

SIMULATIONS OF RUPTURE IN THIN FILMS OF EVAPORATING LIQUIDS

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ABSTRACT

Evolution of dry patches in a thin film of a volatile liquid on a uniformly heated plate is investigated in the framework of a lubrication-type model. The effects of surface tension, evaporation, thermocapillarity, and disjoining pressure are taken into account. Dry areas on the plate are modeled by isothermal microscopic films, which are in thermodynamic equilibrium with the vapor. For non-polar liquids such equilibrium is achieved due to van der Waals forces. Simulations indicate formation of a well-defined capillary ridge around a growing dry patch and show increase in the contact line speed with time. For polar liquids the microscopic film is formed by combined action of van der Waals and electrical double layer forces, the capillary ridge is very small and the contact line speed quickly approaches a constant value. Numerical simulations demonstrate that the proposed model is capable of describing a number of complicated phenomena observed in dewetting of evaporating films.

INTRODUCTION

Moving contact lines in liquid-air systems have been studied extensively. However, a related problem of motion of a contact line between solid, liquid and vapor phase of the same liquid received much less attention. This problem is important for many applications such as micro heat pipes, microfluidic actuators, and spray cooling. Of particular interest for the present study is contact line motion during formation and growth of dry patches in thin evaporating films.

Theoretical investigations of dewetting in thin evaporating films [1,2] suggest that the dynamics of dry patches in polar liquids is determined by the interplay between long-range van der Waals forces and short-range contributions to the disjoining pressure from the electrical double layers. Schwartz et al. [1] accounted for both contributions in their simulations of dewetting in thin films of volatile liquids in the framework of a

simplified evaporation model. Lyushnin et al. [2] used a more elaborate model but did not consider the effects of heat transfer in the film and thermocapillary stresses at the vapor-liquid interface.

Significant progress in understanding the effects of evaporation on viscous flow near contact lines has been made in several studies of steady menisci in contact with heated surfaces [3,4]. Dry areas on heated surfaces are modeled in these studies by microscopic adsorbed films which are in thermodynamic equilibrium with both solid and vapor phases due to van der Waals forces. The contact line is then defined as the region of rapid change of interfacial curvature, i.e. the front between "wet" and "dry" parts of the substrate. This approach was originally developed for steady contact lines and was incorporated into a model of unsteady viscous flow in a recent study of axisymmetric spreading of volatile droplets on heated surfaces [5].

In the present study we describe liquid flow and heat transfer in evaporating films using the general framework of the previous studies [3-5], but our model of disjoining pressure accounts for contributions from both van der Waals forces and electrical double layers. The latter is significant for polar liquids, such as water, on most substrates. The effects of disjoining pressure, thermocapillary stresses, and evaporation intensity on an isolated growing dry patch are investigated. Furthermore, interaction of growing dry patches in evaporating liquid films is studied.

FORMULATION

We consider a thin film of a volatile liquid of density ρ and viscosity μ on a heated rigid plate. The standard one-sided model of evaporation allows us to neglect all dynamical processes in the vapor. The plate temperature is elevated above

the equilibrium saturation temperature at the vapor pressure, T_S^* ; the latter is used as the temperature scale. We use the ratio of the surface tension at the saturation temperature to the length scale in the horizontal direction, σ_0 / R , as the pressure scale. The characteristic velocity U is determined from the interfacial energy balance:

$$U = \frac{kT_S^*}{\rho\ell R}, \quad (1)$$

where ℓ is the latent heat of vaporization and k is the thermal conductivity of the liquid. We define the capillary number as

$$C = \mu U / \sigma_0$$

and develop our mathematical model based on the assumption that the capillary number is a small parameter.

