Motion of a Drop on a Solid Surface Due to a Wettability Gradient

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The hydrodynamic force experienced by a spherical-cap drop moving on a solid surface is obtained from two approximate analytical solutions and used to predict the quasi-steady speed of the drop in a wettability gradient. One solution is based on approximation of the shape of the drop as a collection of wedges, and the other is based on lubrication theory. Also, asymptotic results from both approximations for small contact angles, as well as an asymptotic result from lubrication theory that is good when the length scale of the drop is large compared with the slip length, are given. The results for the hydrodynamic force also can be used to predict the quasi-steady speed of a drop sliding down an incline.

Introduction

Normally, a liquid drop introduced on a horizontal surface may spread, but its center of mass does not move. It is possible, however, to make the drop move by treating the surface to produce a gradient in wettability along the surface. This mechanism, first identified by Greenspan[1] and analyzed by Greenspan[1] and Brochard,[2] was experimentally demonstrated by Chaudhury and Whitesides.[3] Subsequently, additional experimental results were reported by Daniel and Chaudhury,[4] Daniel et al.,[5] and Suda and Yamada.[6] Experiments in which both a wettability gradient and a thermal gradient were simultaneously used are described by Sato et al.[7] Drop motion in a wettability gradient can be important in condensation heat transfer[8] and may eventually find use in microfluidics and for the removal of debris in ink-jet printing.

The main objective of a theoretical analysis is to predict the speed of a drop on a gradient surface. Greenspan,[1] who first considered this problem, was motivated by biological applications involving cell spreading and cell motion on surfaces. He neglected the role of gravity in deforming the drop and used a lubrication analysis, assuming the contact angle to be small, and invoked a slip boundary condition to eliminate the contact-line stress singularity that usually arises in these problems. Greenspan further assumed that the velocity of the contact line normal to itself can be modeled as being proportional to the difference between the dynamic contact angle θ and the equilibrium value θ_s, with a proportionality constant κ that is given. As justification for this model, he cited the work of Blake and Haynes,[9] who postulated that contact-line advancement results from molecules at the contact line overcoming an energy barrier and executing more jumps in the forward direction than in the backward direction. Using averaged equations over the thickness of the drop, Greenspan then developed an orderly perturbation expansion in a small parameter that is related to the capillary number, which is commonly defined as $\mu U/\gamma$, where μ is the viscosity of the liquid, U is the speed of the contact line, and γ is the liquid−gas surface tension. The perturbation parameter used by Greenspan is 3 times the capillary number, divided by θ_s^3. Greenspan developed general equations for the variation of the depth of the liquid with position along the solid surface and showed that at leading order, at any given instant in time, the curvature of the surface of the liquid should be uniform. He then applied the equations to several problems. In one such problem, the equilibrium contact angle is assumed to decrease linearly with distance x, in the form of $\theta_e = \theta_s(1 - \lambda x)$, with a gentle spatial gradient of magnitude $\lambda\theta_s$. Greenspan showed that, in this case, the footprint of the drop rapidly relaxes to its local equilibrium shape, and the drop subsequently moves slowly along the gradient surface at a speed that varies only slowly with time, concomitant with a slow variation of the radius of its footprint with time. The final result for the drop velocity given by Greenspan is $U = \kappa\lambda\theta_s R$, where R is the radius of the footprint. One cannot use Greenspan's equation for U to make a prediction without knowledge of κ, which depends on phenomena occurring at the molecular level. Also, it is worth noting that, in analyzing the motion of a drop in a wettability gradient, Greenspan did not use a force balance on the drop but rather the model for contact-line advancement based on the molecular kinetic theory of Blake and Haynes.[9]

