THERMOCAPILLARY AND GRAVITATIONAL MIGRATION OF A DROP ON A SOLID SURFACE IN TWO- AND THREE DIMENSIONS

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Abstract

We present new models of idealized drops in two and three dimensions that move by thermocapillarity, gravity, or a combination thereof while attached to an inclined solid surface. The drops' shapes, velocities, and temperature fields can be studied. Our models are based on Reynolds equations suitable for these systems, and have options to include a no-slip condition, a precursor film, and the disjoining pressure arising from long-range van der Waals forces. Lubrication theory approximations are used to simplify the derivations. Analytical solutions for the drops' shapes remain elusive, as does the 3D drop's temperature field, so a foundation for follow-up numerical and experimental studies is included. For the 2D case, commentary is given about the equilibrium profile, equilibrium velocity, convection effects, and numerical formulations for the transient height profile and velocity. For the 3D case, a Boundary Integral Method representation to solve for the temperature field numerically is presented.

Keywords: thermocapillary and gravitational migration, three-dimensional drops, surface tension, precursor film, Reynolds equation.

1. INTRODUCTION

In systems having a fluid-fluid interface, the interfacial tension can change according to the temperatures and compositions of the fluids. Manipulation of temperature and/or composition can create tension gradients throughout the interface; the associated tangential stresses cause both fluids to move. Common to problems involving drops spreading, wetting, and migrating across solid surfaces, systems of this sort are ubiquitous in fields, such as life sciences, manufacturing, and mining; optofluidics, coating processes, cladding, soldering, casting, and tertiary oil recovery number among them [16]. The need for useful models of such systems is considerable.

For the system that we aim to model—a drop attached to and migrating across an inclined solid surface bearing a temperature gradient—contact lines add a twist to the already difficult task of modeling the interior dynamics of the drop. Haley and Miksis succinctly describe the challenge: "The motion of a drop on a solid surface is a moving-boundary value problem in fluid mechanics of considerable interest and difficulty...the fluid in the neighborhood of the contact line (three-phase-line) presents an added complication"[25].

Ehrhard and Davis developed a model for the non-isothermal spreading of an axisymmetric viscous drop on a horizontal plate [17]. Five major assumptions and approximations are central to their model: a slip law to relieve stress singularities at the contact lines, linear variation of surface tension with temperature, an adiabatic interface between the drop and air (small Biot number), and—arising from the lubrication theory approximations—small contact angles and small mobility capillary number. They devised a quasi-steady evolution equation for the drop's shape under small mobility capillary number. Mobility of the contact line (not slippage) limits spreading. The slip co-efficient vanishes to leading order in capillary number, a consequence of the non-existence of time derivatives. On this basis, Ehrhard and Davis modeled the spreading of thin drops by capillarity, thermocapillarity, and gravity under a variety of contact angle and speed conditions. Heating prevents the drop from spreading to infinity providing the advancing contact angle is zero.

In a different undertaking, Ehrhard conducted experiments on the isothermal and non-isothermal spreading of viscous drops on glass plates [16]. He discovered that, depending on the time scale, either

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gravitational or capillary forces can dominate the spreading. Heating the plate retarded spreading; cooling, the opposite. Both give rise to thermocapillary phenomena that produce flows altering the dynamics of the spreading. Erhard's experimental results confirm the theoretical predictions of his and Davis' model [17].

Dussan V. and Davis conducted experiments having to do with the motion of a fluid-fluid interface along a solid surface, resulting in what has become one of the better-known studies in this field [15]. They formalized the concept that the fluid-fluid interface rolls on or off the solid. Apart from having demonstrated that the no-slip boundary condition is kinematically compatible with a moving contact line, Dussan V. and Davis illuminated implications of the well-known force singularity at the contact lines. They claim, "It is therefore essential that the solution of posed boundary-value problems containing slip coefficients be able to predict some measurable physical quantities before the imposed slip is taken as a reasonable description of the local boundary condition.[15]"

Ngan and Dussan V. [32] studied the dynamics of liquid spreading on solid surfaces, intending to identify a boundary value problem capable of describing the dynamics of fluid having moving contact line, but excluding the fluid zone lying in the immediate vicinity of the contact line. They reviewed deficiencies in several models of other researchers to evaluate the parameters of their own models. From this perspective, Ngan and Dussan V. claim that many approaches are equivalent, giving rise to velocity fields with the same asymptotic structure near the moving contact line. One identifies the asymptotic structure of the fluid dynamics from the fluid interface's shape in the vicinity of the moving contact line. Of significance, they mentioned that studies of the dynamics of the fluids in the vicinity of the contact line can be categorized according to the mechanism used to alleviate the singularity. A precursor film may exist over the solid, spreading ahead of the apparent location of the contact line. Alternatively, slip may be permitted.

Moriarty and Schwartz [29] used matched asymptotic expansions to study the free surface shape of a thin drop pulled by gravity down a vertical wall. The small parameter in their study was the surface tension term from the lubrication equation. Surface tension forces are significant only in regions of large curvature such as the advancing edge of the drop. Conversely, surface tension plays a negligible role where the curvature is small such as the central region of the drop. Moreover, they modeled the motion of a liquid drop on a horizontal, spinning table, as well as the motion of a drop under the action of an air jet, and used a numerical time-marching scheme to gauge the accuracy of the surface tension theory, for which one does not assume arbitrarily small surface tension. To resolve the associated contact-line singularity in the numerical solution, they included a precursor film in their model. Moriarty *et al.* claim the nodal spacing in the finite difference description of the drop must be smaller than the thickness of the precursor layer, otherwise the wall appears 'dry' ahead of the drop and the contact-line singularity remains.

Haley and Miksis [25] studied the free surface shape of a viscous drop while modeling the effects of contact lines on the spreading of drops; they used a pseudo-spectral method to solve the full non-linear system. In their formulation, Haley and Miksis considered lubrication theory, slip, and the dependence of contact angle on slip velocity. They modeled the initial motion of the drop at a non-equilibrium contact angle using matched-asymptotic methods. Slip coefficients that were either constant or inversely proportional to the drop thickness or its square were considered. After having compared the results of their model with experimental data, Haley and Miksis concluded that it is possible to choose an appropriate model for contact line motion.

Hocking [26] used inter-molecular forces in his model along with a van der Waals force-model to include the contact angle. He concluded that his model can "describe all stages of the spreading process, from the initial formation of a precursor film, through the state in which the drop consists of a central core and tail, to the final stage [all] for infinite time." In Hocking's model, the drop spreads to infinity such that its height tends to zero everywhere; there is no equilibrium shape. Hocking used lubrication theory throughout his analysis, and included contributions from capillarity, viscosity, and inter-molecular forces.

Under the lubrication assumption, Braun *et al.* studied the reactive spreading of drops [6]. Solder drops have a metallic component that diffuses in the liquid towards the metal substrate, whereupon the component undergoes a reaction to form a solid, inter-metallic phase. Consequently, composition gradients arise along the free surface of the drop. Thermal gradients can also exist. The composition and thermal gradients can give rise to Marangoni flow. Within this framework, Braun *et al.* extended lubrication theory to include mass transport and solucapillarity. The model is based largely on Ehrhard and Davis' [17].

On the matter of chemically induced motion, Chaudhury and Whitesides [9] forced a water drop to move uphill (*i.e.,* against gravity) by imposing a chemical gradient across a solid, inclined surface.

Other works relevant to our model include [1] – [8], [10] – [14], [16] – [24], [27] – [28],[30], [31], and [33] – [37].

We continue to focus on tangential stresses arising from temperature gradients, not composition gradients, meaning that a gradient in interfacial tension at a fluid-fluid interface arises when a temperature gradient is applied locally. The rising tangential stresses then cause both fluids to move and thereby set the drop in motion—thermocapillary migration.

Our newest contribution is the expansion of our earlier model—that of a two-dimensional drop moving solely by thermocapillarity on a level solid surface—to the cases of two- and three-dimensional systems having an inclined surface, thereby allowing gravitational migration, too. Depending on the direction and magnitude of the temperature gradient and the inclination angle of the solid surface, thermocapillary migration and gravitational migration can work in tandem or against each other. It is even possible to maintain the drop in a station-keeping position by balancing thermocapillary migration in one direction (by the magnitude of the temperature gradient) against gravitational migration in the other (by the steepness of inclination). We have demonstrated this balancing mechanism experimentally [21].

