

NONLINEAR DYNAMICS OF NON-ISOTHERMAL THIN FILMS AND DROPLETS WITH EVAPORATION AND CONDENSATION ON A RIGID WALL

Pierre Colinet, Séverine Rossomme and Alexey Rednikov

Université Libre de Bruxelles, Chemical Engineering Department, C.P. 165/67

50, av. F.D. Roosevelt, B-1050 Bruxelles, Belgium

Tel : +32-2-6503561, Fax : +32-2-6502910, Email : pcolinet@ulb.ac.be

ABSTRACT

Evaporation/condensation processes of thin films of pure liquids lying on heated or cooled horizontal homogeneous and flat substrates are studied thanks to a lubrication-type equation describing the evolution of their deformable free surface. The one-sided model is restricted to a pure vapour phase at constant pressure, and includes the interfacial kinetic resistance to evaporation, the capillary and disjoining pressures, together with the thermodynamic influence of these last two effects on the saturation conditions. Besides flat liquid films, which are characterized for different forms of the disjoining pressure isotherm, the model also admits drop-like solutions, whose evaporation/condensation dynamics is explored in some details. Note that the analysis is limited to cases where an adsorbed (or precursor) film surrounds the droplets, whatever the regime considered. For a heated plate and attractive molecular interactions with the substrate (favouring complete wetting), the droplets appear as connections between a macroscopic quasi-spherical region and the adsorbed film, and evaporate with slowly receding apparent contact line. For a cooled substrate and molecular interactions promoting partial wetting, provided the initial film profile exceeds some nucleation threshold, similar drop-like solutions are observed after some time, though now growing with slowly advancing contact line. Coalescence of droplets and transition to film condensation is also observed after a certain time.

INTRODUCTION

Thin liquid films and droplets undergoing evaporation or condensation are quite commonly encountered in nature and in industrial applications, such as in coating and drying processes, in sprays ... Moreover, as the latent heat of phase change is typically large, the evaporation/condensation cycle also appears to be much more efficient in transporting energy than conduction or convection. Consequently, there is an intensive research nowadays in the field of two-phase cooling technologies for high-density electronic equipment, where the removal of dissipated heat may in some cases represent the limiting factor preventing further improvement of overall performances.

On the modeling point of view, a number of unanswered fundamental questions remain, however. For instance, the behavior of liquid films undergoing dewetting and droplet formation on a heated or cooled surface (with respect to the saturation temperature corresponding to the prevailing vapor pressure) is far from being completely understood. In the vicinity of contact lines formed by macroscopic liquid zones (such as thick films and droplets) on the substrate, micro-scale effects enter into play, such as non-equilibrium or kinetic effects, disjoining pressure, influence of free surface curvature on saturation conditions, ... Even though their role is typically negligible in purely macroscopic situations, omitting consideration of these effects leads to important inaccuracies (and in some cases even to unphysical divergences) as far as the determination of meaningful quantities is concerned (overall rate of phase change, dewetting speed, final thin-film patterns ...).

Note that the importance of such small-scale effects has already been pointed out quite some time ago by various

authors, and some models have been successfully developed in the past to answer some of these questions [1-6]. This line of research is typically based on the analysis of lubrication-type equations with appropriate disjoining pressure potentials accounting for the intermolecular forces between the liquid and the substrate. In some cases, these thin-film equations allow solutions in the form of macroscopic droplets in contact with adsorbed films of very small thickness lying on the rigid wall [6].

In this presentation, we reconsider some of these models and examine them further, using a combination of analytical results and numerical simulations. The focus is on the determination of the rate of phase change and on nonlinear dynamics in various situations : (i) evaporating droplets where the apparent contact angle formed with the substrate is due to a dynamic equilibrium between spreading and evaporation; (ii) drop-wise and film condensation on a cooled plate.

The paper is organized as follows : after a brief description of the theoretical model, some of its classical steady solutions in the form of evaporating contact lines are described. Then, numerical simulations of the evaporation process of a sessile droplet on a heated plate are presented, followed by simulations in the opposite case of a cooled plate, i.e. when condensation occurs.