Brochard,[2] apparently unaware of the existence of Greenspan's analysis, independently developed a theoretical model of the motion of two-dimensional ridges and three-dimensional drops in a wettability gradient. Brochard considered this motion in the presence and in the absence of temperature gradients and considered both small drops that are negligibly deformed by gravity and relatively large drops. We restrict our discussion to the isothermal case and small drops whose shapes are not influenced by gravity. Brochard recognized that the shape of the drop is influenced negligibly by the motion itself for gentle gradients. In the two-dimensional case of an infinitely long ridge formed by the static shape on a plane translated in the third direction, Brochard obtained a result for the driving force acting on the ridge using energy arguments and equated this to the hydrodynamic resistance offered to the motion of the ridge by the solid surface

(1) Greenspan, H. P. *J. Fluid Mech.* **1978**, *84* (1), 125.
(2) Brochard, F. *Langmuir* **1989**, *5*, 432.
(3) Chaudhury, M. K.; Whitesides, G. M. *Science* **1992**, *256*, 1539.
(4) Daniel, S.; Chaudhury, M. K. *Langmuir* **2002**, *18*, 3404.
(5) Daniel, S.; Sircar, S.; Gliem, J.; Chaudhury, M. K. *Langmuir* **2004**, *20*, 4085.
(6) Suda, H.; Yamada, S. *Langmuir* **2003**, *19*, 529.
(7) Sato, M.; Araki, K.; Matsuura, M.; Hasegawa, K.; Endo, A. Proceedings of the 2nd Pan Pacific Basin Workshop on Microgravity Sciences, Pasedena, CA, 2001; Paper IF-1123.
(8) Daniel, S.; Chaudhury, M. K.; Chen, J. *Science* ~~**1992**~~, *291*, 633.
(9) Blake, T. D.; Haynes, J. M. *J. Colloid Interface Sci.* **1969**, *30*, 421.

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to obtain a result for the quasi-steady velocity of the ridge. In calculating the hydrodynamic force, Brochard used lubrication theory, approximating the ridge by a wedge with a wedge angle equal to the contact angle, and further assumed the angle to be sufficiently small so that trigonometric functions of the angle could be expanded, retaining the first nonzero terms in these expansions. The hydrodynamic force was obtained by integrating the shear stress at the solid surface and truncating the domain slightly before the contact line to avoid the usual contact-line singularity. This cutoff distance, in which slip is assumed to relieve the singularity, is assumed to be of molecular dimensions. In an appendix to the paper, Brochard used a different approach to obtain the same result for the velocity of the ridge. Assuming that the dynamic contact angle is the same at the forward and rear ends of the ridge, Brochard equated the hydrodynamic resistance to the "unbalanced Young force" per unit length of the contact line written as $\gamma(\cos\theta - \cos\theta_e)$, where θ_e is the local equilibrium contact angle. Expanding this for small values of the angles, Brochard showed that, for the ridge to move with negligible deformation, the square of the dynamic contact angle must be approximately equal to the average of the squares of the equilibrium contact angles at the front and rear ends of the ridge. With this result, Brochard found the predictions for the quasi-steady velocity of the drop from the two approaches to be identical. Then, Brochard extended this second approach to the case of a three-dimensional drop, approximated by a spherical cap with a circular footprint. In a manner analogous to the case of the ridge, the unbalanced Young force acting normal to a small segment of the contact line was equated to the hydrodynamic resistance from the lubrication theory solution for the wedge and, in the small angle limit, was shown to lead to a consistent mathematical framework. The result was a prediction for the quasi-steady velocity of the drop $U = \gamma\theta_e^2 R\,(\mathrm{d}\theta_e/\mathrm{d}x)/(3\mu \ln \epsilon)$. Here, θ_e is the equilibrium contact angle at the location of the center of the footprint of the drop (assumed to be a circle), $\mathrm{d}\theta_e/\mathrm{d}x$ is the local rate of change of this equilibrium contact angle with distance, and ϵ is the ratio of the cutoff distance from the contact line (slip length) to the length scale of the drop. In summary, in the case of the spherical-cap drop, Brochard did not employ a force balance on the entire drop but rather a local balance in which only the forces normal to the contact line are balanced. The other crucial approximations made by Brochard are that the drop shape can be approximated by a wedge and that the contact angles are sufficiently small that the first nonzero terms in the expansions of trigonometric functions are adequate approximations.

