THERMOCAPILLARY MIGRATION OF AN ATTACHED DROP ON A SOLID SURFACE

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Abstract — Migration of a small drop of liquid, initially at rest on a level, solid surface, can be induced by means of thermocapillary forces. If a temperature gradient is imposed across the solid, it has the effect of diminishing the surface tension on the warmer side of the droplet. Consequently, migration manifests itself as the difference in surface tension preferentially draws the droplet toward the cooler region of the solid. The study describes the behavior of a droplet modeled as an infinitely long strip of finite width and arbitrary height profile, subject to a uniform temperature gradient imposed along the base. Lubrication theory is employed to determine the velocity and pressure fields within the drop, as well as the net migration velocity of the droplet as a whole. The role of the dynamic boundary condition in the vicinity of the contact lines (including the allowance for slip) on the migration velocity is highlighted.

1. INTRODUCTION

In general, the interfacial tension at a fluid-fluid interface can depend on temperature or composition. If one modifies either of those two variables, separately or in conjunction, a gradient of interfacial tension is expected to develop. Creation of such a gradient leads to the development of tangential stresses on the fluids, one consequence of which is the movement of the bulk fluid phases. This is the most general paradigm used to analyze problems involving interfacially driven drop migration. Composition gradients are relevant in the presence of surfactants, as well as in problems of spreading of molten solder drops which are composed of different elements. This brief note, however, is concerned with the production of surface tangential stresses by temperature gradients alone, in the absence of compositional effects.

Thermocapillary migration of immiscible drops and bubbles, suspended in a bulk liquid, has been the subject of numerous studies in recent years, partly due to its importance in materials processing in space. A comprehensive review of theoretical and experimental work in this area was recently prepared by Subramanian[1]. In addition, our work[2,3] has included

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studies of the effects of surfactants and inertia on thermocapillary migration, as well as the formulation of a reciprocal theorem for an easy calculation of the migration velocity[4]. Most of the contributions to this field have focused on the migration of drops and bubbles that are fully submerged in another liquid, as opposed to those attached to a solid wall. Thermocapillary migration of drops and bubbles in the vicinity of (but not attached to) a solid wall[5–8] has also received some attention. We initiate a similar set of studies, herein, for the case of a single liquid drop attached to a solid surface, on which a temperature gradient is imposed.

Previous work that deals directly with the interfacially-induced motions of liquid drops on solid surfaces includes that of Brochard[9], Ehrhard and Davis[10], Chaudhury and Whitesides[11], Smith[12]. Building on the general formulation by Greenspan[13], Ehrhard and Davis have examined the spreading of a drop on a heated or cooled surface, but without horizontal gradients. Chaudhury and Whitesides have induced an uphill migration of drops on an incline via surface composition gradients. Smith has examined the transient evolution of the drop profile when a temperature gradient is imposed along the surface. Finally, Brochard has examined theoretically the migration caused by either chemical or thermal gradients on a surface. His detailed analysis provides an approximate expression for the migration velocity as a function of the thickness of the drop at its center (for a flat drop). However, the regions of high dissipation near the contact lines (where stress singularities develop) are not fully accounted for. Our analysis is similar to Brochard's, but it applies to droplets having an arbitrary height profile, consistent with lubrication theory. In addition, by allowing for slip in the vicinity of the contact lines, the singularities which otherwise manifest themselves are removed. The migration speed is found to depend strongly on the slip parameter, however. References 14 through 20 provide other examples where the the dynamic condition at the contact line is important in determining the motion of an interface along a solid.

An interesting aspect of the attached drop problem which can be understood based on simple physical arguments is that the drop migrates toward the *cold* side on the surface. This is in contrast with the thermocapillary migration of freely suspended drops and bubbles which migrate toward the hot side. This can be simply explained as follows. Referring to Fig. 1, if the surface temperature is increasing to the right, the surface tension on the drop surface (being a decreasing function of temperature) will be smaller on the right side of the drop than on the left. Thus, a surface flow is established from low to high tension regions — in this case from right to left. As dictated by the resulting viscous flow within the drop and the no-slip boundary condition on the solid surface, the drop has to migrate to the left, toward the cold side.

2. PROBLEM FORMULATION

Consider a long, thin droplet attached to a level, solid plate (Fig. 1). As a simplification, the drop is taken to be infinitely long in the direction perpendicular to the xy-plane, and appears as an infinite strip of finite width when viewed from the top. In addition, suppose the width of the drop is much larger than its average height. In this limit, lubrication theory[21] can be used to obtain the required hydrodynamic quantities analytically. Let x denote the horizontal direction and let the width of the attached drop on the surface be 2ℓ, with $-\ell < x < \ell$ underneath the drop. Denote by $h(x)$ the height profile of the drop as a function of the horizontal coordinate. Validity of the lubrication approximation requires the inequality $h/\ell << 1$ to be true and the derivatives of $h(x)$ to be small.

