# SPREADING AND EVAPORATION
# OF LIQUID DROPS ON SOLIDS

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## ABSTRACT

We consider a volatile liquid droplet on a uniformly heated horizontal surface. We use lubrication theory to describe the effects of capillarity, thermocapillarity, vapor recoil, viscous spreading, contact-angle hysteresis, and mass loss on the behavior of the droplet. A new tri-junction condition, which takes into account the effect of mass loss, is derived and used. We derive an evolution equation for steady and unsteady drop profiles and solve for small and large capillary number. In the steady evaporation case, the steady contact angle is larger than the advancing contact angle. In the unsteady case, effects which tend to decrease (increase) the contact angle promote (delay) evaporation. In the large capillary number limit, we use matched asymptotics to describe the droplet profile; away from the contact line the shape is determined by initial conditions and bulk mass loss, while near the contact line surface curvature and slip are important.

## INTRODUCTION

Many processing systems involve tri-junctions at which phase transformations occur. Czochralski, and other meniscus-defined, crystal growth configurations are examples. They also appear in enclosed configurations such as directional solidification. An important instance of tri-junction behavior involves a contact line across which evaporation/condensation occurs. For example, the behavior of the meniscus is critical in the heat transfer properties of a heat pipe, where a liquid layer is used to remove heat from a hot surface. There has been much theoretical and experimental work done on such systems (e.g. Ripple, 1993; Sujanani and Wayner, 1992; Wayner, 1993; Moosman and Homsy, 1980).

V

J(x,t)          J(x,t)

J(x,t)                          J(x,t)

h(x,t)    z    L
                         θ(t)
                                    X
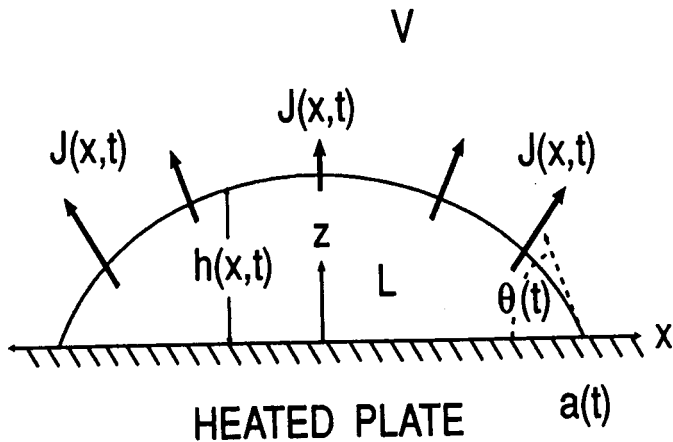
HEATED PLATE          a(t)

Figure 1: THE TWO-DIMENSIONAL EVAPORATING DROPLET.

Ehrhard and Davis (1991) analyzed the behavior of a non-isothermal liquid droplet on a uniformly heated horizontal surface and described the effects of capillarity, thermocapillarity, gravity, and viscous spreading on the dynamics of the droplet. They found that thermocapillarity retards (promotes) spreading when the substrate is heated (cooled). Ehrhard (1993) performed experiments on both isothermal and non-isothermal droplets and found good agreement with the theoretical predictions of Ehrhard and Davis (1991).

In the present work, we consider a volatile liquid droplet on a uniformly heated horizontal surface. We use lubrication theory to describe the effects of capillarity, thermocapillarity, viscous spreading, and mass loss on the behavior of the droplet. The evaporation model and the small slope analysis is analogous to that of Burelbach, et al. (1988) for continuous films; however, in the present case there is a contact-line region which requires additional attention. The current work extends that of Ehrhard and Davis (1991) to the competition between the effects of evaporation and the tendency of the drop to spread or recede.

FORMULATION

We consider a two-dimensional droplet on a uniformly heated horizontal surface as shown in figure 1. The contact line is given by $x = a(t)$, the contact angle by $\theta(t)$, and the liquid-vapor interface by $z = h(x,t)$. The bottom plate, $z = 0$, is uniformly heated resulting in an evaporative mass flux, $J(x,t)$.

We use a one-sided model of evaporation analogous to Burelbach, et al. (1988), where we neglect the vapor phase except where the vapor density is multiplied by the vapor velocity. Using a lubrication approximation applicable to thin droplets, we obtain an evolution equation for the droplet profile, $h(x,\tau)$,