Ford and Nadim[10] presented a lubrication analysis of the thermocapillary motion of a two-dimensional ridge of arbitrary shape on a surface on which a uniform temperature gradient is imposed. The ridge moves toward the cooler region on the surface because of the variation of the gas−liquid surface tension with temperature. The authors permitted the contact angles at the two ends of the ridge to be different and obtained results for the velocity and pressure fields as well as the steady velocity of the ridge. Ford and Nadim[10] also presented a detailed discussion of the role of the slip boundary condition and pointed out that, for a ridge with a semicircular shape (contact angle of 90°), the slip boundary condition is not necessary.

The objective of the present work is to develop an analysis for approximately calculating the hydrodynamic resistance offered by a solid surface to the motion of a drop that has the shape of a spherical cap. As recognized by Greenspan[1] and Brochard,[2] this is the shape that would be assumed by a drop when gravitational effects and shape deformation induced by motion are both negligible. We then balance this resistance with the driving force on the drop on a wettability gradient surface to predict the quasi-steady velocity of the drop. After presenting the result for the driving force, we obtain the hydrodynamic resistance by dividing the drop into a collection of wedges and give an approximate expression for the velocity of the drop in the case when the cosine of the contact angle can be approximated as a linear function of position. Next, we use lubrication theory to obtain a result for the hydrodynamic resistance and a corresponding result for the drop velocity. Also, we provide asymptotic results for the resistance and the drop velocity that are useful when the ratio of the slip length to the length scale of the drop is small. We also give results from the analysis that can be used when the driving force is gravity.

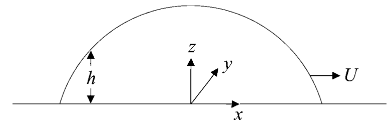

Figure 1. Sketch of a spherical-cap drop, showing the coordinate system.

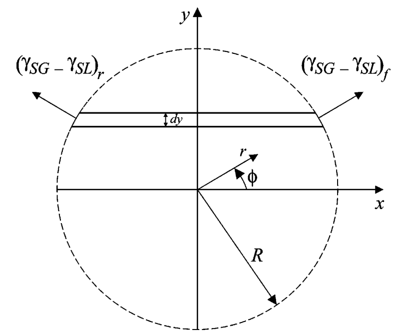

Figure 2. Plan view of the footprint of the drop.

Analysis

Driving Force. We begin by first writing a result for the driving force acting on a spherical-cap drop on a wettability gradient surface, as depicted in Figure 1.

The height of the drop is $h(x,y)$. A plan view of the footprint of the drop, which is a circle, is given in Figure 2.

The result for the driving force, which acts on the drop in the x direction, can be written as

$$F_{\text{driving}} = 2\int_0^{\pi R/2} [(\gamma_{SG} - \gamma_{SL})_f - (\gamma_{SG} - \gamma_{SL})_r] \cos\phi \, \mathrm{d}l \quad (1)$$

Here, γ_{SG} and γ_{SL} are the solid−gas and solid−liquid interfacial tensions, respectively, R is the radius of the footprint of the drop, ϕ is the polar angle identified in Figure 2, and $\mathrm{d}l$ is the length of a differential element of the contact line. The subscripts f and r correspond to "front" and "rear", respectively. One can write $\mathrm{d}l = R\,\mathrm{d}\phi$ and perform the integration in eq 1 when the variation of $\gamma_{SG} - \gamma_{SL}$ around the periphery is known. Young's equation is used to relate the difference $\gamma_{SG} - \gamma_{SL}$ to the local equilibrium contact angle θ_e and the liquid−gas interfacial tension γ, assumed to be constant, as follows.

$$\gamma_{SG} - \gamma_{SL} = \gamma \cos\theta_e \quad (2)$$

(10) Ford, M. L.; Nadim, A. *Phys. Fluids* **1994**, *6*, 3183.