The premise of our new model is based on finding a suitable Reynolds flux equation for describing the 2D- and 3D drops' shapes (i.e., transient height profiles) and velocities as they migrate by temperature gradients and gravity [33]. Even though one can derive the suitable Reynolds equations for these systems (albeit simplified equations using lubrication theory approximations), the analytical solutions for the shapes and velocities from the Reynolds equations remain elusive. Therefore, we include commentary and formulations for numerical solutions that can aid follow-up studies by computer and experiments.

2. THE CASE OF A DROP MODELED IN TWO DIMENSIONS

Problem definition. For the 2D case, we imagine an idealized system having horizontal coordinate x and a solid surface that is inclined by an angle α to the y-axis (Fig. 1). A drop is attached to the solid surface. In a frame of reference that moves with the drop, the solid surface moves with velocity U (x-direction). The drop is two-dimensional and of length 2ℓ, height profile $h(x,t)$ as a function of x and time t, and average height $\bar{h}$ (y-direction). Fluid properties of the drop are density ρ, dynamic viscosity μ, and surface tension σ. Inside the drop exists a velocity field $\vec{\mathbf{v}}(u,v)$ in which (u,v) denote the (x,y)-components of the velocity field, and fluid pressure p. A gradient of surface tension with respect to temperature $d\sigma/dT$ is allowed, as is a temperature gradient G_x in the x-direction. Depending on $d\sigma/dT$, G_x, and α, the drop can move by thermocapillarity, gravity, or a combination thereof.

Governing equations. To simplify the analysis, we use the lubrication theory approximations of $\bar{h}/\ell \ll 1$ and small derivatives of $h(x,t)$ throughout the derivation of our model. In other words, the length of the drop is much larger than its average height. The drop also is considered to be infinitely wide in the direction perpendicular to the xy-plane, appearing as an infinitely wide strip of finite length 2ℓ if it were viewed from above in three dimensions. Under these simplifications, one can derive a suitable Reynolds equation for the 2D case.

One begins with the simplified, lubrication theory approximations to the continuity-, x- and

y-momentum equations

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

$$\frac{\partial^2 u}{\partial y^2} = \frac{1}{\mu}\frac{\partial p}{\partial x} - \frac{\rho g \sin(\alpha)}{\mu} \ , \tag{2}$$

$$\frac{\partial p}{\partial y} = -\rho g \cos(\alpha) \ , \tag{3}$$

respectively. Gravity's influence on the drop's migration comes by way of the inclination angle of the solid surface.

Five boundary conditions are required to solve (1) – (3): one slip condition in the x-direction, one impermeability condition (i.e., the drop cannot penetrate the solid surface) at $y = 0$, one kinematic condition at $y = h(x,t)$, and two stress conditions (one normal, one tangential) on the fluid-fluid interface. The simplified forms of the slip boundary condition and impermeability condition under the lubrication theory approximations are

$$u = b\frac{\partial u}{\partial y} \ , \tag{4}$$

$$v = 0 \ , \tag{5}$$

having an ad hoc slip co-efficient b. The kinematic boundary condition can be derived from the substantial derivative

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \vec{\mathbf{v}} \cdot \nabla \ , \tag{6}$$

and the interface representation

$$f(x,y,t) \equiv y - h(x,t) = 0 \ , \tag{7}$$

such that

$$\frac{Df}{Dt} = 0 \ . \tag{8}$$

The resulting kinematic boundary condition at $y = h(x,t)$ is

$$\frac{\partial h}{\partial t} = v - u\frac{\partial h}{\partial x} \ . \tag{9}$$

The normal stress balance condition and tangential stress balance condition can be approximated by

$$\mu\frac{\partial u}{\partial y} \approx \frac{\partial \sigma}{\partial x} \ , \tag{10}$$

$$p = p_0 - \sigma\frac{\partial^2 h}{\partial x^2} \ , \tag{11}$$

in which the normal viscous stress is neglected in (10).

Equations (1)–(11) represent a well-posed problem for the transient height profile of the 2D drop from which the desired Reynolds equation can be derived.

Derivation of a Reynolds equation for the 2D drop system. One begins the derivation by integrating (1) from $y = 0$ to $y = h(x,t)$ (i.e., from the drop's base to its upper surface) for fixed x, applying Leibniz Rule, then combining the result with the kinematic boundary condition (9) to produce the initial form of the two-dimensional flux equation

$$\frac{\partial h}{\partial t} + \frac{\partial}{\partial x}\int_0^{h(x,t)} u(x,y,t)\, dy = 0 \ . \tag{12}$$

The pressure field comes from integrating (3) with respect to y then combining the result with (11)

$$p = -\rho g \cos(\alpha) y + P(x,t) \ , \tag{13}$$

$$P(x,t) = p_0 + \rho g \cos(\alpha) h(x,t) - \sigma \frac{\partial^2 h}{\partial x^2} \ . \tag{14}$$

One of the more interesting boundary conditions from a physical standpoint is the normal stress balance condition, modified here to incorporate van der Waals forces to compensate for the failure of continuum mechanics at contact lines. De Gennes *et al.* use the moving triple line (i.e., the contact line arising from the solid-liquid-gas interface) as a reference point to create a helpful description of the fluid profile [13]. In close proximity to the triple line, the continuum description fails and van der Waals forces dominate on a molecular domain of a few Angstroms, scaled as a; de Gennes calls this area the "proximal region." For finite equilibrium contact angles θ_e, the proximal region extends $a\theta_e^{-2}$ inward from the contact line and has an approximate thickness $a\theta_e^{-1}$. Moving from the triple line and farther inside the drop, capillary forces and Poiseuille friction dominate the "central region." Farthest from the triple line and well-inside the drop's "distal region," either macroscopic features related to the size of the droplet or gravitational forces prevail. In all three regions, the lubrication theory approximations may be applied to the flow field with a linearized form of capillary number.

The proximal region (i.e., molecular domain) is not well-understood so our model has the option of the conventional ad hoc slip co-efficient. But we go further because there is a better way to model the proximal region without relying on ad hoc parameters. Three simplifications are possible if one considers the height profile to have small slopes: lubrication theory approximations for the flow, linearization of the capillary pressure, and a simplified description of the van der Waals forces. The disjoining pressure Π arising from long-range van der Waals forces is

$$\Pi = \frac{A}{6\pi h^3(x)} \ , \tag{15}$$

having Hamaker constant A for a pure van der Waals fluid. For more complicated fluids (e.g., water), the form of Π is unclear, though reliable data exists for certain solid substrates [1, 11]. The van der Waals contribution arising in the normal stress balance can be included by adding the disjoining pressure term (15) to the pressure (14)

$$P(x,t) = p_0 + \rho g \cos(\alpha) h(x,t) + \frac{A}{6\pi h^3} - \sigma \frac{\partial^2 h}{\partial x^2} \ . \tag{16}$$

The velocity profile can be obtained by substituting (13) and (16) into (2), then twice-integrating

$$u(x,y,t) = \frac{1}{2\mu} \left(\frac{\partial P}{\partial x} - \rho g \sin(\alpha) \right) y^2 + c_1(x,t) y + c_2(x,t) \ . \tag{17}$$

Application of the boundary conditions (4) and (5) generate expressions for the arbitrary functions of integration $c_1(x,t)$ and $c_2(x,t)$

$$c_1(x,t) = \frac{1}{\mu} \left(\frac{\partial \sigma}{\partial x} - Q(x,t) h \right) \ , \tag{18}$$

$$c_2(x,t) = b c_1(x,t) \ , \tag{19}$$

having the convenient expression

$$Q(x,t) \equiv \frac{\partial P}{\partial x} - \rho g \sin(\alpha) \ . \tag{20}$$

Finally, substitution of $Q(x,t)$ in (12) via (17) yields the Reynolds equation that we seek, a flux equation describing the transient height profile of a 2D drop attached to an inclined solid surface and migrating by thermocapillarity, gravity, or a combination thereof

$$\frac{\partial h}{\partial t} + \frac{\partial}{\partial x} F(x, h, \frac{\partial h}{\partial x}, \frac{\partial^2 h}{\partial x^2}, \frac{\partial^3 h}{\partial x^3}) = 0 \quad , \tag{21}$$

$$F \equiv \frac{1}{6\mu} Q h^3 + \frac{1}{2\mu} \left(\frac{\partial \sigma}{\partial x} - Qh \right) \left(h^2 + 2bh \right) \quad . \tag{22}$$