THIN FILM EVOLUTION EQUATION

In two spatial dimensions, denoting the horizontal coordinate by x , the vertical coordinate by z and time by t , we consider the dynamics of a thin liquid film in contact with a flat substrate at $z = 0$ and with its pure vapor at $z = \xi(x, t)$. The vapor is maintained at a constant pressure p_v . Denoting the corresponding saturation pressure by T_{sat} , a non-

equilibrium driving force for phase change is the superheat (or undercooling) $\Delta T = T_w - T_{sat}$, where T_w is the substrate temperature. For $\Delta T > 0$, the film is expected to evaporate, though it is well known that an adsorbed film may still remain on the substrate with a thickness such that intermolecular forces between the liquid and the solid substrate shift the equilibrium temperature by the amount ΔT . Using the linearized Kelvin's law $\Delta T = T_{sat} \Pi(\xi)/\rho\mathcal{L}$ (see Refs [4-9]), where ρ is the liquid density, \mathcal{L} its latent heat, and when the disjoining pressure $\Pi(\xi)$ is assumed to be of the simplest non-polar long-range form $A\xi^{-3}$, we readily get the equilibrium adsorbed film thickness as $\xi_a = (A T_{sat}/\rho\mathcal{L} \Delta T)^{1/3}$. Clearly, the Hamaker constant A must be positive (promoting complete wetting) for such a residual film to exist.

As negative values of A and ΔT will also be considered in what follows, we select as vertical length scale $[z]$ the quantity $\xi_0 = |A T_{sat}/\rho\mathcal{L} \Delta T|^{1/3}$, and define "flags" $s = \pm 1$ and $\theta = \pm 1$ by $A = s|A|$ and $\Delta T = \theta|\Delta T|$. The horizontal scale will be selected such as to balance disjoining pressure with capillarity [9], associated with the interface curvature. Specifically, we choose $[x] = \xi_0^2/\sqrt{3}a$, where $a = (|A|/\gamma)^{1/2}$ is the molecular length scale introduced by de Gennes [10]. The time scale is then conveniently defined by $[t] = \mu \xi_0^5/3|A|a^2$, as seen hereafter.

The analysis is based on the lubrication approximation, i.e. on the hypothesis that the ratio $\varepsilon = [z]/[x] = (\sqrt{3} a)/\xi_0$ remains much smaller than unity. Interestingly, the same condition is also required for the continuum hypothesis to hold, i.e. the film should not reach molecular scale. Then, both hypotheses are found to be satisfied when $|\Delta T|$ is sufficiently small.

Besides the lubrication and continuum assumptions, other basic hypotheses underlying the model are that the Marangoni and vapor recoil effects can be neglected (which is justified in Refs [7,9]), together with thermal conduction, shear stresses and viscous pressure variations in the vapor ("one-sided" model). Omitting details of the derivation for conciseness (see e.g. Refs [1-8] and [9] for the particular scaling used here), the evolution equation for the dimensionless film thickness finally reads

$$\partial_t \xi + E J + \partial_x q = 0 \quad (1)$$

where the evaporative mass loss is given by

$$J = \frac{\theta - \Omega}{K + \xi} \quad (2)$$

and the total horizontal flux is

$$q = \frac{\xi^3}{3} \partial_x \Omega \quad (3)$$

In these expressions, Ω is (minus) the excess pressure in the liquid, induced by disjoining and capillary forces

$$\Omega = \pi(\xi) + 3 \partial_x^2 \xi \quad (4)$$

Note that in Eq. (4), the dimensionless disjoining pressure is kept in general form in order to treat different cases in the following, though its long-range part should always be of the form $s \xi^{-3}$ according to our choice of scales. Apart for the

above-defined flags $s = \pm 1$ and $\theta = \pm 1$, another important dimensionless parameter is the evaporation number

$$E = \frac{\nu \lambda T_{sat}}{3 \rho \mathcal{L}^2 a^2} \quad (5)$$

where ν is the liquid kinematic viscosity and λ the liquid thermal conductivity. Finally, while the kinetic resistance to evaporation is quantified by the number K . If the kinetic expression used for the phase change rate is of the Hertz-Knudsen-Schrage form, we get

$$K = \frac{2-f}{f} \sqrt{\frac{\pi R T_{sat}}{2 M} \frac{\lambda T_{sat}}{\rho_v \mathcal{L}^2 \xi_0}} \quad (6)$$

where f is the accommodation coefficient, R is the universal gas constant, M is the molecular mass of the liquid, and ρ_v is the density of the vapor. Note that in principle, a finite thermal conductivity of the substrate can also be accounted for by adding an additional resistance $d_w \lambda/\lambda_w \xi_0$ in Eq. (6), where d_w and λ_w are the solid wall thickness and thermal conductivity, respectively.