Using eq 2, the result for the driving force can be rewritten as follows.

$$F_{\text{driving}} = 2R\gamma \int_0^{\pi/2} [\cos(\theta_e)_f - \cos(\theta_e)_r] \cos\phi \, d\phi \quad (3)$$

In the special case when $\gamma_{SG} - \gamma_{SL}$ and therefore $\cos\theta_e$ is linear in x, we can write

$$\cos\theta_e = I + Sx \quad (4)$$

where I and S are the intercept and slope, respectively, in a plot of $\cos\theta_e$ with distance x along the gradient. The integral in eq 3 can be evaluated analytically in this case leading to the following result for the driving force.

$$F_{\text{driving}} = \pi R^2 \gamma S \quad (5)$$

Even when $\cos\theta_e$ is not linear in x, a local linear fit is commonly used in interpreting experimental results.[4,5]

Hydrodynamic Force and Quasi-Steady Velocity: Wedge Approximation. In developing a description of the hydrodynamics, we assume incompressible Newtonian flow in the liquid with a constant density ρ and viscosity μ and use a reference frame attached to the moving drop, so that the drop is stationary and the solid surface moves in the negative x direction with a constant speed U. Under these conditions, a steady flow will be established within the drop. The motion in a vertical slab of the spherical cap of differential width dy, located at y, and extending through the entire height of that slab from $x = 0$ to the contact line is modeled as that occurring in a wedge, with θ_w representing the wedge angle. Given the typical length scales, viscosities, and speeds encountered in experiments, it is reasonable to neglect inertial effects and assume Stokes flow. The general solution for two-dimensional Stokes flow in cylindrical polar coordinates is well-known.[11] It has been specialized by Cox[12] for the situation in which motion is created in a fluid wedge immersed in a second fluid by the motion of a solid surface in contact with the two fluids. When Cox's solution is further specialized to the case when the fluid surrounding the wedge is a gas with negligible viscosity, the shear stress exerted by the solid surface on the liquid can be evaluated as

$$\tau_w(x,y) = 2\mu U \frac{\sin^2\theta_w}{(\sin\theta_w \cos\theta_w - \theta_w)(\sqrt{R^2 - y^2} - x)} \quad (6)$$

We can integrate this shear stress over the footprint of the drop to obtain the hydrodynamic resistance F_h in the x direction offered by the solid surface.

$$F_h = \int_\Omega \tau_w(x,y) \, d\Omega \quad (7)$$

where Ω is the circular area occupied by the footprint. To use this solution, one must relate the wedge angle θ_w to the dynamic contact angle θ. We assume that θ is uniform around the periphery of the drop. By using the geometrical result for the shape of the slab being considered, it can be established that $\tan\theta_w = \tan\theta \cos\phi$ on the circular boundary, so that

$$\tan\theta_w = A\sqrt{1 - \frac{y^2}{R^2}} \quad (8)$$

where the constant $A = \tan\theta$. Because of symmetry, the circle can be divided into four quadrants, each contributing equally to the total hydrodynamic force. Therefore, using the results from eqs 6 and 8, the integral in eq 7 needs to be evaluated only in the first quadrant, wherein $x \geq 0$ and $y \geq 0$, and the result multiplied by a factor of 4.

$$F_h = 8\mu UR \int_0^{1-\epsilon} \frac{A^2(1-Y^2)}{A\sqrt{1-Y^2} - [1 + A^2(1-Y^2)]\tan^{-1}(A\sqrt{1-Y^2})} \int_0^{\sqrt{1-Y^2}-\epsilon} \frac{dX}{(\sqrt{1-Y^2} - X)} \, dY \quad (9)$$

The variables (X, Y) used in the integration here are the dimensionless counterparts of the coordinates (x, y), scaled using R. The domain must be truncated at a small distance ϵR from the contact line to avoid singularity in the stress, which is the reason for the choice of the specific upper limits in the integrals in eq 9. The dimensionless parameter ϵ represents the ratio of the length of the slip region in which the no-slip condition is expected to break down to the radius of the footprint of the drop. The former is typically taken to be of molecular dimensions, and the latter is restricted to a maximum value of roughly a millimeter for common liquids, if one wishes to neglect the influence of gravity on the shape of the drop. Therefore, the value of ϵ can vary from 10^{-7} for a millimeter-scale drop to roughly 0.1 for a nanometer-scale drop.