Formulation of the governing equations and boundary conditions for viscous flow and heat transfer in the film is straightforward [5] and therefore is not repeated here. A lubrication-type approach for evaporating films on heated surfaces has been formulated in [5] based on the assumption that the film thickness scales as $C^{1/3}R$. The two-dimensional version of the evolution equation for film thickness h derived in [5] can be written in the form:

$$h_t + J + \frac{1}{3} \nabla [h^3 \nabla (\Delta h + \Pi)] + \frac{M}{2} \nabla [h^2 \nabla (Jh)] = 0 \quad (2)$$

where Π is the disjoining pressure specified below, derivatives are taken with respect to Cartesian coordinates x and y ; both axii are directed along the heated plate. The evaporative flux is expressed in terms of the film thickness and its second derivative as

$$J = \frac{T_0 - \delta(\Delta h + \Pi)}{K + h}. \quad (3)$$

Here the nondimensional substrate temperature T_0 is defined in terms of its dimensional value T_0^* according to

$$T_0 = \frac{T_0^* - T_S^*}{C^{1/3} T_S^*}.$$

The parameters K and δ are defined in [5]; the former measures the significance of non-equilibrium effects at the vapor-liquid interface, the latter determines the effect of changes in the liquid pressure on the equilibrium saturation temperature.

Let us now discuss the physical meaning of different terms in equation (2). The second term on the left hand side of equation (2) represents evaporative mass loss, the third term is due to viscous flow driven by a combination of the capillary and disjoining pressure gradients, and the fourth term is a contribution from the Marangoni stresses. The modified Marangoni number is defined by

$$M = \frac{T_S^*}{\sigma_0} \left| \frac{d\sigma}{dT} \right|, \quad (4)$$

the surface tension is assumed to be a decreasing linear function of temperature. Equation (2) is the key equation in our analysis. Once it is solved for the film thickness h , all other field variables are known.

For polar liquids used in many experiments, e.g. for water on mica surface, the expression for the disjoining pressure is written in the form

$$\Pi = S \exp(-\chi h) + \varepsilon / h^3. \quad (5)$$

This formula allows us to describe uniform microscopic films formed by the combined action of long-range and short-range forces. S is the scaled spreading coefficient defined in [2], χ is the ratio of the initial film thickness and the Debye length, and ε is the scaled Hamaker constant for the van der Waals part of the disjoining pressure.

Shapes of dry patches observed in experiments with evaporating films are often quite complicated, but the basic physical effects contributing to their evolution can be understood using the one-dimensional version of (2). Let us first assume that the film thickness is a function of x and t only and solve the evolution equation numerically on an interval $[0, L]$ using a finite-difference approach. BDF method from the standard *DVODE* solver is used to describe the interface evolution in time numerically.

Let us now specify the boundary conditions for equation (2). We note that the value $x=L$ corresponds to the slowly and uniformly drying region of the film, which implies zero first and third derivatives. Near $x=0$, the solid surface is assumed "dry" from the macroscopic point of view, i.e. it is covered with a microscopic adsorbed film where the evaporative mass flux is suppressed by van der Waals forces. Thickness of this equilibrium film h^* is found based on equation (3) from the condition of zero mass flux ($J=0$) across the interface.

Since the film is flat at $x=0$, all derivatives have to be zero. This was relatively easy to satisfy for steady contact lines: an ordinary differential equation for the interface profile was solved using a shooting method. However, for unsteady interface evolution considered in the present work the number of boundary conditions for the evolution equation is limited and so it is not clear a priori how to ensure that all derivatives are zero near $x=0$. A remarkable feature of the numerical solution illustrated below is that the microscopic film remains flat near $x=0$ when only two boundary conditions are specified in the form:

