MICROREGION MODEL OF A CONTACT LINE INCLUDING EVAPORATION, KINETICS AND SLIP LENGTH

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The evaporation of a liquid into the atmosphere of its pure vapor on a uniformly heated solid substrate is investigated. Five physical phenomena are considered and modeled in the framework of lubrication theory: (i) hydrodynamics, (ii) heat conduction, (iii) phase change, (iv) kinetics of evaporation, and (v) slip length. The model is in fact an inner problem — contact line (CL) vicinity, microregion — of the model investigated by Anderson and Davis [D.M. Anderson and S.H. Davis, “The spreading of volatile liquid droplets on heated surfaces,” Phys. Fluids, vol. 7, pp. 248–265 (1995)] and extends the inner and intermediate solution of Hocking [L.M. Hocking, “On contact angles in evaporating liquids,” Phys. Fluids, vol. 7, pp. 2950–2955 (1995)] to more general considerations of the slip length. Decoupling from the outer problem — the macroscopic part of a liquid object — allows us to quantify the impact of evaporation in the CL vicinity on the apparent contact angle and microregion heat transfer. The linearized problem with respect to the substrate overheating is solved analytically. The analytical solutions are compared with full numerical solutions and to predictions of Hocking. We also define and determine the thermal regularization length associated with the present problem.

KEY WORDS: contact line, evaporation

1. INTRODUCTION

Evaporation of a liquid in contact with a solid substrate is a complex, multiscale phenomenon involving transport processes in both the liquid and vapor phases as well as in the solid substrate. Models describing evaporation can often be separated into those that assume that the rate of evaporation is dominated by the phase transformation kinetics of removing particles from the liquid–vapor interface, sometimes referred to as the ‘transfer-rate-limited’ regime (Ajaev and Homsy, 2001; Maki and Kumar, 2011; Moosman and Homsy, 1980; Potash and Wayner, 1972; Sodtke et al., 2008), and those that assume the evaporation rate is limited by transport processes in the vapor, i.e., diffusion of vapor particles away from the interface (Berteloot et al., 2008; Deegan et al., 1997; Dunn et al., 2008, 2009; Gelderblom et al., 2011; Hu and Larson, 2005; Popov, 2005; Stauber et al., 2014). The first case considers thus an atmosphere of a pure vapor of the corresponding liquid and the second one necessarily requires in addition the presence of some passive gas. Both types of models along with accompanying experiments have recently been discussed in detail by Murisic and Kondic (2011). Our present discussion will focus on the former case in which the evaporative flux is given by a kinetic-type relation. Some forms of these relationships specify the evaporative flux in terms of temperature differences [e.g., Burelbach et al. (1988), Anderson and Davis (1995)]. Other forms prescribe the evaporative flux in terms of a departure of the vapor pressure from its equilibrium value and then use thermodynamic arguments [e.g., Potash and Wayner (1972), Moosman and Homsy (1980) or more recently Morris (2001) and Ajaev and Homsy...
in situations where the relevant length scale $\ell_J$ off evaporation at the contact line (2012), who showed that the inclusion of the Kelvin effect in the setting of a stationary contact line necessarily shuts vanishes at the contact line. Indeed, this scenario has been addressed in detail recently by Janeček and Nikolayev (2012). Perhaps most notably, it was demonstrated [see Janeček et al. (2013); Janeček and Nikolayev (2012); Rednikov and Colinet (2013)] that the inclusion of the Kelvin effect into the moving contact line problem relieves hydrodynamic and thermal singularities at the moving contact line, resulting in a regular solution, even without the inclusion of slip or disjoining pressure. Note that this statement is valid for the case with pure vapor atmosphere but also for the case when an inert gas is present in the atmosphere surrounding the liquid; see a recent study of Janeček et al. (2015). In complete wetting, the Kelvin effect also plays a central role. Its mutual introduction together with disjoining pressure allows the meniscus to extend to an adsorbed liquid layer [e.g., Morris (2001); Rednikov and Colinet (2011)] and has been used in a variety of evaporating droplet models [e.g., Ajaev (2001), Klentzman and Ajaev (2009)] to write the flux in terms of both the deviation of the liquid pressure from the vapor pressure and the deviation of the interface temperature from the saturation temperature.

This same pressure-influenced evaporative flux can also be interpreted as arising from the Kelvin effect, the dependence of saturation temperature on pressure, or effectively interface curvature [e.g., Potash and Wayner (1972), Moosman and Homsy (1980) or more recently Janeček and Nikolayev (2012), Rednikov and Colinet (2013)]. The Kelvin effect has been shown to be important in a variety of situations involving contact lines. Its physical significance and ability to relax heat and viscous stress evaporation singularities has been well shown in the case of partial wetting by Janeček and Nikolayev (2012). Perhaps most notably, it was demonstrated [see Janeček et al. (2013); Janeček and Nikolayev (2012); Rednikov and Colinet (2013)] that the inclusion of the Kelvin effect into the moving contact line problem relieves hydrodynamic and thermal singularities at the moving contact line, resulting in a regular solution, even without the inclusion of slip or disjoining pressure. Note that this statement is valid for the case with pure vapor atmosphere but also for the case when an inert gas is present in the atmosphere surrounding the liquid; see a recent study of Janeček et al. (2015). In complete wetting, the Kelvin effect also plays a central role. Its mutual introduction together with disjoining pressure allows the meniscus to extend to an adsorbed liquid layer [e.g., Morris (2001); Rednikov and Colinet (2011)] and has been used in a variety of evaporating droplet models [e.g., Ajaev (2001), Klentzman and Ajaev (2009)] to write the flux in terms of both the deviation of the liquid pressure from the vapor pressure and the deviation of the interface temperature from the saturation temperature.