The integration in X in eq 9 can be performed immediately, leading to the following final result for the hydrodynamic force exerted by the solid surface on the drop.

$$F_h = 8\mu UR \int_0^{1-\epsilon} \frac{A^2(1-Y^2)}{A\sqrt{1-Y^2} - [1 + A^2(1-Y^2)]\tan^{-1}(A\sqrt{1-Y^2})} \left[\frac{1}{2}\ln(1-Y^2) - \ln\epsilon\right] dY = 8\mu URf(\theta,\epsilon) \quad (10)$$

The integral, which depends on the dynamic contact angle θ and the parameter ϵ, must be obtained numerically. It is useful to give an asymptotic analytical result that can be obtained when the contact angle, and therefore the wedge angle, is small. In this case, the result in eq 6 can be expanded for small θ_w, retaining the leading term.

$$\tau_w(x,y) = -\frac{3\mu U}{\theta_w(\sqrt{R^2 - y^2} - x)} \quad (11)$$

When the result in eq 11 is used to calculate the hydrodynamic resistance, the integration can be performed analytically, yielding

$$F_h = \frac{6\pi\mu UR}{\theta} \ln(2\epsilon) \quad (12)$$

By setting the algebraic sum of the driving force in eq 3 and the hydrodynamic resistance in eq 10 to zero, the

(11) Leal, L. G. *Laminar Flow and Convective Transport Processes*; Butterworth-Heinemann: Boston, 1992.
(12) Cox, R. G. *J. Fluid Mech.* **1986**, *168*, 169.

speed of the drop can be evaluated. In the special case when $\cos\theta_e$ is linear in x, we can write

$$U = -\frac{\pi\gamma RS}{8\mu f(\theta,\epsilon)} = -\frac{\pi R}{8\mu f(\theta,\epsilon)}\frac{\mathrm{d}}{\mathrm{d}x}(\gamma_{SG} - \gamma_{SL}) \quad (13)$$

We see from eq 13 that the speed of the drop in this special case scales linearly with the gradient of the interfacial tension difference ($\gamma_{SG} - \gamma_{SL}$). Also, the speed varies inversely with the viscosity of the liquid. The scaling with the radius of the footprint of the drop is more complex because the dimensionless parameter ϵ varies with R for a given slip length. Likewise, the scaling with the contact angle also is complex.

For small contact angles, when the variation of θ_e with distance is linear, using the result in eq 12 for the hydrodynamic resistance yields the following prediction for the speed of the drop.

$$U = \frac{\gamma R{\theta_e}^2}{6\mu\ln(2\epsilon)}\left(\frac{\mathrm{d}\theta_e}{\mathrm{d}x}\right) \quad (14)$$

To obtain this prediction, we approximated the driving force given in eq 5 by a result valid for small values of the equilibrium contact angle and equated the equilibrium contact angle at the location of the center of the drop to the dynamic contact angle around its periphery. For comparison, the velocity predicted in eq A13 of the paper by Brochard[2] is

$$U = \frac{\gamma R{\theta_e}^2}{3\mu\ln(\epsilon)}\left(\frac{\mathrm{d}\theta_e}{\mathrm{d}x}\right) \quad (15)$$

and therefore twice the velocity predicted by the present wedge approximation to leading order in ϵ. As noted earlier, the result given by Brochard[2] is not based on equating the driving force on the entire drop to the hydrodynamic resistance on it, which is the present approach, but rather on a local balance in which only the forces normal to the contact line on a differential element of the contact line are balanced. This is the reason for the difference between the predictions given in eqs 14 and 15.