An analytical solution for the drop's shape and velocity from this Reynolds equation remains elusive so a non-dimensional version of (21) is given to help advance follow-up research by numerical and experimental means. Variables should be scaled according to the dimensionless groups

$$x^* \equiv \frac{x}{\ell} \ , \ h^* \equiv \frac{h}{\ell} \ , \ t^* \equiv \frac{t}{(\ell/g)^{\frac{1}{2}}} \ , \ \sigma^* \equiv \frac{\sigma}{\rho g \ell^2} \ , \ b^* \equiv \frac{b}{\ell} \ , \ F^* \equiv \frac{F}{(\rho g \ell^3/\mu)} \ , \ Q^* \equiv \frac{Q}{\rho g} \ , \tag{23}$$

in which the asterisk superscripts denote dimensionless quantities. Substitution of (23) into (21) produces the dimensionless version of the Reynolds equation for our problem

$$\frac{\partial h^*}{\partial t^*} + \frac{\rho \sqrt{g \ell^3}}{\mu} \frac{\partial F^*}{\partial x^*} = 0 \ , \tag{24}$$

which is a form that is more suitable for numerical and experimental studies.

Static equilibrium profile. A formula for the shape of the drop in an equilibrium state, known as the static equilibrium profile or free surface shape, can be derived using the normal stress balance condition. One starts by assuming that all transients have vanished and the migrating drop has reached a steady shape. The stress balance condition [23] on the liquid-gas interface describes the the stress exerted by the liquid $\mathbf{P_{liq}}$ counteracting the stress exerted by the surrounding gas $\mathbf{P_{gas}}$

$$\hat{\mathbf{n}} \cdot (\mathbf{P_{gas}} - \mathbf{P_{liq}}) = -\nabla_s \sigma + \hat{\mathbf{n}} \left(\nabla_s \cdot \hat{\mathbf{n}} \right) \sigma \ , \tag{25}$$

having second rank tensors $\mathbf{P_{gas}}$ and $\mathbf{P_{liq}}$, outward unit normal to the interface (a unit vector) $\hat{\mathbf{n}}$, surface gradient along the interface ∇_s, and surface tension σ. By taking the inner product of (25) and the normal vector $\hat{\mathbf{n}}$, the normal stress balance condition can be written as

$$\hat{\mathbf{n}} \cdot (\mathbf{P_{gas}} - \mathbf{P_{liq}}) \cdot \hat{\mathbf{n}} = \left(\nabla_s \cdot \hat{\mathbf{n}} \right) \sigma \ . \tag{26}$$

Equation (26) is evaluated on the interface, which is the drop's upper surface $y = h(x)$; $\hat{\mathbf{n}} \cdot (\nabla_s \sigma)$ is zero by definition. Since the drop is thin and flat in the limit of the lubrication theory approximations, its upper surface is approximately parallel to the supporting plate. An expression equivalent to the LHS of (26) is

$$\hat{\mathbf{n}} \cdot \mathbf{P_{gas}} \cdot \hat{\mathbf{n}} - \hat{\mathbf{n}} \cdot \mathbf{P_{liq}} \cdot \hat{\mathbf{n}} = p_{liq} - p_{gas} - \hat{\mathbf{n}} \cdot \boldsymbol{\tau} \cdot \hat{\mathbf{n}} \quad \text{at} \quad y = h(x) \ , \tag{27}$$

in which the components of the normal vector and the viscous stress tensor $\boldsymbol{\tau}$ are

$$\hat{\mathbf{n}} = (n_1, n_2, n_2) \ , \quad \text{and} \tag{28}$$

$$\boldsymbol{\tau} = \mu \begin{pmatrix} 2\frac{\partial u}{\partial x} & \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} & \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \\ \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} & 2\frac{\partial v}{\partial z} & \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} \\ \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} & \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z} & 2\frac{\partial w}{\partial z} \end{pmatrix} \ . \tag{29}$$

Using (27)–(29), the LHS of (26) can be written as

$$p_{liq} - p_{gas} - \mu \left[2\frac{\partial u}{\partial x} n_1 n_1 + \left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y} \right) n_1 n_2 + \left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right) n_1 n_3 + \right.$$

$$\left(\frac{\partial v}{\partial x}+\frac{\partial u}{\partial y}\right)n_2n_1+2\frac{\partial v}{\partial y}n_2n_2+\left(\frac{\partial w}{\partial y}+\frac{\partial v}{\partial z}\right)n_2n_3+$$

$$\left(\frac{\partial u}{\partial z}+\frac{\partial w}{\partial x}\right)n_3n_1+\left(\frac{\partial w}{\partial y}+\frac{\partial v}{\partial z}\right)n_3n_2+2\frac{\partial w}{\partial z}n_3n_3\Bigg]\Bigg|_{y=h(x)} . \tag{30}$$

Several simplifications to (30) are possible. For the 2D case, derivatives with respect to the the third dimension $\partial/\partial z$ vanish, as does the associated component of the the velocity field w. Furthermore, the unit vector that is normal to the upper surface of the drop is roughly equal to $\hat{\mathbf{j}}$, meaning $n_1 = 0$, $n_2 = 1$, and $n_3 = 0$

$$p_{liq} - p_{gas} - 2\mu\frac{\partial v}{\partial y} = \sigma\left(\nabla_s \cdot \hat{\mathbf{n}}\right) \quad \text{at} \quad y = h(x) . \tag{31}$$

The curvature term $(\nabla_s{\cdot}\hat{\mathbf{n}})$ on the RHS of (31) for the given height profile $h(x)$ can be expanded by representing the interface as

$$f(x,y) \equiv y - h(x) . \tag{32}$$

The normal to the newly defined surface can be found from the well-known expression

$$\hat{\mathbf{n}} = \frac{\nabla f(x,y)}{\left|\nabla f(x,y)\right|} , \tag{33}$$

the result being

$$\hat{\mathbf{n}} = \frac{\hat{\mathbf{j}} - h'(x)\hat{\mathbf{i}}}{(1+h'(x)^2)^{\frac{1}{2}}} . \tag{34}$$

It is then straightforward to find the divergence of the normal along the upper surface of the drop

$$\nabla_s \cdot \hat{\mathbf{n}} = -h''\left\{\left(1+h'(x)^2\right)^{-\frac{1}{2}} - h'(x)^2\left(1+h'(x)^2\right)^{-\frac{3}{2}}\right\} . \tag{35}$$

Under the lubrication theory approximations, the derivative of the height profile $h'(x)$ is small (i.e., much less than 1), which is characteristic of a nearly flat and thin drop. Equation (35) can be simplified to

$$\nabla_s{\cdot}\hat{\mathbf{n}} \approx -h''(x) . \tag{36}$$

One can further reduce the normal stress balance (31) using (36) to

$$p_{liq}(x) - p_{gas} - 2\mu\frac{\partial v}{\partial y} = -\sigma(x)h''(x) . \tag{37}$$

Under the lubrication theory approximations, $\partial v/\partial y$ is negligible by comparison to the other terms of (37) and the static shape of the drop can be found by a perturbation expansion, the most natural perturbation parameter being the dimensionless capillary number ϵ,

$$\epsilon \equiv \frac{\mu U}{\sigma_0} \ll 1 , \tag{38}$$

in which U represents the velocity scale (75), enabling one to write the perturbation expansions as

$$p_{liq}(x) \approx p_{liq,0} + \epsilon p_{liq,1} + \ldots , \tag{39}$$

$$\sigma(x) \approx \sigma_0 + \epsilon\sigma_1(x) + \ldots , \tag{40}$$

$$h(x) \approx h_0(x) + \epsilon h_1(x) + \ldots . \tag{41}$$

In (39)–(41), variables with '0' and '1' subscripts denote zeroth- (equilibrium) and first-order terms, respectively. An argument can be made based entirely on physical grounds that small viscous forces do not significantly deform the shape of the drop. Since the entire problem is confined to the regime of small capillary number, it is reasonable to assume that there is no significant deviation of the profile from its equilibrium configuration. Substitution of the perturbation expansions (39)-(41) into (37) yields

$$\begin{aligned} -p_{gas} + p_{liq,0} + \epsilon p_{liq,1}(x) &= -\left(\sigma_0 + \epsilon\sigma_1(x)\right)\left(h_0''(x) + \epsilon h_1''(x)\right) \\ &= -\sigma_0 h_0''(x) - \epsilon\sigma_0 h_1''(x) - \epsilon\sigma_1(x) h_0''(x) + O(\epsilon^2) \ . \end{aligned} \tag{42}$$