In the present work we are interested in examining the microregion near a stationary contact line in the absence of a precursor film. An issue to be aware of in this setting is the potential for a kinematic inconsistency at the free surface evaluated at the contact line when evaporation is present. This was recently illustrated by Maki and Kumar (2011) in their work on the ‘coffee-ring effect’ in axisymmetric evaporating droplets of colloidal suspensions. Basically, one cannot have a stationary contact line with nonzero evaporation at a heated substrate (with or without slip and Marangoni effects) in the standard context of lubrication theory. Maki and Kumar avoided this inconsistency in their work by including a precursor film (established through van der Waals interactions and the Kelvin effect) where evaporation shuts off. The kinematic inconsistency at a stationary contact line is resolved if the evaporative flux $J$ vanishes at the contact line. Indeed, this scenario has been addressed in detail recently by Janeček and Nikolayev (2012), who showed that the inclusion of the Kelvin effect in the setting of a stationary contact line necessarily shuts off evaporation at the contact line ($J = 0$) and effectively removes the inconsistency identified by Maki and Kumar.

The Kelvin effect is thus from the physical point of view an essential phenomenon (Janeček et al., 2013). However, in situations where the relevant length scale $\ell_K$ [identified in Janeček et al. (2013)] is small with respect to length scales associated with other microscale phenomena (e.g., slip, interface thermal resistance), the Kelvin effect still relaxes thermal and shear stress singularities, but is strongly localized in the contact line vicinity that does not significantly impact the apparent contact angle or the integrated mass flux. These quantities are controlled by phenomena with larger characteristic scales such as slip or interface thermal resistance. Here, we treat the asymptotic limit $\ell_K \to 0$. Note that this limit corresponds to the model introduced by Anderson and Davis (1995). Indeed the model of Anderson and Davis in the present context can be viewed as an outer solution model closed by a condition on the apparent contact angle. Hocking (1995) has investigated the full problem of a stationary evaporating sessile droplet based on the model of Anderson and Davis with the assumption of a local equilibrium contact angle at the contact line and a transition to an apparent contact angle over a region where interface slip is important. One of the key predictions of the matched asymptotic analysis of Hocking, which is based on a small slip parameter with inner and outer expansions joined by an intermediate expansion, is a closed-form relationship for the deviation, due to evaporation, of the apparent contact angle from the equilibrium contact angle. Morris (2001) later recognized the possibility of identifying the dependence of the apparent contact angle on evaporation for a stationary meniscus through a local analysis alone — decoupled from the outer, large-scale geometry. We take advantage of this possibility here to derive, based on a purely local analysis, a new analytical relationship between the apparent contact angle and the local equilibrium, or Young, contact angle in the presence of evaporation that extends Hocking’s result to general values of the slip parameter. Comparisons of our apparent contact angle results with those of Hocking will be presented in more detail below. We also give predictions for the dependence of the thermal regularization length on evaporation.

In the absence of the Kelvin effect the mass evaporation flux is coupled with hydrodynamics only through the thickness of the liquid layer, $h$. Note that length scales related to the slip length and the nonequilibrium parameter, as identified in Janeček and Nikolayev (2013), are $\ell_s = 3l_s/\theta_Y$ and $\ell_\beta = \beta/\partial Y$, where $\beta = R^* k$, $R^*$ is the interface...
thermal resistance, \( k \) is the liquid thermal conductivity, \( l_s \) is the slip length, and \( \theta_Y \) is the constant microscopic contact angle. The length scale \( \beta \) can be viewed as an additional thickness of the liquid layer across which evaporative heat transfer takes place (Nikolayev, 2010). This provides a thermal regularization effect that can also be viewed in terms of an effective thermal resistance \( R^* + h/k = (\beta + h)/k \), which remains nonzero even at the contact line where \( h = 0 \). The viscous and thermal singularities are thus “removed” by considering a slip length \( l_s \) and a nonequilibrium parameter (interface thermal resistance) \( R^* \).

Three particular objectives of the present study are as follows. First, we shall determine the slope of the free interface far from the CL (i.e., the apparent contact angle), which we accomplish using a regular perturbation method. Our results extend to more general values of slip, the previous work of Hocking (1995), whose analysis was based on an asymptotic limit of small slip. The interest in larger slip lengths has been promoted in part by an interest in understanding contact line and fluid motion on super-hydrophobic and/or patterned surfaces [e.g., Lauga and Stone (2003)]. For example, the slip lengths reported by Fetzer et al. (2006, 2007) for polymer films on coated silicon wafers were in the range 100 nm up to 10 \( \mu \)m. Münch et al. (2005) explored the influence of large values of slip on the rupture dynamics in thin films, in particular thin polymer films on coated silicon wafer (Fetzer et al., 2005). In their large slip asymptotics they assumed the slip parameter was inversely proportional to a power of the typical thin-film aspect ratio. Our work here assumes the slip length and film thickness are comparable and so we do not formally reach their “large” and “intermediate” slip regimes. Second, our work provides a means in which the macroscale evaporating droplet model of Anderson and Davis (1995) may be closed consistent with the local physics of the contact line. And third, we shall identify a thermal regularization length, \( \ell_T \), that is associated with the total integrated mass flux in the contact line region.

2. PROBLEM

Stationary evaporation in the vicinity of the triple gas–liquid–solid contact line (CL) in two-dimensional space is considered; see Fig. 1. The contact line is placed at the origin \( (x = 0) \) of the Cartesian coordinate system. The solid is perfectly conductive and overheated with respect to the saturation temperature \( T_s \), given by the ambient vapor pressure. The coupled dynamics of the liquid and vapor phases are simplified by adapting the one-sided model of evaporation; see Burelbach et al. (1988), which allows one to treat only the dynamics of the liquid domain. This is based on the approximation that density, viscosity, and thermal conductivity in the vapor phase are negligible compared with that in the liquid phase.