DYNAMICS OF FLAT FILMS

For flat films $\xi = \xi(t)$, Eqs (1-4) reduce to

$$\partial_t \xi = E \frac{\pi(\xi) - \theta}{K + \xi} \quad (7)$$

which can be easily interpreted by representing its right-hand-side as a function of ξ , as done in Fig. 1 for two different cases. First, we consider $s = +1$, hence $\pi = \xi^{-3}$, for which we expect an equilibrium adsorbed film to exist for a superheated plate (i.e. $\theta = +1$). Indeed, Fig. 1 shows that $\partial_t \xi > 0$ for $\xi < 1$ while $\partial_t \xi < 0$ for $\xi > 1$. Hence, there is only one equilibrium thickness at $\xi = 1$ and it is stable. It is also easy to see that the case $s = +1$, $\theta = -1$ corresponds to a film thickness growing without bound by condensation of the saturated vapor phase. The case $s = -1$, $\theta = 1$, on the other hand, has no equilibrium thickness either and leads to continuous thinning of the film by evaporation down to $\xi = 0$ (where our approach breaks down).

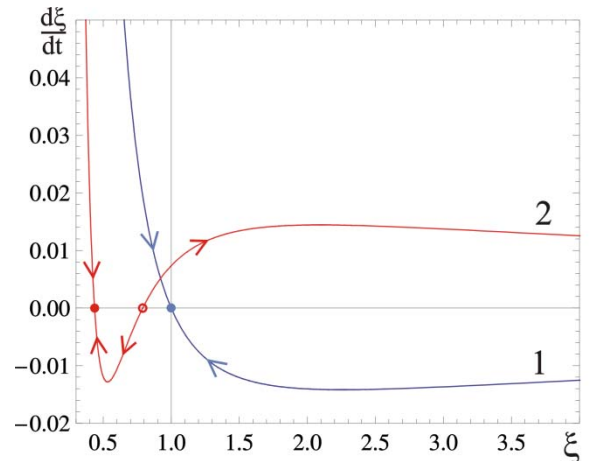


Figure 1 : determination of equilibrium film thicknesses and their stability for flat films of ammonia at $T_{sat} = 300$ K with $|\Delta T| = 1$ K ($E = 0.124, K = 5.74$). Case 1 (blue) : $\pi = \xi^{-3}$ and $\theta = 1$. Case 2 (red) : $\pi = -\xi^{-3} - R \xi^{-4}$ with $R = -0.4$ and $\theta = -1$.

Finally, for the case $s = -1$ and $\theta = -1$, there is a steady solution at $\xi = 1$, but it is unstable : starting with $\xi > 1$, condensation occurs and ξ grows without bound. If $\xi < 1$ initially, the film evaporates down to zero, once again. Therefore, the value $\xi = 1$ appears as a nucleation threshold for film condensation, as studied in more details in the last section of this paper. Note that in order to avoid continuous thinning of the film as encountered in this last case, it will appear convenient to consider a repulsive contribution in the disjoining pressure, i.e. $\pi = -\xi^{-3} - R \xi^{-4}$. This case is represented in Fig. 1 for $R = -0.4$, which shows that besides the nucleation threshold (now shifted to $\xi \approx 0.791$), there is a stable equilibrium value at $\xi \approx 0.436$.

NON-EQUILIBRIUM CONTACT LINE PROFILES

Next, we numerically consider steady solutions of Eq. (1), connecting the adsorbed film on the left (say, at $x = 0$) with a constant positive slope region on the right (limited for numerical reasons at some sufficiently large $x = L$). This is accomplished by using an accurate finite difference scheme, with imposed boundary conditions $\xi(0) = 1, \xi'(0) = 0, \xi(L) = \xi_{max} \gg 1, \xi''(L) = 0$.

Such steady solutions are indeed found, and were actually obtained earlier (see e.g. [4] in the context of heat pipe modeling). As illustrated in Fig. 2, the evaporation flux calculated from Eq. (2) presents a sharp peak at the location of the contact line. Even though the latter occurs on a very small distance, it generally represents a significant contribution to the overall evaporation rate (hence, to the heat transfer coefficient), which points to the importance of correctly modeling small-scale effects for estimating the performances of heat exchangers [4,11].