According to standard perturbation methods, terms with 'like-powers' of ϵ are equated

$$p_{liq,0} - p_{gas} = -\sigma_0 h_0''(x) \ , \tag{43}$$

$$-p_{liq,1}(x) = \sigma_0 h_1''(x) + \sigma_1 h_0''(x) \ . \tag{44}$$

The terms of (43) are associated with ϵ^0, whereas those of (44) are associated with ϵ^1. Information about the equilibrium profile $h_0(x)$ can be extracted from (43). To do so, one starts with the difference between the external and internal pressures

$$\Delta p \equiv p_{liq,0} - p_{gas} \ . \tag{45}$$

The sign of Δp is generally positive, meaning that the pressure within the drop is greater than p_{gas}. The x-dependent parts in the liquid pressure p_{liq}, the surface tension

$$\sigma(x) = \sigma_0 + \sigma_T G x \ , \tag{46}$$

and the viscous stresses are linear with respect to the temperature gradient G or the migration velocity U. In the limit of small capillary number, the x-dependent terms are negligible to leading order. By neglecting these terms and gravity contributions, an equation for the leading order height profile $h_0(x)$ can be produced

$$h_0''(x) = -\frac{\Delta p}{\sigma_0} \ . \tag{47}$$

The height profile, therefore, is the same as a stationary drop. The general solution of (47) is the quadratic

$$h_0(x) = -\frac{\Delta p}{\sigma_0}\frac{x^2}{2} + a_1 x + a_2 \ , \tag{48}$$

having constants a_1 and a_2. The boundary conditions at the contact lines require

$$\begin{cases} h_0(x) = 0 & \text{at} \quad x = \pm\ell \\ h_0'(x) = \tan(\theta_S) & \text{at} \quad x = -\ell \\ h_0'(x) = -\tan(\theta_S) & \text{at} \quad x = +\ell \end{cases} \tag{49}$$

in which the advancing and receding contact angles are equal to a static value θ_S (i.e., the case of a stationary drop)

$$\theta_A = \theta_B = \theta_S \ . \tag{50}$$

Application of the boundary conditions (49) produces the constants $a_1 = 0$ and $a_2 = \left(\Delta p\, \ell^2 / 2\sigma_0\right)$, which gives an inverted parabola for the equilibrium height profile.

$$h_0(x) = \frac{\Delta p}{2\sigma_0}\left(\ell^2 - x^2\right) \ . \tag{51}$$

The analysis can be taken one step further to incorporate the important effect of the contact angles on the drop's shape. After having specified the contact angle θ_S, the constant part of the pressure in the drop can be determined. In addition, the boundary conditions involving the first derivatives of the height profile offer a way to express $h_0(x)$ in terms of θ_A and θ_B. The result of these considerations is a relation for Δp as function of the contact angles

$$\frac{\Delta p}{\sigma_0} = \frac{\tan(\theta_S)}{\ell} \ . \tag{52}$$

By combining (51) and (52), one can write an alternative formulation of the height profile

$$h_0(x) = \frac{\tan(\theta_S)}{2\ell}\left(\ell^2 - x^2\right) \ . \tag{53}$$

An important consequence of the first-derivative boundary conditions is $\theta_A = \theta_B$, which is expected for a drop that has developed a static equilibrium shape.

It is useful to replace the length ℓ in (53) with the drop's volume, a static quantity that is often easier to measure. One knows the volume of the drop *a priori*. In transforming the problem from three dimensions to two, volume is replaced by area, namely, a lengthwise, vertical slice through the drop. The contact angles can also be measured. From the area A and reference surface tension σ_o, the length of the drop and pressure difference can be predicted. To create a formula for the area, $h_0(x)$ is integrated along the total base length of the droplet

$$\begin{aligned} A &\equiv \int_{-\ell}^{\ell} h_0(x)\,dx \\ &= \frac{\Delta p}{2\sigma_0}\left(\ell^2 x - \frac{x^3}{3}\right)\Bigg|_{-\ell}^{+\ell} , \end{aligned} \tag{54}$$

which reduces to

$$A = \frac{2\Delta p \ell^3}{3\sigma_0} \ . \tag{55}$$

Eliminating Δp from (52) and (55) yields

$$\ell = \left(\frac{3A}{2\tan(\theta_S)}\right)^{\frac{1}{2}} \tag{56}$$

Back-substitution of (56) into (55) generates the corresponding expression for Δp

$$\Delta p = \left(\frac{\sigma_0^2}{12A}\right)^{\frac{1}{2}} (2\tan(\theta_S))^{\frac{3}{2}} \ . \tag{57}$$

Using $\Delta p = \Delta p(\sigma_0, A, \theta_S)$ and $\ell = \ell(\theta_S, A)$, the equilibrium height profile is

$$h_0(x) = \frac{(\tan(\theta_S))^{\frac{3}{2}}}{2\sqrt{3A}}\left(\frac{3A}{\tan(\theta_S)} - x^2\right) \ . \tag{58}$$

The height profile, therefore, is parabolic, at least to leading-order under the lubrication theory approximations. The profile can be substituted into the expression for the migration velocity to produce a value for a thin drop. The first order correction $h_1(x)$ to the drop's shape can also be found by a dual expansion in capillary number and lubrication parameter.

For small capillary numbers, the height profile of the drop is well-approximated by its form for a stationary drop, given by (58). If the expression for $h_0(x)$ is substituted into the integral (73), J can be written as

$$J = \frac{1}{\ell\tan(\theta_S)}\frac{2\tanh^{-1}[1/\sqrt{1+B}]}{\sqrt{1+B}} , \tag{59}$$

having the dimensionless slip parameter B

$$B \equiv \frac{6b}{\ell\tan(\theta_S)} \ . \tag{60}$$

As B tends to zero, J tends to infinity logarithmically and the migration velocity approaches zero. This is consistent with the fact that infinite forces are required to move the drop if a no-slip boundary condition is imposed at the contact line. If one can measure the migration velocities of small drops on solid surfaces, the data can be used to obtain a value of the slip coefficient b indirectly, which can be difficult to measure by other means directly.

The role of convection. Convection might play an important role in the dynamics of the migrating drop. For a drop hanging from a solid surface (Fig. 1.4), the liquid density near the drop's cooler side is greater than the density near its warmer side. Gravity pulls the denser cell of cooler liquid toward the inverted apex of the hanging drop, displacing the less dense, warmer cell upward. The convective motion of descending cooler liquid and ascending warmer liquid could cause the drop to migrate, which might likewise happen in the case of a drop attached to the top of a solid surface. In the hanging configuration, convection should cause the drop to move toward the warmer region of the solid, whereas the supported drop should move to the cooler region. Depending on the whether the drop is hanging or supported, convection could either assist or impede thermocapillary migration. Convection may or may not dominate thermocapillary migration, and to understand the extent of its influence, one can turn to the Boussinesq approximation to gain insight.