The liquid is considered to be incompressible and Newtonian. Consistent with the lubrication approximation (small slope of the free interface) only the thermal conductive term from the energy equation is retained. Thermocapillary and vapor recoil terms [e.g., see Anderson and Davis (1995), Eq. (9)] are neglected for the sake of simplicity. Two equations can be written in the lubrication approximation for the thickness of the liquid wedge \( h(x) \) and pressure jump (difference between the pressure in the vapor and the liquid) \( \Delta p(x) = p_V - p_L \):
\[
\frac{\rho}{\eta} \frac{d}{dx} \left[ (h + 3l_s) \frac{h^2}{3} \frac{d\Delta p}{dx} \right] = -J = \frac{k}{L} \Delta T \frac{\Delta p}{\beta + h},
\]

(1)

\[
\Delta p = \gamma \frac{d^2 h}{dx^2},
\]

(2)

where \( \eta \) is the dynamic viscosity, \( \rho \) the liquid density, \( \Delta T \) the heater overheating, \( L \) the latent heat, \( k \) the liquid thermal conductivity, \( J \) the evaporative mass flux, and \( \gamma \) the surface tension. Similar local fluid wedge regions have been considered in the perfectly wetting cases with the Kelvin effect and disjoining pressure [e.g., DasGupta et al. (1993); Moosman and Homsy (1980); Morris (2001, 2003)]. The study by Renk and Wayner (1979) focused on a stationary evaporating contact line problem without a precursor film (extended meniscus) and no explicit incorporation of the effects of slip. They proposed an equation for the volumetric flow that results in an equation for the interface shape that differs from the one studied here. Our problem, which does not include the presence of a precursor fluid layer, identifies the contact line \( x = 0 \). Our boundary conditions at the contact line and far from the contact line are described below.

Boundary conditions for Eqs. (1) and (2) are at the contact line (\( x = 0 \)):

\[
h(0) = 0; \quad \frac{dh}{dx} = \theta_Y,
\]

(3)

and far from the contact line (\( x \to \infty \))

\[
\frac{d^2 h}{dx^2} = 0,
\]

(4)

where \( \theta_Y \) is the microscopic (Young) contact angle. The fourth boundary condition comes from the requirement of a regular solution, i.e., finite slope at the CL or in other words for \( x \to 0 \)

\[
\frac{d^2 h}{dx^2} \text{ integrable.}
\]

(5)

We are primarily interested in two main quantities.

— The slope of the free interface established far from the contact line, i.e., the apparent contact angle \( \theta_{app} \).

— The total mass transferred through the microregion \( Q = \int_0^x J dx \). Note that far from the contact line we expect local mass evaporation flux \( J \) to have the form

\[
J(x \to \infty) \sim \frac{k \Delta T}{L} \frac{1}{\theta_{app} x}.
\]

(6)

Then \( Q \) is expected to be of the following form far from the contact line:

\[
Q(x \to \infty) \sim \frac{k \Delta T}{\theta_{app} L} \ln \left( \frac{x}{\ell_T} \right),
\]

(7)

where \( \ell_T \) is a thermal regularization length that we discuss in more detail below. It is in some sense an analogue of the Voinov length (Eggers, 2005; Janeček et al., 2013; Voinov, 1976) in the Cox-Voinov expression (due to log term).

2.1 Dimensionless Equation

Similarly to Janeček et al. (2013), the variables \( x \) and \( h \) are scaled by the characteristic lengths \( X \) and \( Y \), whose ratio is set by the microregion contact angle \( \theta_Y \): \( Y = \theta_Y X \). This eliminates \( \theta_Y \) from the boundary conditions. We can identify three basic length scales \( X \) associated with the problem (1)–(5). Two have been already mentioned (\( \ell_B, \ell_s \)).
The last one can be identified if we assume that $l_s$ and $\beta$ scale with $Y$. In this case, comparing prefactors of the left and right side of (1) leads to

$$\frac{Y^5}{X^3} \sim \frac{3\eta \Delta T k}{\rho L \gamma}.$$  

From the latter expression, we can identify the third length related to evaporation as $\ell_e = 3 \eta \Delta T k / (\rho L \gamma \delta^3)$. When $\ell_s, \ell_\beta,$ and $\ell_e$ are specified, the problem $1$–$(5)$ can be solved. Note that the scale for mass flux $J$ is $k \Delta T / (\theta Y X \ell)$ (i.e., $J = [k \Delta T / (\theta Y X \ell)] j$, where $j$ is a dimensionless mass flux) and that for $Q$ is $k \Delta T / (\theta Y \ell)$ (i.e., $Q = [k \Delta T / (\theta Y \ell)] q$, where $q$ is dimensionless). In the following, it is convenient to choose $\ell_\beta$ as the characteristic length scale of the problem, i.e., $X = \ell_\beta$.

Equation (1) reduces to

$$[(H + N_s) H^2 H''']' = -\epsilon j = -\frac{\epsilon}{1 + H}, \tag{8}$$

where prime denotes differentiation with respect to the dimensionless variable $\zeta = x/X$, $N_s = \ell_s / \ell_\beta$ measures ratio of slip and kinetics effect on evaporation, and $\epsilon = \ell_e / \ell_\beta$ is the overheating parameter. The boundary conditions $(3)$–$(5)$ are in dimensionless form:

$$H(0) = 0; \quad H'(0) = 1; \quad H''(\zeta \rightarrow \infty) = 0; \quad H''(\zeta \rightarrow 0) \text{ integrable.} \tag{9}$$

The problem listed here is similar in spirit to the local problem explored by Morris (2001) for perfectly wetting systems that incorporates the effects of disjoining pressure and the Kelvin effect. Our problem more closely resembles the inner solution problem studied by Hocking (1995). Besides slight notational differences between Hocking’s work and ours, we note that the present model does not make the assumption of a small slip parameter — we treat $N_s$ as an $O(1)$ parameter. The slip parameter $N_s$ in our model is defined with respect to the thermal regularization parameter $\ell_\beta$. Hocking’s slip parameter ($\beta$ in that work) is scaled relative to a macroscopic droplet height. The boundary conditions used by Hocking on his inner solution are the first three listed above but we note that our fourth that requires $H''(\zeta \rightarrow 0)$ integrable is also an eventual property of Hocking’s inner solution. We make further comparison’s to Hocking’s work below.