## Table 1: Nomenclature

| | |
|---|---|
| $a_0$ | initial droplet radius |
| $\bar{C}$ | capillary number |
| $\bar{E}$ | evaporation number |
| $h_0$ | initial droplet height at center |
| $K$ | non-equilibrium parameter |
| $K'$ | dimensional non-equilibrium constant |
| $k$ | thermal conductivity of liquid |
| $L$ | latent heat of vaporization |
| $M$ | Marangoni number |
| $m$ | mobility exponent |
| $\Delta T$ | temperature difference |
| $\beta$ | slip coefficient |
| $\beta^*$ | dimensional slip length |
| $\gamma$ | linear thermocapillarity constant |
| $\eta$ | measure of viscous spreading |
| $\theta_A$ | advancing contact angle |
| $\theta_R$ | receding contact angle |
| $\nu$ | kinematic viscosity of liquid |
| $\bar{\rho}$ | density ratio |
| $\rho_L$ | liquid density |
| $\rho_V$ | vapor density |
| $\sigma_0$ | reference surface tension |

$$h_\tau + \frac{\bar{E}}{K+h} + \frac{\partial}{\partial x}\left[\bar{C}^{-1}h^2\left(\beta + \frac{1}{3}h\right)h_{xxx}\right.$$

$$\left. + MK\frac{h\left(\beta + \frac{1}{2}h\right)h_x}{(K+h)^2} + \frac{2\bar{E}^2}{\bar{\rho}}\frac{h^2\left(\beta + \frac{1}{3}h\right)h_x}{(K+h)^3}\right] = 0 \ . \tag{1}$$

The scales for time, horizontal lengths, and vertical lengths are $a_0 h_0/\nu$, $a_0$, and $h_0$, respectively. Also

$$\bar{E} = \frac{k\Delta T a_0}{\rho_L \nu L h_0}, \quad K = \frac{1}{K'}\frac{k}{h_0 L}, \quad \bar{C} = \frac{\rho_L \nu^2 a_0^3}{\sigma_0 h_0^4}, \quad \beta = \frac{\beta^*}{h_0}, \quad M = \frac{\gamma \Delta T h_0^2}{\rho_L \nu^2 a_0}, \quad \bar{\rho} = \frac{\rho_V a_0^3}{\rho_L h_0^3}. \tag{2}$$

Equations related to equation (1) have been derived by other authors (e.g. Greenspan, 1978; Hocking, 1981; Hocking, 1983; Burelbach, et al., 1988; Ehrhard and Davis, 1991). This equation is subject to initial conditions, boundary conditions, a contact-line condition, and the global mass balance condition.

Empirical studies (see Dussan V., 1979) on the spreading behavior of nonvolatile liquid droplets have led to the use of a constitutive relation between fluid velocity at the contact

line, $u_{CL}$, and the contact angle given by $u_{CL} = \eta f(\theta)$, where $f(\theta)$ is an increasing function of $\theta$ given by

$$f(\theta) = \begin{cases} (\theta - \theta_A)^m & \text{for } \theta > \theta_A \\ 0 & \text{for } \theta_R < \theta < \theta_A \\ (\theta - \theta_R)^m & \text{for } \theta < \theta_R \end{cases} \tag{3}$$

where $\eta$ and $m$ are empirically determined constants (in general the value of $\eta$ may have different values for $\theta > \theta_A$ than for $\theta < \theta_R$; however, for simplicity, we take a single value). Measured values have this form. We shall presume that this form persists down to micron scale where effective slip occurs. From the mass-balance condition evaluated at the contact line and from the above constitutive relation we obtain the contact-line condition,

$$a_\tau(\tau) = -\frac{\bar{E}}{K\theta(\tau)} + \bar{\eta}f(\theta(\tau)) \tag{4}$$

where $\bar{\eta} = (\eta/\nu)(h_0^{m+1}/a_0^m)$. We see here that the speed of the contact line is *not* equal to the fluid velocity there, the difference being related to the mass loss.

The global mass balance is

$$\int_0^{a(\tau)} \left( h_\tau(x,\tau) + \frac{\bar{E}}{K + h(x,\tau)} \right) dx = 0. \tag{5}$$

First, we shall look at the steady case. Then we shall look at the unsteady case for $\bar{C} = 0$, $\bar{C} \ll 1$, and $\bar{C} \gg 1$.


## STEADY SPREADING AND EVAPORATION

In order to focus on the effects of the mass loss on contact-angle dynamics, we shall define a steady, evaporating droplet which can be achieved by introducing mass through the base of the droplet and balancing evaporative mass loss (see figure 2). In this case, we immediately find that the contact-line condition (4) gives the steady value $\theta_S$ of $\theta$,

$$\theta_S(\theta_S - \theta_A)^m = \frac{\bar{E}}{K\bar{\eta}} . \tag{6}$$

This shows that $\theta_S > \theta_A$ *always*; evaporation gives an apparent angle *greater* than, possibly much greater than, $\theta_A$.


## UNSTEADY SPREADING AND EVAPORATION

### Zero Capillary Number

Consider $\bar{C} = 0$ with all other parameters $O(1)$. As discussed by Ehrhard and Davis (1991), this limit leads to an outer solution in time for the drop profile; the initial conditions on $h$ are dropped while those at the contact line are enforced.