Consider the general form of the Navier-Stokes equation

$$\rho \frac{D\vec{v}}{Dt} = -\nabla P + \mu \nabla^2 \vec{v} + \rho \vec{g} \ . \tag{61}$$

According to the Boussinesq approximation, the density ρ can be expanded in terms of a reference density ρ_0 and the variation of density with respect to temperature

$$\rho = \rho_0 + \left(\frac{d\rho}{dT} \right)_0 (T - T_0) \ . \tag{62}$$

In 2D and at zero angle of inclination, the Boussinesq approximation contributes only to the lubrication version of the y-momentum equation

$$0 = \frac{\partial p}{\partial y} + (\rho_0 + \beta' G x)\, g \cos(\alpha) \ , \tag{63}$$

where $\beta' \equiv (d\rho/dT)_0$. The reference temperature T_0 is measured at the drop's center base. Using an expression for the van der Waals force, it can be shown that

$$P(x,t) = (\rho_0 + \beta' G x) g \cos(\alpha) h + p_o + \frac{A}{6\pi h^3} - \sigma \frac{\partial^2 h}{\partial x^2} \ . \tag{64}$$

Dimensionless groups help to determine the relative contributions of convection and surface tension

$$\begin{cases} \rho^* \equiv \rho/\rho_0 \ , & T^* \equiv T/T_0 \ , \quad \sigma^* \equiv \sigma/\sigma_T G \ell \ , \\ P^* \equiv P/\rho_0 g \bar{h} \ , & x^* \equiv x/\ell \ , \quad h^* \equiv h/\bar{h} \ . \\ \beta^* \equiv \beta' G \ell/\rho_0 & \end{cases} \tag{65}$$

Ignoring van der Waals effects, the relevant pressure gradient for the two-dimensional Reynolds equation is

$$\frac{\partial P^*}{\partial x^*} = \left(h^* + x^* \frac{\partial h^*}{\partial x^*} \right) \beta^* \cos(\alpha) + \frac{\partial h^*}{\partial x^*} \cos(\alpha) - \frac{\partial}{\partial x^*} \left(\sigma^* \frac{\partial^2 h^*}{\partial x^{*2}} \right) \frac{\sigma_T G}{\ell g \rho_0} \ . \tag{66}$$

Consider the dimensionless group

$$\frac{\sigma_T G}{\ell \rho_0 g} \ , \tag{67}$$

and the parameter β^*. The convection terms play less of a role as the angle of inclination increases to 90-degrees, as when β^* is small, too. For the case of $\beta^* \equiv 0$, the pressure gradient reduces to a dimensionless form analogous to the dimensional one of (20)

$$\frac{\partial P^*}{\partial x^*} = \frac{\partial h^*}{\partial x^*} \cos(\alpha) - \frac{\partial}{\partial x^*} \left(\sigma^* \frac{\partial^2 h^*}{\partial x^{*2}} \right) \frac{\sigma_T G}{\ell \rho_0 g} \ . \tag{68}$$

For liquids such as glycerol, the variation in density with respect to temperature over the temperature range 0–100 C is only several percent. If the surface tension variation with respect to temperature σ_T is large, then capillary forces will dominate the system. One might counter-argue that even if the variation of β is much greater than several percent, capillary forces still dominate under micro-gravity conditions, in which the dimensionless group (67) becomes very large. In the absence of data for the physical parameters of this system, one cannot comment definitively on the extent of convection's contribution to the drop's migration.

Numerical representation. Equation (24) is a scalar problem involving a non-linear partial differential equation. Techniques for solving such equations are well-known [2], such as the Lax Method, the Lax-Wendroff Method, the MacCormack Method (a predictor-corrector version of the Lax-Wendroff Method), and the Rusanov Method. We recommend the MacCormack Method because, unlike the Lax-Wendroff Method, the MacCormack Method does not have a Jacobian and is easier to apply. Another point in the MacCormack Method's favor is that it provides good resolution at discontinuities, which can occur at the contact lines of our problem.

The MacCormack Method representation of (24) is

$$h^{*\overline{n+1}}_{j} = h^{*n}_{j} - \frac{\Delta t}{\Delta x}\left(F^{*n}_{j+1} - F^{*n}_{j}\right) \ , \tag{69}$$

$$h^{*n+1}_{j} = \frac{1}{2}\left[h^{*n}_{j} + h^{*\overline{n+1}}_{j} - \frac{\Delta t}{\Delta x}\left(F^{*\overline{n+1}}_{j} - F^{*\overline{n+1}}_{j-1}\right)\right] \ , \tag{70}$$

a finite-element system that is first-order in time and fourth-order in space.

The finite-element system was coded using CM-FORTRAN and run on a Connection Machine CM-5 supercomputer. A finite-element mesh having 500 nodes with constant inter-nodal spacing Δx represents the solid surface; nodes are numbered left-to-right from 1 to 500 (Fig. 2). A single 500-element parallel array represents the 500 nodes, corresponding to the index j in (69) and (70). Each element in the array contains a real number: the drop's dimensionless height at each node. The array's size strikes a balance between computational speed and resolution. The time index is n, with temporal increments Δt. A precursor film was added to the system and slip was excluded to handle contact line singularities.

Transient height profile (numerical solution). Thermocapillary migration and gravity migration were simulated individually and together. Using data[2] from the experimental component of our investigation, dimensionless groups were calculated [21]. Relevant values include: length of drop ℓ (0.0075 m), mean thickness of drop $\bar{h}$ (0.005 m), spatial gradient of temperature G (-460 C/m), reference surface tension σ_0 (2.87×10^{-2} N/m), thermal gradient of surface tension σ_T (-8.91×10^{-5} N/mC), fluid density ρ (1.0717×10^{-3} kg/m^3), and Hamaker constant A (book value 10^{-20} Nm/s). Simulation runs reached equilibrium after approximately 5,000 time-steps. Numerical instabilities were not found, even beyond 20,000 time steps.

Figure 2 shows the drop's shape when it migrates only by thermocapillarity. The drop's dimensionless height is measured along the vertical axis; length, the horizontal axis. The simulation was run with $\Delta t/\Delta x = 1$. In the top frame, the drop is initially 300 nodes long and semi-circular, having a maximum radius 0.5. Although the drop cannot be more than 500 nodes long, it can 'wrap-around' to node-0 as its advancing edge migrates beyond node-500. The system can also be thought of as an infinite train of drops with periodic boundary conditions. A uniform temperature gradient heats the solid surface such that the drop's left side is warmer than its right side. Instead of using slip, a precursor film of thickness 0.01 covers the entire solid surface. During the first 5,000 time-steps of the simulation, the drop moves to the right and starts to deform (middle frame). By 12,000 time-steps (bottom frame), the drop reaches its steady-state equilibrium, and has different contact angles at the advancing and receding edges. In the final frame, the forward shift of the apex is pronounced and the drop spreads to some extent.

[2]Based on engine oil: CD SAE 30, specific gravity 1.0717 at 25 C).

Variations in the drop's height can also be visualized as a color density plot. In Fig. 3, the horizontal axis represents successive time-steps, progressing left-to-right as the system evolves in time. The vertical axis denotes distribution of the drop over the solid surface as viewed from above. From this point-of-view, the top and bottom of the plot correspond to left and right sides of the solid surface, respectively. Rather than the cross-sectional view of the height profile as in Fig. 2, the initially semi-circular drop appears as a narrow strip of color that is one time-increment wide and 300 nodes long (far left 'slice' of plot). Red denotes regions of maximum height; blue are minima. One can easily identify the red zone as the apex of the semi-circle, initially located in the middle of the drop. Migration direction is 'down' the page (i.e., left-to-right across the solid surface). As the simulation progressed, successive color snapshots were taken, all viewed from above the drop. Though individual snapshots look like narrow strips of color, when placed side-by-side and left-to-right, the resulting composite plot appears as a wide band of rainbow-like color. At the far right of the plot, the drop has reached a steady state shape, and its apex has shifted markedly forward. Note spreading and development of a faint structure trailing the drop (thin, light-blue line above the main band of color).

Thermocapillary and gravity effects are both in play for the simulations of Fig. 4. The frames represent the shape of the drop at different time-steps. The parameters and axes are as in Fig. 2 with one major difference—the solid surface slopes to the left. A 'tug-of-war' exists between the thermal gradient that drivers the drop to the right by thermocapillarity and the angle of inclination that drives pulls the drop to the left by gravity. In Fig. 4-a,b, the inclination angle is 2-degrees. Gravity wins in this scenario; during the first 2,000 time-steps, the drop shifts from its original shape and position (Fig. 4-a) to the left (Fig. 4-b), and starts to deform. Limited spreading occurs. Combinations of inclination angles and temperature gradients produce a variety of dynamics. Certain combinations, for example, fully impede migration in perfect balance of gravity against thermocapillarity. Under sufficiently large temperature gradients and small angles of inclination, the drop moves 'uphill' by thermocapillary effects, a rather exotic case shown in Fig. 4-c (initial shape) and Fig. 4-d (after 2,000 time-steps).