We expect the dimensionless mass evaporation flux $j$ to be of the following form far from the contact line:

$$j(\zeta \rightarrow \infty) \sim \frac{1}{\ell_H(\zeta \rightarrow \infty)}, \tag{10}$$

where $H'(\zeta \rightarrow \infty) = \theta_{app} / \theta_Y$. From a practical point of view, it is important to know the total mass evaporated near the contact line: $q = \int_0^{\infty} j d\zeta$. We expect $q$ to be of the following form far from the contact line:

$$q(\zeta \rightarrow \infty) \sim \frac{1}{H'(\zeta \rightarrow \infty)} \ln \left( \frac{\ell_H}{\ell_T} \right). \tag{11}$$

2.1.1 Perturbation about Isothermal Condition

We seek a solution of $(8)$–$(9)$ by expanding $H$ and $j$ in regular perturbation series in $\epsilon$:

$$H = H_0 + \epsilon H_1 + \cdots, \tag{11}$$

$$j = j_0 + \epsilon j_1 + \cdots. \tag{12}$$

At the zero order obviously $H_0 = \zeta$. Next, one needs to substitute $(11)$–$(12)$ into $(8)$–$(9)$ and collect terms of the same order in $\epsilon$. Moosman and Homsy (1980) have also exploited this near-isothermal limit in their evaporating meniscus study.

The first-order problem for $H_1$, which also identifies the leading-order mass flux $j_0$, is

$$[(\zeta + N_s) \zeta^2 H''_1]' = -j_0 = -\frac{1}{1 + \zeta}. \tag{13}$$
This equation for $H_1$ is nearly identical to the inner problem studied by Hocking (1995) (see his second equation on p. 2953) with the exception that here we retain the right-hand side $-1/(1 + \zeta)$ whereas Hocking’s right-hand side is $-1$. This difference follows from the assumption that in Hocking’s case the interface shape is scaled with the small slip parameter and hence the corresponding non-constant term in Hocking’s right-hand side is neglected. The new result in our work is that by treating $N_s$ as an order-one quantity we retain the $\zeta$ term in the denominator of the right-hand side and can obtain a prediction for the apparent contact angle that applies for more general values of slip. The solution for $H_1'$ is detailed in Appendix A.

From the solution $H_1'$ we are able to obtain an explicit formula for the dependence of the apparent contact angle on slip, evaporation, and other key physical effects in this problem. Specifically we find that the first-order approximation for the apparent contact angle is

$$\theta_{app} = \theta_Y + \epsilon \theta_Y H_1'(\zeta \to \infty) + o(\epsilon).$$

where, depending on the parameter $N_s$, we find

$$H_1'(\zeta \to \infty) = \begin{cases} 
\frac{1}{2N_s} \left\{ \ln \left( \frac{1}{1 - N_s} \right) \left[ \ln \left( \frac{1}{1 - N_s} \right) + 2 \ln(N_s) \right] + 2 \text{Li}_2 \left( \frac{N_s}{N_s - 1} \right) \right\} & \text{for } N_s < 1 \\
\frac{\pi^2}{6} & \text{for } N_s = 1 \\
\frac{1}{6N_s} \left[ 2\pi^2 + 3 \ln^2 (N_s - 1) + 6 \text{Li}_2 \left( \frac{1}{1 - N_s} \right) \right] & \text{for } N_s > 1
\end{cases}$$

(15)

where $\text{Li}_2$ is a dilogarithm function (see Appendix A).

Formulas (14) and (15) are central results of this paper and will be discussed in detail in the next section. To close this section we point out two limiting cases for these general results. First, in the limit $N_s \ll 1$ we find that

$$H_1'(\zeta \to \infty) \sim \ln \left( \frac{\epsilon}{N_s} \right) + \mathcal{O}[N_s \ln (N_s)].$$

(16)

For $N_s \gg 1$ we find that

$$H_1'(\zeta \to \infty) \sim \frac{\ln^2 (N_s)}{2N_s} + \frac{\pi^2}{3N_s} + \mathcal{O}[N_s^{-2} \ln (N_s)].$$

(17)

### 3. APPARENT CONTACT ANGLE RESULTS

One of the key points of comparison of our apparent contact angle results in the previous section is with formula (14) of Hocking (1995). In particular, his expression gives the difference between the fourth power of the apparent contact angle and the fourth power of the equilibrium angle. In terms of our notation, Hocking’s equation (14) can be expressed as

$$\theta_{app}^4 = \theta_Y^4 + 4\epsilon \theta_Y^4 \ln \left( \frac{\epsilon \theta_Y}{\theta_{app}N_s} \right),$$

(18)

where we have used the following notational correspondences between our work and Hocking’s work ($\epsilon \theta = \Theta \rightarrow \theta_{app}$, $\epsilon \theta_0 = \Theta_0 \rightarrow \theta_Y$, $\nu \rightarrow \eta/\rho$, $K^* \rightarrow LR^*$, $\tilde{\beta} \rightarrow l_s$, $\sigma \rightarrow \gamma$) and have corrected what we believe to be a typographical error of a 2 instead of a 3 in the denominator of the logarithmic argument in his equation (14).\(^1\) The power of four that appears in Hocking’s work was also recognized by Morris (2001), who characterized both the mathematical and physical origin of the appearance of this particular power. Our expression for the apparent contact angle comes out of our regular perturbation analysis in the linearized form (14). However, motivated by the work of both Hocking and Morris, we can express an equivalently valid expression for the fourth power of our $\theta_{app}$ by a simple