Hydrodynamic Force and Quasi-Steady Velocity: Lubrication Theory. While the results obtained using the wedge approximation can be used in interpreting experimental observations, calculation of the hydrodynamic resistance requires that the integral in eq 10 be evaluated numerically. Therefore, we present an alternative analytical solution of the problem obtained using lubrication theory. Again, we use a reference frame in which the drop is stationary and the solid surface moves in the negative x direction with a speed U and invoke the same assumptions employed earlier. However, we make an additional assumption that $h_0/R \ll 1$, where h_0 is a characteristic length scale representing the height of the drop. Scaling all velocities in the Navier−Stokes and continuity equations with U, distances in the x and y directions with R, and distances in the z direction normal to the solid surface with h_0, in the limit as $h_0/R \to 0$, the leading order equations one obtains are the lubrication equations. One finds that, at leading order, there are no pressure variations in the z direction, and the velocity component v_z is zero. Also, because the only reason for motion in the drop is the translation of the surface at $z = 0$ in the negative x direction, it can be shown that the velocity component v_y and the pressure gradient in the y direction also are zero. Therefore, the only nontrivial problem at leading order is that for v_x. The governing equations for v_x are

$$\mu\frac{\partial^2 v_x}{\partial z^2} = \frac{\mathrm{d}p}{\mathrm{d}x} \quad (16)$$

$$v_x(x,y,0) = -U \quad (17)$$

$$\frac{\partial v_x}{\partial z}(x,y,h) = 0 \quad (18)$$

and the condition of no net volumetric flow is

$$\int_0^h v_x(x,y,z)\,\mathrm{d}z = 0 \quad (19)$$

The solution for the velocity distribution can be obtained as

$$v_x = -U\left(1 - 3\frac{z}{h} + \frac{3}{2}\frac{z^2}{h^2}\right) \quad (20)$$

Therefore, the shear stress exerted by the solid surface on the liquid is

$$\tau_w(x,y) = -\mu\frac{\partial v_x}{\partial z}(x,y,0) = -3\mu\frac{U}{h(x,y)} \quad (21)$$

This shear stress can be used in the area integral in eq 7 to obtain the hydrodynamic resistance offered by the solid surface to the motion of the drop.

The shape of a spherical cap is described by

$$h(x,y) = \sqrt{R^2\csc^2\theta - r^2} - R\cot\theta \quad (22)$$

where θ is the dynamic contact angle, assumed uniform around the periphery of the drop, and r is the radial coordinate shown in Figure 2. Because the height h is independent of the polar angle ϕ, the area integration in eq 7 can be conveniently performed in polar coordinates, leading to

$$F_h = -6\pi\mu U\int_0^{R(1-\epsilon)}\frac{r\,\mathrm{d}r}{h(r)} = -6\pi\mu U\int_0^{R(1-\epsilon)}\frac{r\,\mathrm{d}r}{\sqrt{R^2\csc^2\theta - r^2} - R\cot\theta} \quad (23)$$

As in the previous analysis, to avoid the contact-line singularity, the integration is performed from the center to a radial location that is ϵR away from the contact line. The final result for the hydrodynamic resistance can be written as

$$F_h = -6\pi\mu UR[g(\theta,1-\epsilon) - g(\theta,0)] \quad (24)$$

where

$$g(\theta,\xi) = -[\cot\theta\ln(\sqrt{\csc^2\theta - \xi^2} - \cot\theta) + \sqrt{\csc^2\theta - \xi^2} - \cot\theta] \quad (25)$$

The result for the hydrodynamic resistance given in eq 24 can be easily evaluated, so that there is no need to further approximate it; however, it is instructive to work out some asymptotic results for comparison with those from the wedge solution. First, when the contact angle is small, it is possible to obtain the following leading order result good for $\theta \ll 1$.

$$F_{\mathrm{h}} = \frac{6\pi\mu UR}{\theta}\ln(2\epsilon - \epsilon^2) \tag{26}$$

Comparing this with the small angle expansion of the result from the wedge solution, given in eq 12, we see that the wedge solution and the lubrication solution are in agreement to leading order in ϵ for small angles.