When the temperature gradient is removed and the drop is allowed to move by gravity alone, it migrates *and* spreads (not shown). The apex shifts quickly towards the advancing edge and the gentle, bulbous front produced by thermocapillary migration is absent. Rather, the apex is pointed and part of an almost vertical, advancing front.

Finally, under conditions of no-slip and no precursor film, the drop deforms as in Fig. 2, but does not move.

Velocity (numerical solution). At least two numerical methods are at one's disposal to determine velocities of thermocapillary migration. One method tracks nodal position of the virtual center-of-mass of the simulated drop as a function of time-step (Fig. 5). Center-of-mass velocity $U^*_{c.of.m}$ is constant and equal to the slope of the line:

$$U^*_{c.of.m} = 1.12 \times 10^{-3} \ . \tag{71}$$

The other method [22] numerically verifies the formula from our earlier work that predicts the velocities of drops migrating on solid surfaces by thermocapillarity

$$U = -\frac{(d\sigma/dT)G}{6\mu J} + \frac{(d\sigma/dT)Gb}{2\mu} - \frac{\sigma_B \cos(\theta_B) - \sigma_A \cos(\theta_A)}{6\mu\ell J} \ , \tag{72}$$

in which

$$J \equiv \frac{1}{2\ell}\int_{-\ell}^{\ell} \frac{dx}{h(x) + 3b} \ . \tag{73}$$

For a semi-circular drop, (72) and (73) reduce to

$$U = -\frac{(d\sigma/dT)G\ell}{3\pi\mu} \ . \tag{74}$$

Using the velocity scale based on (30)

$$U_{scale} = \frac{(d\sigma/dT)G\bar{h}}{\mu} \ , \tag{75}$$

the velocity formulae (73) and (74) can be written in dimensionless form as

$$U^* = -\frac{1}{6J^*} \ . \tag{76}$$

Equation (76) is valid when contact forces do not dominate. From the two-dimensional simulation of thermocapillary migration, an equilibrium height profile was obtained after sufficient iteration. From the equilibrium height profile, a value for the J^*-integral was calculated, followed by a value for U^*, yielding

$$U^* = 1.43 \times 10^{-3} \ . \tag{77}$$

Though the two methods use different equations, their respective velocity predictions should be in agreement, since all equations were derived from the same theoretical starting point. In other words, the results should be self-consistent. Velocities U^* and $U^*_{c.of.m}$ differ by approximately 21%. Though not a perfect match, the comparison indicates fair self-consistency, insofar as the numerical analysis can produce. Furthermore, this result could be interpreted as a measure of the numerical method's accuracy.

Verification of velocity. It is prudent to check if the velocity formula of the 2D migrating drop can be reproduced by an alternate approach. The basic premise is to extract an ordinary differential equation describing the height profile $h(x)$ (when steady state is reached) from the 2D Reynolds equation, which must have a solution corresponding to a unique velocity U for a given height profile. This U should be identical to the two-dimensional velocity formula, a steady state quantity.

To do so, one starts the derivation from (21). The original velocity formula describes migration in the context of zero-gravity and with

$$\sigma_T G \equiv \frac{\partial \sigma}{\partial x} \ . \tag{78}$$

To compensate for the moving reference frame, a co-ordinate translation is performed with the definition

$$\eta \equiv x - Ut \ , \tag{79}$$

and with U as yet unspecified. The profile $h(x,t)$ is then assumed to be of the form $h(\eta)$. With the dimensionless scales of (23) (here, η is scaled with ℓ), the dimensionless version of (79) is

$$\eta^* = x^* - U^* t^* \ . \tag{80}$$

The governing equation can then be transformed to the new reference frame after integrating once with respect to η^*

$$-U^* h^* + F^* = 0 \ . \tag{81}$$

Using $h = h(\eta)$, and thereafter integrating (81) with respect to η^*, it can be shown that

$$h^* \left\{ 1 + \left(\frac{\bar{h}}{\ell}\right)^2 \left[\frac{h^*}{3} + b^*\right] \left[{h^*}'' + \left(\frac{\sigma_0}{(d\sigma/dT)G\ell}\right)\right] {h^*}''' \right\} + b^* - U^* = 0 \ , \tag{82}$$

a non-linear ordinary differential equation for h^*. If it is true that

$$\frac{\sigma_0}{(d\sigma/dT)G\ell} >> 1 \ , \tag{83}$$

then (83) can be simplified to

$$h^* \left\{ 1 + \left[\frac{h^*}{3} + b^*\right] \left[\left(\frac{\bar{h}}{\ell}\right)^2 \left(\frac{\sigma_0}{(d\sigma/dT)G\ell}\right) {h^*}''' \right] \right\} + b^* - U^* \approx 0 \ , \tag{84}$$

with associated boundary conditions that include static contact angle θ_S, namely

$$\begin{cases} h^*(x^*) = 0 & \text{at} \quad x^* = \pm 1 \\ h^{*\prime}(x^*) = \tan(\theta_S) & \text{at} \quad x^* = -1 \\ h^{*\prime}(x^*) = -\tan(\theta_S) & \text{at} \quad x^* = +1 \end{cases} \tag{85}$$

Perhaps the best way to solve this problem is by the shooting method whereby one must find a particular value of U for which (84) has a solution.

2. THE CASE OF A DROP MODELED IN THREE DIMENSIONS

Problem definition. For the 3D case, we imagine an idealized system having cartesian coordinates x, y, and z, and a solid surface that is inclined by an angle α to the y-axis (Fig. 1). A drop is attached to the solid surface. In a frame of reference that moves with the drop, the solid surface moves with speed U (x-direction) or V (y-direction). The drop is three-dimensional and has initial maximum length l along the x-axis, initial maximum width l along the y-axis, height profile $h(x, y, t)$ as a function of x, y and time t, and average height $\bar{h}$ (z-direction). Fluid properties of the drop are density ρ, dynamic viscosity μ, and surface tension σ. Inside the drop exists a velocity field $\vec{\mathbf{v}}(u, v, w)$ for which (u, v, w) denote the (x, y, z)-components of the velocity field, and fluid pressure p. Gradients of surface tension with respect to temperature $d\sigma/dT$ are allowed, as are temperature gradients G_x and G_y in the x- and y-directions, respectively. Depending on $d\sigma/dT$, G_x, G_y, and α, the drop can move by thermocapillarity, gravity, or a combination thereof.

Governing equations. To simplify the analysis, we use the lubrication theory approximations of $\bar{h}/\ell \ll 1$ and small derivatives of $h(x, y, t)$ throughout the derivation of our model. Under these simplifications, one can derive a suitable Reynolds equation for the 3D case.

One begins with the simplified, lubrication theory approximations to continuity-, x-, y-, and z-momentum equations

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \ , \tag{86}$$

$$\frac{\partial^2 u}{\partial z^2} = \frac{1}{\mu}\frac{\partial p}{\partial x} - \frac{\rho g}{\mu}\sin(\alpha) \ , \tag{87}$$

$$\frac{\partial^2 v}{\partial z^2} = \frac{1}{\mu}\frac{\partial p}{\partial y} \ , \tag{88}$$

$$\frac{\partial p}{\partial z} = -\rho g \cos(\alpha) \ , \tag{89}$$

respectively. Gravity's influence on the drop's migration comes by way of the inclination angle of the solid surface.