\(^1\)This typographical error has been confirmed by analytical review of Hocking’s work as well as by our numerical simulations.
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In particular, taking the fourth power of the right-hand side of Eq. (14) and expanding it in powers of the regular perturbation parameter \( \epsilon \) yields the result

\[
\theta_{app}^4 = \theta_Y^4 + 4\epsilon \theta_Y^4 H'_1(\zeta \to \infty) + o(\epsilon),
\]

which carries the same \( o(\epsilon) \) asymptotic approximation error as the original expression for \( \theta_{app} \). Our first observation is that for the case \( N_s \ll 1 \) with \( H'_1(\zeta \to \infty) \) given by Eq. (16) this result is in agreement with Hocking’s equation (14) if one additionally applies the approximation \( \theta_{app}/\theta_Y \approx 1 \) for the terms inside the logarithm of his equation (14) [e.g., Eq. (18) above].

As our Eq. (19) is not restricted to small values of \( N_s \), it is now instructive to explore the predictions for general values of \( N_s \) and compare them to numerical solutions of the full problem as specified in Eqs. (8) and (9). Details of the numerical procedure are outlined in Appendix B. Plots of \( \theta_{app}/\theta_Y \) versus \( \epsilon \) for three different values of \( N_s \) are shown in Fig. 2. We see from these figures that our expression (19) agrees very well with our numerical simulations of the full problem. The linearization expressed in Eq. (14) clearly captures the small \( \epsilon \) trends. Hocking’s equation (14) does well where expected for smaller values of \( N_s \) but departs from the numerical solution as \( N_s \) increases. The results by Hocking and Morris showing that evaporation drives a difference between the fourth power of the apparent contact angle and the fourth power of the equilibrium contact angle is the inspiration behind our Eq. (19). The agreement between Eq. (19) and the numerical simulations of the full problem clearly shows that this same fourth power feature of the apparent contact angle holds even away from the small \( N_s \) limit. In all of the cases shown in Fig. 2 we observe an increase in apparent contact angle with imposed overheating. This increase in contact angle with evaporation is in general agreement with the well-known trend observed in related contact line/evaporation models [e.g., Berteloot et al. (2008); Janěček and Nikolayev (2012); Morris (2001)].

The premise of Hocking’s paper can be echoed here: the difference between the apparent (macroscopic) contact angle and static (microscopic) contact angle is established local to the contact line where slip is important. Our results in Eqs. (14) and (15) along with the recast version in Eq. (19) capture this relationship for general values of our slip parameter \( N_s \). The result in Eq. (19), while formally derived for small \( \epsilon \) appears to be very accurate even for non-small \( \epsilon \). Our results for general values of \( N_s \) may be of interest in the context of the larger effective slip lengths that occur for super-hydrophobic and patterned surfaces and/or for polymeric fluids [e.g., Choudhary et al. (2015); Fetzer et al. (2005, 2006, 2007); Lauga and Stone (2003); Münch et al. (2005); Vinogradova and Belyaev (2011)].

For further discussion of our apparent contact angle result, we turn to Fig. 3, which shows the solution \( H'_1(\zeta \to \infty) \) vs. parameter \( N_s \). We see that the change in apparent contact angle relative to the equilibrium contact angle driven by evaporation [i.e., \( H'_1(\zeta \to \infty) \)] is always positive; that is, evaporation increases the apparent contact angle. As can be noted above for the case \( N_s \gg 1 \) (e.g., relatively large slip length) the limiting result is \( \theta_{app} \sim \theta_Y \), indicating that in cases of large slip length there is little increase in apparent contact angle. Also as noted above, \( H'_1(\zeta \to \infty) \) logarithmically diverges for \( N_s \to 0 \) [as also recognized in the analysis of Hocking (1995)]. However, recalling that \( N_s = \ell_s/\ell_B = (3\ell_s/\beta) \) and \( \epsilon = \ell_c/\ell_B \) allows us to make the observation that for a large thermal resistance length scale \( \ell_B(\beta) \) the apparent contact angle remains finite, in fact \( \theta_{app} = \theta_Y + \epsilon \theta_Y H'_1(\zeta \to \infty) \to \theta_Y \), in the large \( \ell_B \) limit. The results of Mathieu (2003) show that the value of \( \beta \) decreases strongly with decreasing pressure. For example, for mercury \( \beta \) can range from \( O(1–10 \mu m) \) [at 1 bar] up to \( O(mm) \) [at \( 10^{-3} \) bar]. If a typical slip length is taken to be \( \sim O(\mu m)–O(mm) \) then \( N_s \ll 1 \). In such a case, that is with \( \epsilon \ll 1 \) and \( N_s \ll 1 \), we expect a weak influence of evaporation on apparent contact angle so that \( \theta_{app}(T) \sim \theta_Y \). These different limits (large slip and large thermal resistance) suggest that the increase in apparent contact angle is in some sense a geometric response of the system toward regularization and that strong regularization with respect to slip and/or thermal kinetics reduces the degree to which this geometric regularization is required.