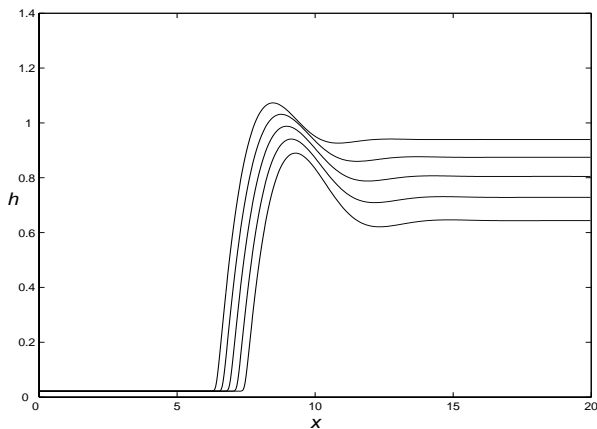
$$h(0) = h^* \quad h_x(0) = 0.$$

The initial condition is a discontinuous function equal to h^* for $[0, L/3]$ and equal to 1 on the remaining two thirds of the interval.

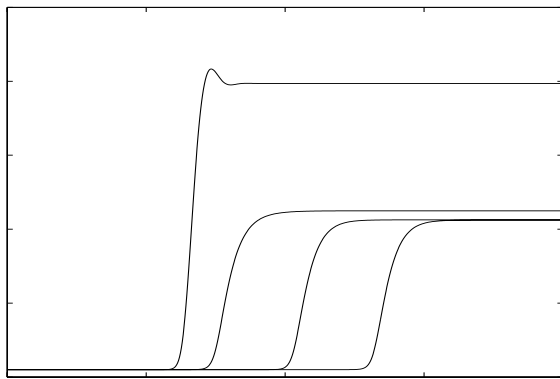
RESULTS AND DISCUSSION

Let us first study liquid-vapor interface evolution in non-polar liquids by running the simulation with $S=0$ in the expression for the disjoining pressure given by equation (5). After a very

short transient period the solution becomes smooth and evolves further on relatively slow time scales. Snapshots of typical interface shapes are shown in Fig. 1a for $L=20$ and 600 mesh points for $\delta = 10^{-2}$, $\varepsilon = 10^{-4}$, $T_0 = 0.1$. Formation of the capillary ridge observed in experiments is clearly seen in the simulations as well. The region of interface deformation is localized, curvature is very high near the dry area. Far away from it the film simply dries out by evaporation in a uniform fashion. The adsorbed film thickness is constant. We find that the dependence of contact line position on time is almost linear which agrees with the experimental studies of dry-out. The contact line speed increases slightly with time, which can be explained by a higher intensity of evaporation in films of smaller thickness at the late stages of dry-out.



a.



b.

FIG 1. Snapshots of interface deformation for 2D growing dry patches for non-polar (a) and polar (b) liquids; $K=0.02$, $M=0$.

Let us now consider polar liquids and use the appropriate form of the expression for the disjoining pressure, equation (5) with $S=1$ and $\chi = 10.9$. We choose parameter values that are relevant for experimental studies of dry-out in polar liquids, as discussed in [2]. The initial condition is again a discontinuous function that jumps from the unit thickness to the adsorbed film value. Typical results are illustrated in Fig. 1b. Initially the evolution is similar to the case of non-polar liquids shown above: the thicker part of the film decreases its height by

evaporation and capillary ridge is formed ahead of the moving contact line. However, at the later stages of evolution, the presence of electrical double layer results in rapid decrease of thinning rate of the film and significant decrease in the height of the capillary ridge. The latter in fact becomes very small. The motion of the contact line can then be describes as propagation of a front between two different equilibrium values of film thickness and the contact line speed becomes essentially constant. This regime has been studied in [2] in the framework of a slightly different model of evaporating films.