The solution of the evolution equation (1) with $\bar{C} = 0$ is given simply by a parabolic droplet profile; the lubrication version of a constant curvature profile, where surface
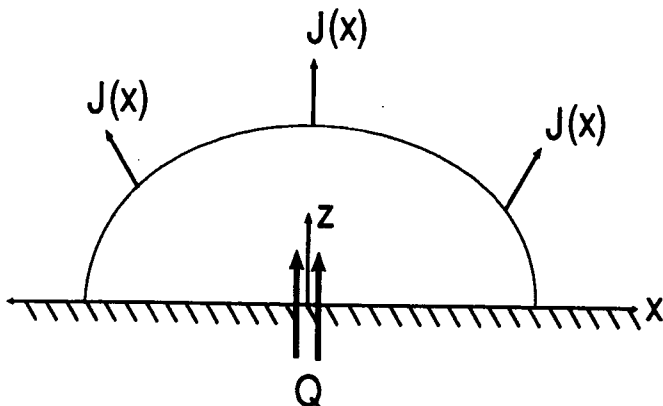
Figure 2: THE STEADY TWO-DIMENSIONAL EVAPORATING DROPLET WITH MASS FLUX THROUGH THE BASE WHICH BALANCES THE EVAPORATIVE MASS FLUX THROUGH THE LIQUID-VAPOR INTERFACE.

tension is dominant. Note that with $\bar{C} = 0$ the results are independent of slip, thermocapillarity, and vapor recoil. With this, the global mass balance and the contact-line condition give an evolutionary system for $a$ and $\theta$. The solution represents a quasi-steady solution where the drop profile equilibrates instantaneously and depends on time only through $a$ and $\theta$, which evolve due to viscous spreading and bulk mass loss.

There are two typical regimes; the 'strong' evaporation regime where $a_\tau(0) < 0$, and the 'weak' evaporation regime where $a_\tau(0) > 0$. That is, although the droplet disappears, the droplet radius may decrease monotonically (strong evaporation regime) or increase initially before decreasing (weak evaporation regime).

## Small Capillary Number

Here we obtain a solution for $h$ using a regular perturbation expansion in small capillary number. The results are again quasi-steady but we now can identify thermocapillary, vapor recoil, and unsteady and mass loss effects. We find that the mass flux is strongest where the droplet is thinnest; that is, at or near the contact line. Therefore, mechanisms which tend to increase $\theta$ *delay* evaporation while those which tend to decrease $\theta$ *promote* evaporation.

We find that the inclusion of the unsteady and mass-loss terms, the thermocapillary term, and the vapor recoil term each alter the profile, making the droplet contract, and as a result, each delay evaporation.

## Large Capillary Number

We now consider $\frac{1}{\bar{C}\bar{E}} \ll 1$, $\frac{\bar{\eta}}{\bar{E}} \ll 1$, and ignore thermocapillary and vapor recoil effects. Here we use matched asymptotic expansions to obtain representations for the droplet profile, contact angle, and droplet radius. In this limit, the spatial derivatives drop out of the evolution equation (1) and therefore the bulk of the drop has a shape

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given by the initial conditions and there is a boundary-layer correction near the contact line where the spatial derivatives cannot be neglected. We find that the inner solution is spatially oscillatory and decays away from the contact line. If the contact angle has $f > 0$ ($< 0$) the oscillations start out as a slight dip (bulge) near the contact line. Furthermore, if $f = 0$ there are no oscillations, and to $O(\frac{1}{CE})$, the outer solution is the uniformly valid solution. The droplet radius decreases monotonically in time while the contact angle may increase or decrease.

## SUMMARY

We have considered the evaporation of a liquid droplet on a uniformly heated horizontal surface and have studied the effects of capillarity, thermocapillarity, vapor recoil, viscous spreading, contact-angle hysteresis, and mass loss on the dynamics of the droplet profile and contact-line region. We have used a one-sided model of evaporation of Burelbach, et al. (1988), which is modified to include the presence of contact lines. Our model also extends that of Ehrhard and Davis (1991) of non-isothermal spreading to include evaporation.

We have derived a new contact-line condition (4) which takes into account the effects of evaporative mass loss. Using a lubrication theory, we derived an evolution equation for the droplet profile.

In the steady case, the steady contact angle is always larger than the advancing contact angle, $\theta_A$. This steady angle corresponds to that angle which balances viscous spreading with mass loss.

For the unsteady case, we obtained solutions for zero capillary number, small capillary number, and large capillary number.

For zero and small capillary number, we found that, although evaporation always causes the droplet to completely disappear, there are two basic regimes in which the dynamics of the contact lines differ. The first is the 'strong' evaporation regime where the droplet radius decreased monotonically in time. The second is the 'weak' evaporation regime where the droplet radius increases initially. Effects which tend to decrease the contact angle and thin the drop promote evaporation while those which tend to increase the contact angle and contract the drop delay evaporation. Thermocapillarity, vapor recoil, and the unsteady and mass loss terms in the evolution equation all tend to contract the droplet profile and therefore delay evaporation.

For large capillary number and small $\frac{f}{E}$ we found that the droplet profile could be described by an outer region, away from the contact line where surface curvature can be neglected, and an inner region near the contact line where the effects of curvature and slip are important. We find that the inner region corresponds to a spatially oscillating solution which decays away from the contact line and may correspond to either a dip or bulge in the liquid/vapor interface immediately adjacent to the contact line.

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