We can relate the present results back to the evaporative contact angle model of Anderson and Davis (1995). In particular, their equation (20) for a steady, evaporation-modified contact angle expressed in terms of the present notation is

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A similar algebraic manipulation was performed by Hocking when he matched his interface slope function \( S \) in his inner and outer solutions to his intermediate solution, which involved a formula for \( S^I \). See his equation (12) and two others for \( S \) that follow on p. 2953.
FIG. 2: $\theta_{app}/\theta_Y$ vs. $\epsilon$ for (a) $N_s = 0.2$, (b) $N_s = 1$, and (c) $N_s = 2$. The green dotted curve shows the result of our Eq. (14), the red dotted curve shows the result of our Eq. (19), the solid black curve shows the results of our numerical simulation, the magenta dash-dotted curve shows the result of Eq. (23), and the blue dashed curve shows the result of Hocking’s equation (14) [e.g., our Eq. (18)].

\[ \theta_{app} f(\theta_{app}) = \epsilon \theta_Y \left( \frac{\gamma}{\eta} \right)^{3} \eta_{AD}, \]  

(20)

where $\eta_{AD}$ is the prefactor used in their assumed contact line speed $u_{CL} = \eta_{AD} f(\theta_{app})$ for the nonvolatile limit and $f(\theta_Y) = 0$. Anderson and Davis investigated one particular form of $f(\theta)$ but here we consider another of the form.

FIG. 3: $H_f(\zeta \rightarrow \infty)$ vs. $N_s$. Note that the function is of logarithmic form as $N_s \rightarrow 0$. Interfacial Phenomena and Heat Transfer
$f(\theta) = \theta^3 - \theta_Y^3$ studied elsewhere [e.g., Berteloot et al. (2008); Eggers (2005); Voinov (1976)]. Inserting our relation $\theta_{app} = \theta_Y + \epsilon \theta_Y H'_1(\zeta \to \infty)$ into Eq. (20) and linearizing with respect to $\epsilon$ gives

$$H'_1(\zeta \to \infty) \frac{f'(\theta_Y)}{\theta^2_Y} = \frac{(\gamma/\eta)}{3\eta_{AD}}. \tag{21}$$

With $f(\theta) = \theta^3 - \theta_Y^3$ it follows that

$$\eta_{AD} = \frac{(\gamma/\eta)}{3H'_1(\zeta \to \infty)}, \tag{22}$$

where $H'_1(\zeta \to \infty)$ is the function of $N_s$ given by Eq. (15). Therefore, the choice for $\eta_{AD}$ expressed in Eq. (22) gives an explicit form for the coefficient $\eta_{AD}$ that could be used in the evaporating droplet model of Anderson and Davis to yield a macroscopic contact angle boundary condition that is consistent with the contact line physics examined in the present local model.

In particular, doing so we obtain

$$\theta_{app}(\theta_{app}^3 - \theta_Y^3) = 3\epsilon \theta_Y^3 H'_1(\zeta \to \infty), \tag{23}$$

where $H'_1(\zeta \to \infty)$ is given by Eq. (15). This formula, denoted by AD/IA, is plotted along with others in Fig. 2.

4. THERMAL REGULARIZATION LENGTH RESULTS

The leading-order approximation for mass evaporation flux in dimensionless form is $j = 1/(1 + \zeta)$. The integrated mass flux is

$$q = \int_0^\zeta j d\zeta = \ln (1 + \zeta). \tag{24}$$

Note that $q(\zeta \to \infty) \sim \ln \zeta$ and for the zero-order approximation the thermal regularization length expressed in Eq. (10) is simply: $\ell_T = \ell_B$. That is, the thermal regularization length is proportional to the product of the thermal conductivity $k$ and the interface thermal resistance $R^*$. The scaled thermal regularization length $\ell_T$ vs. overheating parameter $\epsilon$ is shown in Fig. 4. The thermal regularization length $\ell_T$ obtained by fitting the expression in Eq. (7) to the numerically calculated value of $Q$. The thermal regularization length is smaller with imposed overheating. That is, as overheating is increased, the distance over which the integrated mass flux is regularized decreases. This trend is further enhanced by a reduction of the slip length (i.e., smaller $N_s$) for overheating parameter $\epsilon < 7$. We draw an analogy here to the Voinov length and its dependence on capillary number (contact line speed times viscosity divided by surface tension) as identified by Eggers (2005) in his equation (9). In that expression the Voinov length (i.e., the length scale over which the hydrodynamic singularity is regularized) is to leading order proportional to the slip length and, at least for small capillary number, decreases with increasing capillary number. So enhancing the source of the hydrodynamic singularity — contact line motion — shortens the regularization scale. Our thermal regularization length is to leading order in substrate overheating, proportional to the thermal resistance length scale $\ell_B$ and decreases with enhanced substrate heating. That is, enhancing the source of the thermal singularity — substrate overheating — shortens the regularization scale.

5. CONCLUSIONS

A microregion model describing hydrodynamics and heat transfer in the vicinity of the contact line using the lubrication approximation is studied. Although not discussed in detail in the results, the characteristic scale at which the apparent contact angle $\theta_{\text{app}}$ is established corresponds to the maximum of the slip and kinetics/thermal resistance length scales, i.e., $\max(\ell_B, \ell_s)$. We presented a linearized approximation based on the limit of small overheating and identified closed-form expressions for the dependence of the apparent contact angle on the overheating parameter and the ratio of length scales, $N_s$, associated with hydrodynamic slip and interface thermal resistance. Inspired by previous observations in work by Hocking (1995) and Morris (2001) on closely related problems, we derived a modified approximation for the fourth power of the apparent contact angle valid in the same small overheating limit and showed that this result agreed very well with numerical simulations of the full problem for general values of our slip parameter $N_s$. Perhaps more surprisingly, this approximation for the apparent contact angle, derived using a regular perturbation expansion for small values of the overheating parameter $\epsilon$, when expressed in terms of a fourth power of the contact angle, agreed extremely well with numerical simulations of the full problem even when $\epsilon$ was not small. We demonstrated that for $N_s \ll 1$ our analytical formula for apparent contact angle is in agreement with the result derived by Hocking (1995). Our new analytical formulas for the apparent contact angle thus extend Hocking’s seminal result to general values of this slip/thermal resistance ratio. In other words, the general scaling observed by Hocking, namely the difference in the fourth power of the apparent contact angle, $\theta_{\text{app}}^4$, and the fourth power of the equilibrium contact angle, $\theta_Y^4$, is proportional to the dimensionless overheating parameter, $\epsilon$, is found to still be true for the case of non-small slip $N_s = O(1)$. Unlike Hocking’s formula, our new result is shown to be in good agreement with the numerical solutions for a wide range of $N_s$ values, not limited to small slip conditions. We also showed that the present results provide a closure condition for the proposed apparent contact angle relationship developed and used in the evaporating droplet model of Anderson and Davis (1995). A leading-order result for the thermal regularization length in the total integrated mass reveals that it is jointly proportional to the interfacial thermal resistance and thermal conductivity. The model framework, asymptotic limits, and new apparent contact angle formulas developed here for more general values of the slip parameter complement existing literature on evaporating contact lines and may prove useful in the further exploration and understanding of moving contact line models with evaporation.