Thermocapillary effect can have a significant influence on dewetting in evaporating films. Since thermocapillary stresses are coupled to temperature field in the liquid, they cannot be described in the framework of models that do not include heat transfer in the film. The present model is free from this limitation: the lubrication-type equation (2) provides a consistent description of thermocapillary stresses in terms of the modified Marangoni number, M . An interesting feature of the present simulation results for non-zero M is that the effect of thermocapillarity on the contact line speed can be different depending on film thickness. For thicker films, the contact line speeds up due to Marangoni effect, while for thinner films thermocapillarity has the opposite effect. This is illustrated in Fig. 2 for $M=2$ (solid line), where both effects are captured at different stages of film evolution (dashed line corresponds to $M=0$). The speed-up of the contact line is not difficult to explain: it has to do with the fact that temperature near the contact line is higher and so Marangoni flow tends to speed up the removal of liquid. In order to understand the slow-down observed for thinner films, we investigated the interface shape for different values of M and observed that liquid tends to accumulate in the capillary ridge. This accumulation results in a significant reduction of the evaporation rate and thus slows down the contact line.

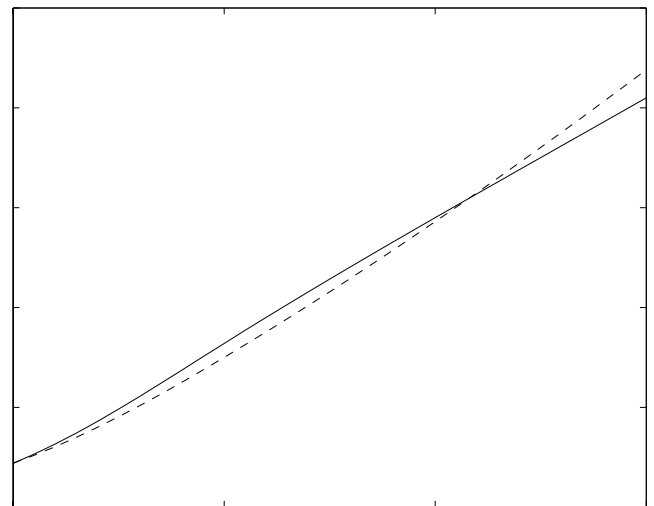


FIG 2. Contact line speed for different values of the modified Marangoni number: $M=0$ (solid line), $M=2$ (dashed line)

Let us now study formation and interaction of dry patches using the full two-dimensional numerical solution of the differential equation (2) for film thickness. Significant potential of disjoining pressure models for such simulations has been

demonstrated in the literature in the framework of simplified evaporation models [1]. In the simulations discussed below we assume the liquid to be non-polar, i.e. choose the expression for disjoining pressure that includes only van der Waals forces, although similar results can be obtained for polar liquids. Computational domain is a 40 by 40 square box.

We start by considering a single dry patch. The initial condition for the simulation is chosen as an axisymmetric step-function that jumps from the ultra-thin film to a macroscopic film of uniform thickness. The vapour-liquid interface becomes rather smooth on a very fast time scale and then propagates without changing its shape significantly. A typical snapshot of the dry patch is shown in Fig. 3. This dynamics is similar to that discussed in 2D context. We note that the characteristic capillary ridge is formed ahead of the boundary of the expanding dry area. The rate of expansion can be recorded from the numerical simulation based on the position of the contact line.

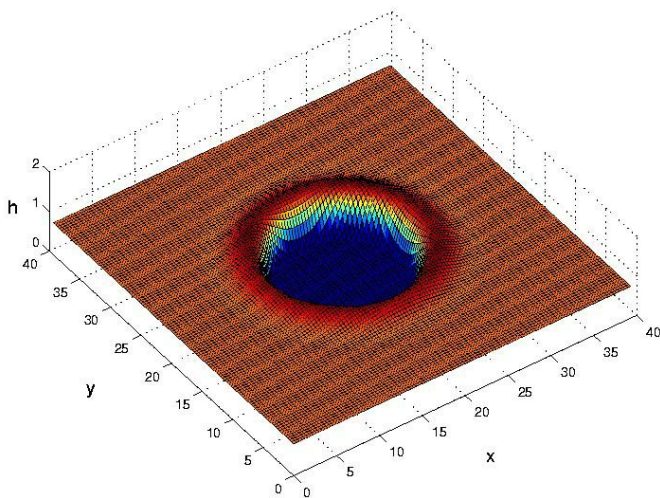


FIG. 3 Snapshot of an expanding axisymmetric dry patch.