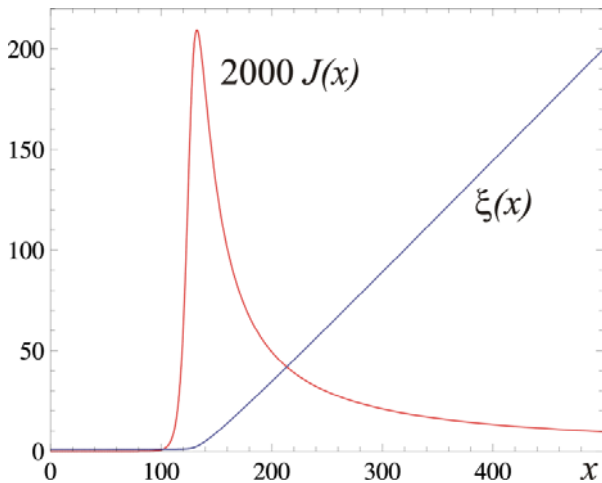


Figure 2 : steady film thickness profile (blue curve) and corresponding evaporation flux (red curve) for ammonia at $T_{sat} = 300\text{K}$ with $|\Delta T| = 1\text{K}$ ($E = 0.124, K = 5.74$), $s = \theta = 1, R = 0$, and $\xi_{max} = 200$. Domain size is $L = 500$, with 500 mesh points.

As the expression selected for the disjoining pressure favors complete wetting, the contact angle visible on Fig. 2 clearly results from a dynamic equilibrium between spreading and evaporation, i.e. it is an apparent contact angle, depending on ΔT . Its value for Fig. 2 is $b = \xi'(L) \approx 0.556$, which corresponds quite well with the analytical formula obtained in the limit $E \rightarrow 0$ by matched asymptotic expansions [9]. Note also that due to our choice of scale, the actual apparent slope is in fact $b \varepsilon \approx 0.322$, i.e. the apparent angle is about 18° .

EVAPORATION OF SESSILE DROPLETS

Now, starting with a sufficient initial mass $m = \int_0^L \xi dx$ of fluid localized within a limited portion of the domain (e.g. near its center), and with periodic boundary conditions, evaporating droplets may be studied, as depicted in Fig. 3. Whatever the initial shape of the “droplet”, it evolves rapidly to a nearly spherical cap (more precisely, parabolic in the lubrication approximation) shrinking slowly in time. Hence, the apparent contact line is not steady anymore but now slowly recedes as time progresses.

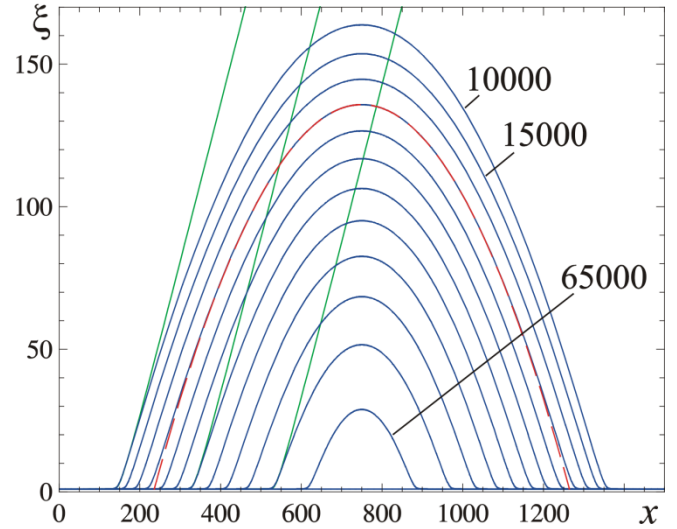


Figure 3 : simulation of the evaporation of an ammonia droplet, at $T_{sat} = 300\text{K}$ with $|\Delta T| = 1\text{K}$ ($E = 0.124, K = 5.74$), $s = \theta = 1$, and $R = 0$. Domain size is $L = 1500$, with 1500 mesh points. Time is indicated for some droplet profiles. The red dashed curve represented for $t = 25000$ is the osculating parabola at the corresponding droplet apex. The green profiles reproduce the steady contact line profile calculated in Fig. 2, with some shift along x .

Still, as shown in Fig. 3, the steady profiles calculated in the previous section compare fairly well with droplet shapes in the region where they join with the adsorbed film, and even more so for large droplets where a significant part of the free surface lies outside the domain of intermolecular forces with the substrate. In this “macroscopic” domain, the drop is very close to a parabolic cap, as also visible in Fig. 3 (see the red dashed curve). The evolution always leads to complete droplet disappearance, though leaving the substrate covered by an adsorbed microscopic film.

DROP-WISE CONDENSATION

Finally, we consider the opposite case of a cooled plate ($\theta = -1$). For $s = 1$ and $R = 0$ (complete wetting at equilibrium), condensation occurs in the form of a flat film growing without bound, as already noted above. More interesting is the situation where the long-range part of the disjoining pressure favors dewetting, i.e. $s = -1$. In this case, as argued in our study of flat film solutions, we need to consider a repulsive contribution to the disjoining pressure, here chosen in the form $\pi = -\xi^{-3} - R \xi^{-4}$ with $R = -0.4$. Then, there is a nucleation threshold, i.e. condensation will occur provided initial fluctuations of the density of vapor molecules near the substrate are such that the film thickness exceeds $\xi \approx 0.791$, at least locally. At the contrary, regions of

the film where this threshold is not reached are expected to evaporate, down to the stable film thickness $\xi \approx 0.436$.