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REFERENCES


APPENDIX A. CALCULATION OF $H_1''(\zeta)$

Equation (13) can be easily solved for $H_1''$:

$$H_1'' = \frac{C_1 - \ln (1 + \zeta)}{\zeta^2 (N_s + \zeta)},$$

(A1)

where $C_1$ is an integration constant. Next, we are interested in the solution for $H_1''$ (assuming $N_s > 0$). It can be easily checked that the asymptotic behavior of $H_1''(\zeta)$ at the CL ($\zeta \to 0$) is

$$H_1''(\zeta \to 0) = -\frac{C_1}{N_s \zeta} + \cdots,$$

(A2)

where three dots represents some integrable terms. This implies $C_1 = 0$ as boundary condition (9d) has to be satisfied. The solution for the first-order approximation for the slope reads

$$H_1'' = \frac{1}{N_s^2} \left[ N_s \frac{\ln (1 + \zeta)}{\zeta} + N_s \ln \frac{1 + \zeta}{\zeta} - \text{Li}_2(-\zeta) + G(\zeta) \right],$$

(A3)
where

\[ G(\zeta) = \begin{cases} 
-\ln(N_s + \zeta) \ln(1 - N_s) + \text{Li}_2 \left( \frac{N_s + \zeta}{N_s - 1} \right) + C_2 & \text{for } N_s < 1 \\
-\frac{1}{2} \ln^2(1 + \zeta) + C_3 & \text{for } N_s = 1 \\
\ln \left( \frac{N_s - 1}{N_s + \zeta} \right) \ln(1 + \zeta) - \text{Li}_2 \left( \frac{1 + \zeta}{1 - N_s} \right) + C_4 & \text{for } N_s > 1 
\end{cases} \quad (A4)\]

\( C_2, C_3, C_4 \) are integration constants and \( \text{Li}_2 \) is a dilogarithm function defined by the integral \((\text{Abramowitz and Stegun, 1965})\)

\[ \text{Li}_2(z) = \int_z^1 \ln (1 - t) t^{-1} dt. \]

From \( H''(\zeta \to \infty) = 0 \) it follows that

\[ C_2 = 0.5 \ln^2(1 - N_s) \quad (A5) \]

\[ C_3 = -\frac{\pi^2}{6} \quad (A6) \]

\[ C_4 = -\frac{\pi^2}{3} - 0.5 \ln^2(N_s - 1). \quad (A7) \]

An integration of Eq. (A3) reveals the slope

\[ H'_1(\zeta) = \frac{1}{N_s^2} \left[ -N_s \text{Li}_2 (-\zeta) + N_s \left[ (\zeta + 1) \ln(\zeta + 1) - \zeta \ln \zeta - 1 \right] \right. \]

\[ \left. - [\zeta \text{Li}_2 (-\zeta) + (1 + \zeta) \ln(1 + \zeta) - (1 + \zeta)] + g(\zeta) \right] \quad (A8) \]

where \( g'(\zeta) = G(\zeta) \); in particular,

\[ g(\zeta) = \begin{cases} 
-(\zeta + N_s) \ln(1 - N_s) \left[ \ln(\zeta + N_s) - 1 \right] - \zeta + (1 + \zeta) \ln \left[ \frac{1 + \zeta}{1 - N_s} \right] & \text{for } N_s < 1 \\
+ (N_s + \zeta) \text{Li}_2 \left( \frac{N_s + \zeta}{N_s - 1} \right) + C_2 \zeta + C_5 & \text{for } N_s = 1 \\
- \zeta + N_s \ln(N_s - 1) + (1 + \zeta) \ln(1 + \zeta) - (1 + \zeta) + C_3 \zeta + C_6 & \text{for } N_s > 1 \\
- (N_s + \zeta) \text{Li}_2 \left( \frac{1 + \zeta}{1 - N_s} \right) + C_4 \zeta + C_7 & \text{for } N_s > 1 
\end{cases} \quad (A9) \]

where integration constants \( C_5, C_6, C_7 \), chosen to satisfy \( H'_1(0) = 0 \), are

\[ C_5 = N_s - 1 + \ln(1 - N_s) [N_s \ln N_s - N_s + 1] - N_s \text{Li}_2 \left( \frac{N_s}{N_s - 1} \right) \quad (A10) \]

\[ C_6 = 1 \quad (A11) \]

\[ C_7 = N_s - 1 - N_s \ln(N_s - 1) + N_s \text{Li}_2 \left( \frac{1}{1 - N_s} \right). \quad (A12) \]

**APPENDIX B. NUMERICAL SOLUTION**

Consider the ordinary differential equation (ODE) (8) subject to the boundary conditions (9). In order to solve this problem numerically we first identify asymptotic forms for \( H \) and its derivatives in the limit \( \zeta \to 0 \). Note that the numerical solution does not require that the overheating parameter \( \epsilon \) be small.

