic term depending on a macroscopic scale $\mathcal{L}_{\rm macro}$, at which contact angle is defined. Replacing the latter length scale by a fraction of radius R modifies the wetting law

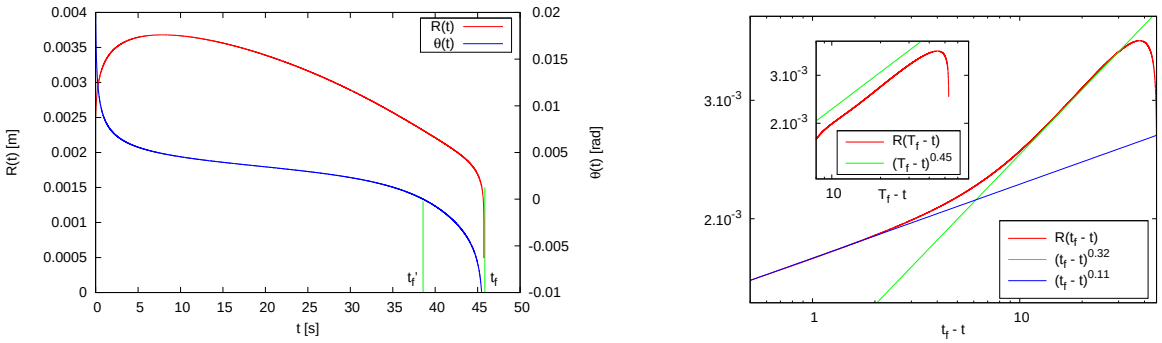

Figure 2: (Left) Plot versus time $t_{\rm f} - t$ of the radius R of an evaporating totally wetting droplet together with the angle θ. Time $t_{\rm f}$ corresponds to the time of vanishing radius whereas time $t'_{\rm f}$ if the time at which angle θ gets to zero. (Right) Plot of the dynamics of radius R in log-log scale. Depending on the choice of reference final time $T_{\rm f}$, one obtains a different scaling and recovers that found in experiments.

and shall delay the singularity (the smaller $\mathcal{L}_{\rm macro} \equiv R$, the smaller constant B). We performed numerical simulation of the dynamics using this modified wetting law and find no major changes in the dynamics: the final time of singularity is slightly shifted but the scaling exponents remain the same.

3. Conclusions

In this paper, we have proposed a model for completely wetting liquid under evaporation. A wetting law relating the apparent contact angle to the speed of the contact line was proposed and used to numerically study the dynamics of an evaporating droplet in total wetting conditions. This model correctly describes the early stages of spreading and retraction of a droplet. However, at late times, the contact angle vanishes before the radius itself vanishes, yielding non-physical scalings. Usual dynamical scalings found in experiments can only be recovered by extrapolating a final reference time.

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