Let (u, v) denote the (x, y)-components of the velocity field within the drop, and p the pressure. Under the lubrication approximation, the continuity, x- and y-momentum equations reduce to

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0\,, \tag{1}$$

$$\mu \frac{\partial^2 u}{\partial y^2} = \frac{\partial p}{\partial x}\,, \tag{2}$$

$$\frac{\partial p}{\partial y} = 0\,, \tag{3}$$

where μ denotes the viscosity of the drop. Moreover, a coordinate system is chosen such that the observer translates with the drop. Thus, the wall appears move to the right with velocity U. With this in mind, and assuming that a steady state shape has been reached, the continuity condition (1) is integrated at a given x, from 0 to $h(x)$, with respect to y. Use of Leibnitz rule with the kinematic condition,

$$v = uh'(x) \quad \text{at} \quad y = h(x)\ , \tag{4}$$

eventually yields

$$\int_0^{h(x)} u(x, y)\, dy = 0\ . \tag{5}$$

Physically, (5) indicates that there is no net mass flux across any vertical cross section of the drop, in the moving reference frame.

The problem of finding the temperature field within the drop can be simplified based on a similar approximation. For small Peclet numbers, when the drop is a good thermal conductor, the temperature field within the drop satisfies Laplace's equation. In the lubrication limit, the latter simply requires the second derivative of temperature with respect to

y to vanish. On assuming minimal heat loss to the air (which can be achieved experimentally by taking steps to minimize convection in the surrounding air), the temperature field within the drop is found to be exactly the same as that along the base of the drop, with no y-variation. Therefore, the temperature field throughout the drop is given by

$$T = T_o + Gx \, , \tag{6}$$

where G is the temperature gradient along the solid surface and T_o is the instantaneous value of temperature at the wall at the centerline of the drop.

The hydrodynamics boundary conditions to be imposed are as follows: Along the base of the drop the no-penetration condition requires $v = 0$; this condition was previously used in the integration of the continuity expression, above. In problems which involve contact line motion, the no-slip boundary condition creates singularities in the stresses at the contact lines[14]. To compensate, an *ad hoc* slip coefficient b (which has units of length and can be called a slip length) is introduced, and the boundary condition modified to

$$u = U + b\frac{\partial u}{\partial y} \quad \text{at} \quad y = 0 \; . \tag{7}$$

If b is identically zero, (7) simply reduces to the no-slip boundary condition. For small b, the fluid is allowed to slip in regions where the velocity gradient (or shear stress) becomes large, near the contact lines.

At the interface, the kinematic boundary condition (4) was already employed in the derivation of (5). Of the dynamic conditions, the normal stress balance cannot be imposed because the shape profile has been assumed as a known function. The tangential stress balance which accounts for surface tension variation along the surface, reduces, under the lubrication approximation, to the form

$$\mu\frac{\partial u}{\partial y} = \frac{\partial \sigma}{\partial x} = \sigma_T\frac{dT}{dx} = \sigma_T G \quad \text{at} \quad y = h(x) \; . \tag{8}$$

Here σ is the surface tension and σ_T is the rate of change of surface tension with temperature (generally a negative number) which is assumed to be constant.

When the drop reaches its terminal migration velocity, the sum of forces acting on the drop must be zero. Consider the x-component of these forces. There is no force on the drop in the x-direction by the surrounding air, taken to be inviscid and of uniform pressure. The only forces on the drop are from shear stress at the wall and from the contact lines at the two ends. Per unit length in the z-direction, the force-free condition reduces to

$$-\int_{-\ell}^{\ell} \mu \left.\frac{\partial u}{\partial y}\right|_{y=0} dx + \sigma_B \cos\theta_B - \sigma_A \cos\theta_A = 0 \; , \tag{9}$$

where the subscripts A and B are associated with the cool and warm ends, respectively. The angles θ are shown in Fig. 1.

The above set of equations constitutes a well-posed problem that can be solved for the migration velocity U, as well as the entire pressure and velocity fields in the drop. The solution is presented in the next section.

3. SOLUTION FOR GENERAL $h(x)$

The general solution to equations (2) and (3) is the quadratic function

$$u(x,y) = \frac{1}{2\mu}\frac{dp}{dx}y^2 + c_1(x)y + c_2(x) \ . \tag{10}$$

Application of boundary conditions (7) and (8) produces expressions for coefficients $c_1(x)$ and $c_2(x)$ of the form

$$c_1(x) = \frac{\sigma_T G}{\mu} - \frac{1}{\mu}\frac{dp}{dx}h(x) \ , \tag{11}$$

$$c_2(x) = U + \frac{b}{\mu}\sigma_T G - \frac{b}{\mu}\frac{dp}{dx}h(x) \ . \tag{12}$$

If one substitutes (10)–(12) into the continuity formula (5), an expression for the pressure gradient can be obtained:

$$\frac{dp}{dx} = \frac{\frac{3}{2}\sigma_T G h + 3\mu U + 3b\sigma_T G}{h^2 + 3bh} \ . \tag{13}$$