Seven boundary conditions are required to solve (86) – (89): two slip conditions (one each for the x- and y-directions), one impermeability condition (i.e., the drop cannot penetrate the solid surface) at $z = 0$, one kinematic condition, and three stress conditions (one normal, two tangential) on the fluid-fluid interface. The simplified forms of the slip boundary conditions and impermeability condition under the lubrication theory approximations are

$$u = b\frac{\partial u}{\partial z} \ , \tag{90}$$

$$v = b\frac{\partial v}{\partial z} \ , \tag{91}$$

$$w = 0 \ , \tag{92}$$

having an ad hoc slip co-efficient b, and all of which are evaluated at $z = 0$. The kinematic condition can be derived from the substantial derivative

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \vec{\mathbf{v}} \cdot \nabla \ , \tag{93}$$

and the interface representation

$$f(x, y, z, t) \equiv z - h(x, y, t) = 0 \ , \tag{94}$$

such that

$$\frac{Df}{Dt} = 0 \ . \tag{95}$$

The resulting kinematic boundary condition at $z = h(x, y, t)$ is

$$\left. \frac{\partial h}{\partial t} + u\frac{\partial h}{\partial x} + v\frac{\partial h}{\partial y} - w = 0 \right|_{z=h(x,y,t)} \ . \tag{96}$$

The normal stress balance condition

$$p = p_0 + \frac{A}{6\pi h^3} - \sigma \left(\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} \right) \Bigg|_{z=h(x,y,t)} \ , \tag{97}$$

has a disjoining pressure Π with Hamaker constant A of the form

$$\Pi = \frac{A}{6\pi h^3(x)} \ . \tag{98}$$

Equation (98) is for a pure van der Waals fluid and arises from long-range van der Waals forces. The tangential stress balance boundary conditions can be simplified with the lubrication theory approximations

$$\mu \left. \frac{\partial u}{\partial z} \approx \frac{\partial \sigma}{\partial x} \right|_{z=h(x,y,t)} \ , \tag{99}$$

$$\mu \left. \frac{\partial v}{\partial z} \approx \frac{\partial \sigma}{\partial y} \right|_{z=h(x,y,t)} \ , \tag{100}$$

which are evaluated at the interface.

Equations (86)–(100) represent a well-posed problem for the transient height profile of the 2D drop from which the desired Reynolds equation can be derived.

Derivation of a Reynolds equation for the 3D drop system. One begins the derivation by restricting net mass flux across any vertical cross-section of the drop in the moving reference frame by integrating the continuity equation (86) from $z = 0$ to $z = h(x, y, t)$ (i.e., from the drop's base to its upper surface) for fixed x and y

$$\int_0^{h(x,y,t)} \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) dz = 0 \ . \tag{101}$$

applying the Leibnitz rule, then applying the kinematic boundary condition (96) to produce the initial form of the three-dimensional flux equation

$$\frac{\partial h}{\partial t} + \frac{\partial}{\partial x} \int_0^{h(x,y,t)} u(x, y, z, t)\, dz + \frac{\partial}{\partial y} \int_0^{h(x,y,t)} v(x, y, z, t)\, dz = 0 \ . \tag{102}$$

The velocity field components $u(x, y, z, t)$ and $v(x, y, z, t)$ arise from twice integrating (87) and (88) with respect to z, yielding

$$u(x, y, z, t) = \frac{1}{2\mu} \left(\frac{\partial p}{\partial x} - \rho g \sin(\alpha) \right) z^2 + c_1(x, y, t) z + c_2(x, y, t) \ , \tag{103}$$

$$v(x, y, z, t) = \frac{1}{2\mu} \frac{\partial p}{\partial y} z^2 + d_1(x, y, t) z + d_2(x, y, t) \ . \tag{104}$$

The integration functions are found by applying the slip, impermeability, and tangential stress balance boundary conditions (90), (91), (92), (99), and (100) to (18) and (19):

$$c_1(x,y,t) = \frac{1}{\mu}\left[\frac{\partial\sigma}{\partial x} - \left(\frac{\partial p}{\partial x} - \rho g \sin(\alpha)\right) h(x,y,t)\right] \ , \tag{105}$$

$$c_2(x,y,t) = \frac{b}{\mu}\left[\frac{\partial\sigma}{\partial x} - \left(\frac{\partial p}{\partial x} - \rho g \sin(\alpha)\right) h(x,y,t)\right] \ , \tag{106}$$

$$d_1(x,y,t) = \frac{1}{\mu}\left[\frac{\partial\sigma}{\partial y} - \left(\frac{\partial p}{\partial y}\right) h(x,y,t)\right] \ , \tag{107}$$

$$d_2(x,y,t) = \frac{b}{\mu}\left[\frac{\partial\sigma}{\partial y} - \left(\frac{\partial p}{\partial y}\right) h(x,y,t)\right] \ . \tag{108}$$

An equation for the pressure field can be found by integrating (4) with respect to z:

$$p = -\rho g \cos(\alpha) z + P(x,y,t) \ . \tag{109}$$

The new function $P(x,y,t)$ describes the pressure field along the base of the drop and must be characterized, which can been done by combining the normal stress balance condition (8) with (24). By taking partial derivatives $\partial/\partial x$ and $\partial/\partial y$, the pressure gradients can then be formulated:

$$\frac{\partial P}{\partial x} = \left(\rho g \cos(\alpha) - \frac{A}{2\pi h^4}\right)\frac{\partial h}{\partial x} - \frac{\partial\sigma}{\partial x}\left(\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2}\right) - \sigma\left(\frac{\partial^3 h}{\partial x^3} + \frac{\partial^3 h}{\partial x \partial y^2}\right) \ , \tag{110}$$

$$\frac{\partial P}{\partial y} = \left(\rho g \cos(\alpha) - \frac{A}{2\pi h^4}\right)\frac{\partial h}{\partial y} - \frac{\partial\sigma}{\partial y}\left(\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2}\right) - \sigma\left(\frac{\partial^3 h}{\partial y \partial x^2} + \frac{\partial^3 h}{\partial y^3}\right) \ . \tag{111}$$

Using the convenient definition

$$Q \equiv \frac{\partial p}{\partial x} - \rho g \sin(\alpha) \ , \tag{112}$$

substitution of (18) and (19) in (17) creates the Reynolds equation that we seek for our system:

$$\frac{\partial h}{\partial t} + \frac{\partial}{\partial x}\left[\frac{1}{6\mu}Qh^3 + \frac{1}{2\mu}\left(\frac{\partial\sigma}{\partial x} - Qh\right)\left(h^2 + 2bh\right)\right] + \tag{113}$$
$$\frac{\partial}{\partial y}\left[\frac{1}{6\mu}\frac{\partial p}{\partial y}h^3 + \frac{1}{2\mu}\left(\frac{\partial\sigma}{\partial y} - \frac{\partial p}{\partial y}h\right)\left(h^2 + 2bh\right)\right] = 0 \ .$$

Central to our model, (28) governs the transient height profile $h(x,y,t)$ of a 3D drop migrating on inclined solid surface by gravity and thermocapillarity. Equation (28) is fourth-order in space and first-order in time, and includes the effects of surface tension, slip, a possible precursor film, van der Waals forces, and viscosity.

Temperature Field. To solve (28), the temperature distribution field of the drop must be formulated. In our earlier work, we found an exact, analytical solution for the temperature field of a drop simplified to two-dimensions and having a semi-circular profile. The hydrodynamic equations for the system, however, are intractable analytically so we applied the lubrication theory approximations as a further simplification before solving for the velocity field. Although the lubrication theory approximations restricts whatever solution arises for the velocity field to idealized systems of thin drops, our experimental studies revealed the velocity field actually works well in the real world for predicting the behavior of fat drops, too [21].

Analytical solutions for 2D- and 3D drops of arbitrary profile continue to be elusive so we outline a Boundary Integral Method (BIM) formulation here to help readers conduct their own numerical analyses according to their personal preferences of programming languages and computing power. A detailed treatment of the BIM is in [2].

Consider the system of a liquid drop attached to a level solid surface in a gaseous environment and free to convect heat with the gas. The drop, initially at rest, has an arbitrary height profile

$h(x)$ and total base-length $2l$. A linear temperature gradient is imposed on the surface having one end at a constant hotter temperature; the other end, at a constant cooler one. Alternatively, one can stipulate that an arbitrary temperature distribution $f(x)$ exists on the surface. The interfacial boundary of the drop can be parameterized into two curves C_1 and C_2 using a parameterization variable s. The curve C_1 runs counterclockwise from the point s_1 across the top of the drop to the endpoint s_n at $x = l$. From s_n to s_1, the curve C_2 is defined at the interface between the drop and the surface. The region bounded by C is denoted by D: the drop's body. A unit normal $\hat{n}$ points outward from the drop's body at every point $s \in C$ for which $C \equiv C_1 + C_2$. Under these conditions, one can solve for the temperature field along C.