Since we expect, to first approximation, that \( H \sim \zeta \) as \( \zeta \to 0 \) the ODE reduces to
\[
N_s[\zeta^2 H''']' \approx -e. \tag{B1}
\]
Then,
\[
H''' \approx -\frac{e}{\zeta N_s} + \frac{a_0}{\zeta^2}, \tag{B2}
\]
where \( a_0 \) is an integration constant. It follows that
\[
H'' \approx -\frac{e}{N_s} \ln \zeta - \frac{a_0}{\zeta} + a_1, \tag{B3}
\]
where \( a_1 \) is an integration constant. However, for \( H'' \) integrable as \( \zeta \to 0 \) we must have \( a_0 = 0 \), so
\[
H'' \approx -\frac{e}{N_s} \ln \zeta + a_1 \quad \text{as} \quad \zeta \to 0. \tag{B4}
\]
Then,
\[
H''' \approx -\frac{e}{\zeta N_s} \quad \text{as} \quad \zeta \to 0. \tag{B5}
\]
Consistent with these forms and boundary conditions \( H(0) = 0 \) and \( H'(0) = 1 \) we have, as \( \zeta \to 0 \),
\[
H' \approx -\frac{e}{N_s} (\zeta \ln \zeta - \zeta) + a_1 \zeta + 1, \tag{B6}
\]
and, as \( \zeta \to 0 \),
\[
H \approx -\frac{e}{N_s} \left( \frac{1}{2} \zeta^2 \ln \zeta - \frac{3}{4} \zeta^2 \right) + \frac{1}{2} a_1 \zeta^2 + \zeta. \tag{B7}
\]
We now use \( a_1 \) as a shooting parameter and integrate the ODE (8) with initial conditions for \( H \), \( H' \), \( H'' \), and \( H''' \) as outlined above applied at \( \zeta = \zeta_{\text{min}} > 0 \) (but near 0). The integration proceeds out to a large but finite value of \( \zeta = \zeta_{\text{max}} \) where we require \( H''(\zeta_{\text{max}}) = 0 \) [to approximate \( H''(\zeta \to \infty) \to 0 \)] in order to determine \( a_1 \). The value \( \zeta_{\text{max}} = 1000 \) is found to be sufficiently large to approximate \( \infty \) in this case. The case \( e = 0 \) has exact solution \( H(\zeta) = \zeta \) (so that \( a_1 = 0 \)) which is useful in establishing some initial shooting solutions.

The numerical calculations described here and shown in the main text have been performed using the mathematical software Matlab.

**APPENDIX C. PHYSICAL PROPERTIES**

The fluid properties and calculated values of parameters used here are listed in Table C1. The interfacial thermal resistance \( R^* \) is calculated from the following expression Stephan and Hammer (1994):
\[
R^* = \frac{2 - f}{2f} \frac{T_s \sqrt{2\pi RT_s/M(\rho - \rho_V)}}{\mathcal{E}^2 \rho \rho_V}, \tag{C1}
\]
where \( M \) is the molar mass, \( R \) is the universal gas constant, and \( f \) is the accommodation coefficient taken here to be unity.

According to available data (Lauga et al., 2007), the slip length \( l_s \) varies from nm to \( \mu m \) depending on state of the solid substrate, wettability, and molecular parameters of liquid (Snoeijer and Andreotti, 2013). For water, the value 10 nm seems to be a reasonable value to be used (Nikolayev, 2010). For water at ambient pressure \( \ell_\beta \) and \( \ell_s \) are of a comparable order (\( N_s = 0.69 \)), see Table C1.

*Interfacial Phenomena and Heat Transfer*
**TABLE C1:** Fluid properties and calculated values of system parameters for water and toluene

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<thead>
<tr>
<th></th>
<th>Water</th>
<th>Toluene</th>
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<tr>
<td>$T_s$ (K)</td>
<td>373.12</td>
<td>293.15</td>
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<tr>
<td>$p_{sat}$ (Pa)</td>
<td>101325</td>
<td>2919</td>
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<tr>
<td>$p_V$ (kg/m$^3$)</td>
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<td>0.11</td>
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<td>$\rho$ (kg/m$^3$)</td>
<td>958.4</td>
<td>866.8</td>
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<tr>
<td>$L$ (kJ/kg)</td>
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<tr>
<td>$k$ (W/mK)</td>
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<td>0.14</td>
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<tr>
<td>$M_{gas}$ (g/mol)</td>
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<td>92.1</td>
</tr>
<tr>
<td>$\eta$ (Pa·s)</td>
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<td>$5.8\times10^{-4}$</td>
</tr>
<tr>
<td>$\gamma$ (mN/m)</td>
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<td>28.5</td>
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<tr>
<td>$l_s$ (nm)</td>
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<td>10</td>
</tr>
<tr>
<td>$R^*$ (Km$^2$/W)</td>
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<td>$3.1\times10^{-6}$</td>
</tr>
<tr>
<td>$\ell_s \theta_Y^2 / \Delta T$ (nm/K)</td>
<td>$4.5\times10^{-3}$</td>
<td>$2.4\times10^{-2}$</td>
</tr>
<tr>
<td>$\ell_s \theta_Y$ (nm)</td>
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<td>30</td>
</tr>
<tr>
<td>$\ell_{qY} \theta_Y$ (nm)</td>
<td>40.3</td>
<td>443</td>
</tr>
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<td>$N_s$ (−)</td>
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<td>0.07</td>
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<td>$\epsilon \theta_Y^2 / \Delta T$ (1/K)</td>
<td>$10.4\times10^{-5}$</td>
<td>$5.4\times10^{-5}$</td>
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