As a study of the dynamics of thermodynamic fluctuations (i.e. nucleation kinetics) is beyond the scope of the present work, and in order to illustrate some interesting aspects of the drop-wise condensation regime, we select a particular initial condition in the form of the simple profile $\xi(t = 0) = 1 + 0.5 \cos[2\pi(x/L - 0.5)]$, i.e. exceeding the nucleation threshold in the center of the simulation domain, but not near its boundaries. Three phases of the subsequent evolution of the film profiles are represented in Fig. 4 : (A) droplet nucleation, where the shape of the film is still dependent upon the selected initial condition; (B) quasi-spherical droplet growth; (C) droplet coalescence with neighboring droplets and transition to film condensation.

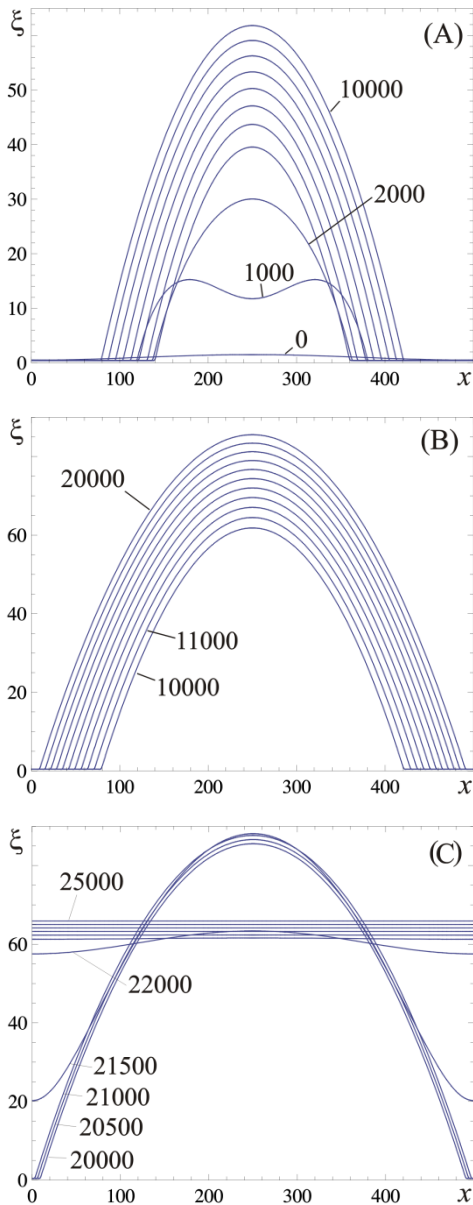


Figure 4 : three different stages of drop-wise condensation of ammonia at $T_{sat} = 300\text{K}$ with $|\Delta T| = 1\text{K}$ ($E = 0.124, K = 5.74$) and $\theta = -1$ on a partly wetted substrate ($s = -1, R = -0.4$). (A) : nucleation; (B) : spherical growth; (C) : coalescence and transition to film condensation. The size of the periodic domain is $L = 500$, with 1500 mesh points. Time is indicated for some of the film profiles.

Note that as the simulation domain is periodic, the growing droplet actually coalesces (at $t \approx 21000$) with a chain of

equally spaced identical neighbors, such that there is a quite abrupt transition to film condensation. In reality, the transition is more gradual, as was checked using less symmetric initial conditions (two droplets or more).

As a conclusion, several micro-scale physical mechanisms of films and droplets evaporation/condensation processes can be studied within lubrication-type models incorporating at least capillarity and disjoining pressure (and their effect on the saturation conditions), together with the kinetic resistance to evaporation. Moreover, some analytical results are available in some limiting cases [2,5,9], and it appears that other predictive theories can be build on some of the observations made above (spherical cap, quasi-steady contact line motion), which will be explored in more details in future works.

ACKNOWLEDGMENTS

This work was partly funded by the European Space Agency MAP and PRODEX programmes, and by the Communauté Française de Belgique through the ARCHIMEDES project (ARC 04/09-308). PC and SR gratefully acknowledge financial support of the Fond de la Recherche Scientifique – F.N.R.S., and of the Fond pour la Formation à la Recherche dans l’Industrie et l’Agriculture – F.R.I.A., respectively.

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