As for the BIM formulation, Laplace's equation governs the temperature field $T(x, y)$ inside the drop:

$$\nabla^2 T(x, y) = 0 \ , \tag{114}$$

with two boundary conditions, one being a Dirichlet boundary condition that constrains a known temperature distribution function $f(x)$ to exist along the base of the drop (at $y = 0$). The Dirichlet boundary condition represents the contact of the drop's base with the differentially heated surface on which it sits. Convection effects must be considered throughout the drop's upper free surface $h(x)$, which gives rise to the other boundary condition, a mixed one. The Dirichlet- and mixed boundary conditions are

$$T = f(x) \ \text{ at } y = 0 \ , \tag{115}$$

$$-k\hat{n} \cdot \vec{\nabla} T = h(T - T_{air}) \ \text{ at } y = h(x) \ , \tag{116}$$

in which the thermal conductivity of the liquid, the convection co-efficient, and ambient air temperature are represented by the constants k, h, and T_{air}, respectively.

Consider the following integral equation:

$$\int_D G(\vec{x}, \vec{x}_0) \ dA_{\vec{x}} = 0 \ , \tag{117}$$

in which the Green's function is given by $G(\vec{x}, \vec{x}_0)$ and the actual position of the source in the Green's functions is denoted by $\vec{x}_0$.

One starts the development the Boundary Integral Equations by expanding (32) by parts:

$$\int_D T(\vec{x}) \, \nabla^2 G(\vec{x}, \vec{x}_0) \, dA_{\vec{x}} + \int_C (G(\vec{x}, \vec{x}_0) \frac{\partial T}{\partial n} - T(\vec{x}) \frac{\partial G}{\partial n}(\vec{x}, \vec{x}_0)) \, dS_{\vec{x}} = 0 \ . \tag{118}$$

The key to using the boundary conditions is to note that the normal partial derivative $\partial/\partial n$ can be written as

$$\frac{\partial}{\partial n} \equiv \hat{n} \cdot \vec{\nabla} \longrightarrow \frac{\partial T}{\partial n} = \vec{n} \cdot \vec{\nabla} T \ . \tag{119}$$

Substitution of the boundary conditions (30) and (31) in (33) gives

$$-\int_C G(\vec{x}, \vec{x}_0) \frac{\partial T}{\partial n} \, dS_{\vec{x}} = \int_{C_1} G(\vec{x}, \vec{x}_0) \, \frac{h}{k}(T - T_{air}) \, dS_{\vec{x}} - \int_{C_2} G(\vec{x}, \vec{x}_0) \, \hat{n} \cdot \vec{\nabla} f(x) \, dS_{\vec{x}} \ . \tag{120}$$

At the base of the drop, the unit normal points from the $-\hat{j}$ direction outward such that

$$\frac{\partial T}{\partial n} = \frac{\partial f(x)}{\partial n} = \hat{n} \cdot \vec{\nabla} f(x) \ . \tag{121}$$

For a linear temperature gradient, (35) reduces to

$$(0, -1) \cdot (\frac{\partial f}{\partial x}, 0) = 0 \ , \tag{122}$$

and the integral associated with C_2 vanishes. By contrast, a non-trivial contribution is made by (31). The Boundary Integral Equations for the system can now be written in terms of the element of boundary arc length ds as

$$\frac{1}{2}T(s_0) - \int_0^{S_{max}} T(s)\, G'(s, s_0)\, ds = \frac{h}{k}\int_0^{S_n} T(s)\, G(s, s_0)\, ds - \frac{hT_{air}}{k}\int_0^{S_n} G(s, s_0)\, ds\ . \tag{123}$$

In tensor form, (38) is

$$\mathbf{B}\cdot\vec{T} - \frac{1}{2}\vec{T} = \mathbf{A}\cdot\vec{T} - \vec{C}\ , \tag{124}$$

in which the bold-faced quantities represent second-rank tensors. The discretized version of the Boundary Integral Equation becomes

$$(\mathbf{A} + \mathbf{B} - \frac{1}{2})\cdot\vec{T} = \vec{C}\ , \tag{125}$$

and the entire problem has been reduced to solving (40) for the temperature distribution values contained in $\vec{T}$.

Equation (40) can be solved numerically. The first step is to discretize the boundary C. It can be shown analytically that an inverted parabola describes the static equilibrium profile of the drop, at least to a first order approximation from the lubrication theory approximations. One can use a simple hemisphere, therefore, to represent the drop's shape. Equal increments of ds along C_1 and C_2 can be generated during the discretization process, which includes parameterizations for $x(s)$ and $y(s)$. It should be noted that the ds increments along C_1 are not equal to those along C_2 because $C_1 \neq C_2$. An illustrative example of a discretization of $\mathbf{A}$ is

$$\frac{h}{k}\int_0^{S_{max}} T(s)\, G(s, s_i)\, ds = \frac{h}{k}\sum_{j=1}^{sn}(f_l(i,j)\, T_j + f_r(i,j)\, T_{j+1}\,)\, ds\ , \tag{126}$$

in which

$$f_l(i,j) = \int_{S_j}^{S_{j+1}} G(s, S_i)(\frac{S_{j+1} - s}{S_{j+1} - S_j})\, ds\ , \tag{127}$$

$$f_r(i,j) = \int_{S_j}^{S_{j+1}} G(s, S_i)(\frac{s - S_{j+1}}{S_{j+1} - S_j})\, ds\ . \tag{128}$$

Discretization of $\mathbf{B}$ is similar to $\mathbf{A}$ with the exception that $G(s, S_i)$ is replaced by $G'(s, S_i)$ in $\mathbf{B}$'s discretization. To include contributions from all nodal points, the indices range over $i \in \{1, smax\}$ and $j \in \{1, smax\}$.

A five-point integration scheme such as *qgaus* [3] can be used to integrate (41). Because the integrating engine requires interpolation of points within each ds element of the boundary, cubic splines must be calculated; *spline* and *splint* [3] provide interpolations of the $x(s)$ and $y(s)$ for any value of s. These subroutines require first- and second derivatives of $x(s)$ and $y(s)$ so it is prudent to plot the derivatives as functions of s before attempting any integration as a way to detect anomalies. This ensures reasonable benchmark values for interpolation are generated. To validate, curvatures at each nodal point may be computed according to

$$-x'(s)y''(s) + x''(s)y'(s) \approx 4/l \tag{129}$$

Since $G'(s, s_i)$ requires interpolation between first derivatives of the mesh, third derivatives must also be supplied to the cubic spline subroutines.

3. DISCUSSION

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FIGURE CAPTIONS

Figure 1 — The system of a 2D drop migrating by thermocapillarity and gravity while attached to an inclined solid surface. Temperature gradients can be imposed in the x-direction as well as inclination angle α to the y-axis.

Figure 2 — Simulated transient height profile of a 2D drop migrating by thermocapillarity and gravity while attached to an inclined solid surface. The solid surface slopes to the left by 2-degrees. Depending on the inclination angle, either gravity or thermocapillarity act in tandem or against each other. Gravity causes leftward migration; thermocapillarity, rightward. ((a) initial shape; (b), after 2,000 time-steps). In (c) and (d), combinations of temperature gradient and inclination angle can be chosen for which there is no migration: a balance of gravity against thermocapillarity. The drop can even be made to migrate uphill given sufficiently small inclination angle in proportion to the and large and thermal gradient sufficiently large ((c) initial shape; (d) after 2,000 time-steps).

Figure 3 — Simulated transient height profile of a 2D drop migrating by thermocapillarity and gravity while attached to an inclined solid surface. The solid surface slopes to the left by 2-degrees. When the drop is viewed from 'above' (i.e., along the y-axis looking down), a color map of the motion is possible. Colors range from blue (height profile minima of the drop) to red (drop's apex). Migration is apparent; the apex shifts markedly forward as the simulation progresses.

Figure 4 — Simulated velocity of a 2D drop migrating by thermocapillarity and gravity while attached to an inclined solid surface. The line's slope equals the velocity of the center-of-mass of the drop. The horizontal axis is a measure of time (i.e., time-step in the numerical integration) and the vertical axis denotes the nodal position of the center-of-mass as the drop migrates. The plot contains 14,500 data generated from a CM-5 supercomputer.

Figure 5 — Convection cells in a differentially heated drop. The existence of these cells is based on physical arguments. Convection might contribute to—or impede—migration by thermocapillarity and gravity.

Figure 6 — The system of a 3D drop migrating by thermocapillarity and gravity while attached to an inclined solid surface. Temperature gradients can be imposed in the x- and y-directions as well as inclination angle α to the y-axis.