An important advantage of the description of contact line proposed in the present study is that it allows one to simulate topological changes in films with many dry areas of arbitrary shape without any special subroutines for tracking contact lines. In order to illustrate this we consider interaction and merger of dry patches into a single dry area. The results of simulations for the two patches are presented in Fig. 4. Snapshots of contact lines are shown at equal time intervals. As a result of interaction, both patches clearly change their shape. Initially, interaction slows down growth of each dry patch. This stage is followed by rapid acceleration of fronts towards each other until the dry areas merge completely. This rapid dynamics can be explained by the decrease of the amount of liquid in the film between the patches. If one would try to impose a fixed contact angle condition at the contact line, this merger process would be rather difficult to describe. However, the present method allows us to carry out the simulation without specifying contact angles. In principle, the value of the dynamic contact angle can be defined based on the present set of numerical results.

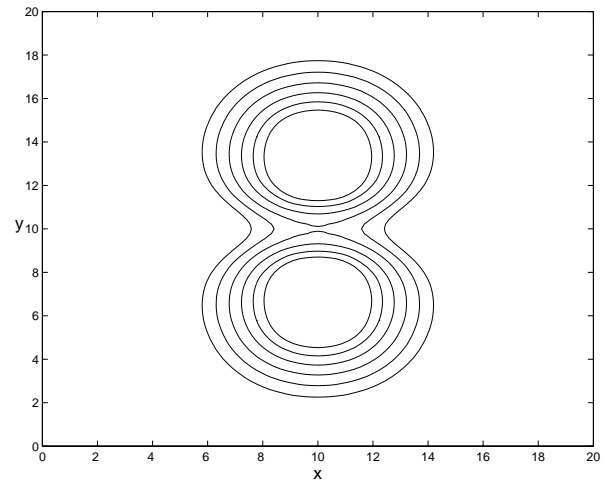


FIG. 4. Snapshots of contact line for interacting dry patches that merge together to form a single dry area.

We note that merger of the dry areas is easily handled by the code without any numerical difficulties which clearly indicates the significant potential of the moving contact line model, developed in [5] and extended to polar liquids in the present work, for simulations of complicated wetting phenomena in evaporating liquid films. The present approach is somewhat analogous to phase field methods for simulations of moving interfaces.

CONCLUSIONS

Dewetting in evaporating liquid films is characterized by nucleation of localized macroscopically dry patches. Several investigations suggested that these dry areas are in fact covered by microscopic films which are in equilibrium with the vapor due to disjoining pressure. In the present work, this idea is incorporated in a carefully developed model of viscous flow, heat transfer, and evaporation in the film around growing dry patches. We demonstrate that the model can be used to describe complicated evolution of a two-dimensional interface in three-dimensional space and is capable of handling topological changes in the system, e.g. merger of two dry patches.

We have found two different scenarios for growth of dry patches. For non-polar liquids, the equilibrium microscopic film is formed due to van der Waals forces and contact line speed slightly increases with time as the dry patch grows. For polar liquids the equilibrium in the adsorbed film is due to a combination of van der Waals forces and formation of electrical double layers and the contact line speed quickly approaches a constant value.

Simulations indicate that capillary ridges are formed ahead of growing dry patches. The ridge is more well-defined for non-polar liquids and provides a possible physical mechanism for an instability of the moving contact line which is indeed observed in experiments. Thermocapillary forces are shown to decrease the expansion rate of the dry patch if the film is sufficiently thin. For thicker films, Marangoni stresses tend to speed up expansion since they assist in removal of liquid from the regions near the dry area. Studies of two interacting dry patches indicate that at high separation distances the patches slow each other down, while rapid dynamics is observed as they come closer and finally merge.

ACKNOWLEDGMENTS

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