Expressions (10) and (13) represent a complete solution to the lubrication equations. [Eq. (13) can be integrated to find the pressure field everywhere.] The only remaining unknown is the migration speed U, which appears in (12) and (13). To find U, we finally impose the requirement that the droplet is force-free, as expressed by (9). To make the derivation easier, we note that boundary condition (7) permits the velocity gradient at $y = 0$ to be expressed in terms of u itself. After making this substituting for the integrand in the first term in (9) and noting that u is itself equal to $c_2(x)$ at $y = 0$ [cf. (10)], one finds the following explicit expression for the migration velocity:

$$U = -\frac{\sigma_T G}{6\mu J} + \frac{\sigma_T G b}{2\mu} - \frac{\sigma_B \cos(\theta_B) - \sigma_A \cos(\theta_A)}{6\mu \ell J} \ , \tag{14}$$

in which

$$J \equiv \frac{1}{2\ell}\int_{-\ell}^{\ell} \frac{dx}{h(x) + 3b} \ . \tag{15}$$

4. DISCUSSION

The principal result of our analysis is expression (14) for the thermocapillary migration velocity of a thin two-dimensional drop, having an arbitrary height profile, on a solid surface. Its evaluation requires determining the value of the integral J, defined by (15), involving the height profile $h(x)$ and the slip length b. Note that the contact angles θ_A and θ_B appearing in (14) are not independent of the given height profile. Rather, they are simply related to the derivatives of $h(x)$ at the two end points. Furthermore, as a consequence of the assumed linear dependence of σ on T, one has $\sigma_A = \sigma_o - \sigma_T \ell G$ and $\sigma_B = \sigma_o + \sigma_T \ell G$.

The limiting case of the slip coefficient b tending to zero is worth considering. In that limit, the second term on the RHS of (14) is negligible. However, depending on the height profile $h(x)$, the parameter J defined by (15) might not have a finite limit as b vanishes. In particular, if the height profile $h(x)$ has a finite slope at $x = \pm\ell$ (corresponding to a contact angle less than $\pi/2$) the integral (15) would be infinite for $b = 0$. For instance, near $x = -\ell$, if $h(x) \sim a(x+\ell)^m$, then J becomes singular as b tends to zero, for $m \geq 1$. On the other hand, the singularity is not present for $0 < m < 1$. A similar argument holds at $x = \ell$.

For the case of a drop whose height profile corresponds to an exact semicircle, $h(x) = \sqrt{\ell^2 - x^2}$, the foregoing suggests that the limiting case of no-slip ($b \to 0$) is well-defined, producing a droplet migration velocity of

$$U = -\frac{\sigma_T G \ell}{3\pi\mu} \ , \tag{16}$$

The profile forms contact angles of $\pi/2$ at the endpoints. Of course, the case of a semicircular drop does not strictly conform to the lubrication approximation.

A case more closely conforming to the lubrication limit is the "cylindrical cap" drop which is the solution to the static equations when the contact angles at the two ends are both very small and equal to their static values, θ_S. In that case, the drop profile is approximately an inverted parabola in the form

$$h(x) = \frac{\tan(\theta_S)}{2\ell}\,(\ell^2 - x^2)\,. \tag{17}$$

If this expression for $h(x)$ is substituted into (15), the resulting value of J is

$$J = \frac{1}{\ell\tan(\theta_S)} \frac{2\tanh^{-1}[1/\sqrt{1+B}]}{\sqrt{1+B}} \ , \tag{18}$$

where B is a dimensionless slip parameter defined by

$$B \equiv \frac{6b}{\ell\tan(\theta_S)} \ . \tag{19}$$

As B tends to zero, J tends to infinity (logarithmically) and the migration speed (14) approaches zero. This is consistent with the fact that if a no-slip boundary condition is imposed at the contact line, an infinite force is required to overcome the stress singularity. The migration velocity of the drop has a sensitive dependence on the slip parameter. Therefore, if one can design careful experiments to measure the steady migration speeds of small drops on solid surfaces, the results can be used to obtain an indirect evaluation of the slip coefficient b, which might be difficult to measure directly.

Finally, a comment about the contribution from the contact force at the ends on the migration speed is in order. The effect of the contact forces is represented by the last term on the RHS of (14). It is known[22] that the contact angle at a liquid/solid contact line is itself dependent on temperature. More importantly, the contact angle is also a function of the velocity of the contact line on the solid surface, (the angle is larger than the static value on the advancing side of the drop and smaller on the receding side[14]). Accounting for both of these effects, as well as for the difference in the surface tension itself at the two ends, is straightforward if the exact dependence of the contact angle on temperature and relative velocity is known for the system under consideration. It should be recognized, however, that the present analysis only provides the steady state value of the migration velocity of the drop, given its final height profile. An equally important problem involves the determination of the height profile itself as it evolves in time. The latter evolution is strongly influenced by the conditions at the dynamic contact lines.

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FIGURE CAPTION

Figure 1 — Side view of an infinite two-dimensional drop attached to a solid surface. Temperature increases linearly to the right on the surface. In a coordinate system translating with the migrating drop, the wall appears to move to the right with velocity U.