Given the prospect that ϵ can assume values that are very small compared with unity, it also is useful to develop an asymptotic approximation of the hydrodynamic resistance given in eqs 24 and 25 for any value of the dynamic contact angle θ as $\epsilon \to 0$. This can be obtained by straightforward means as

$$F_{\mathrm{h}} \sim -6\pi\mu UR\left[-\cot\theta\ln\epsilon + \cot\theta\ln\left(\frac{\cos\theta}{1+\cos\theta}\right) + \tan\frac{\theta}{2} + O(\epsilon)\right] \tag{27}$$

For a fixed value of the contact angle, we see that $F_{\mathrm{h}} \sim 6\pi\mu UR\cot\theta\ln(\epsilon)$ as $\epsilon \to 0$.

By setting the algebraic sum of the driving force in eq 3 and the hydrodynamic resistance in eq 24 to zero, the speed of the drop can be calculated. In the special case when $\cos\theta_{\mathrm{e}}$ is linear in x, we can write

$$U = \frac{\gamma RS}{6\mu[g(\theta,1-\epsilon) - g(\theta,0)]} \tag{28}$$

with an asymptotic approximation for small ϵ as

$$U = \frac{\gamma RS}{6\mu\left[-\cot\theta\ln\epsilon + \cot\theta\ln\left(\frac{\cos\theta}{1+\cos\theta}\right) + \tan\frac{\theta}{2} + O(\epsilon)\right]} \tag{29}$$

Contribution to the Resistance from the Slip Region. We must note here that we have neglected the contribution to the drag from the slip region in our analysis of this problem. It is instructive to estimate the order of magnitude of this contribution. As noted by Cox,[12] a variety of models have been proposed for relieving the stress singularity at the contact line. The most common approach is to assume that the difference in velocity between the solid and the fluid at the solid surface, called the slip velocity, is proportional to the shear stress at the solid surface. Using this model, Huh and Mason[13] solved the fluid mechanical problem of the advancement of a meniscus within a tube when the contact angle is close to 90° by the method of matched asymptotic expansions using the ratio of the length scale of the slip region to the tube radius as a small parameter. These authors showed that, instead of becoming unbounded as the inverse of the distance from the contact line, the shear stress at the solid surface achieves a constant value in the slip region that is $O(1/\epsilon)$ in the present notation. Because the scaled length of the slip region is $O(\epsilon)$, this leads to an additional contribution to the hydrodynamic resistance of $O(1)$. The implication to our analysis is that the results from both the wedge solution and the lubrication solution, when expanded for small ϵ, will need to be corrected at $O(1)$, but the hydrodynamic resistance is correct to $O(\ln\epsilon)$, which is the leading order, subject to the assumptions made in our models. Huh and Mason[13] also consider a second option, in which they set the shear stress at the solid surface in the slip region to zero. Such a model will, of course, yield a zero correction to the hydrodynamic resistance calculated in the present work.

Validity of the Quasi-Steady Approximation. In the present work, we have made the quasi-steady approximation, equating the driving force at a given location to the steady hydrodynamic resistance to calculate the instantaneous velocity of the drop. The key assumptions are that transients in the velocity can be neglected and that the hydrodynamic resistance can be approximated as that from steady flow. The validity of the quasi-steady approximation is evaluated here by examining the unsteady problem in an approximate manner. Newton's law yields the following force balance on the drop.

$$m\frac{\mathrm{d}U}{\mathrm{d}t} = F_{\mathrm{driving}} - \beta U \tag{30}$$

In eq 30, m is the mass of the drop, and its speed U is allowed to vary with time t. The driving force and the drag are evaluated locally at the current position of the drop, and we assume F_{driving} and β are constants during the unsteady evolution of the velocity to its quasi-steady value for the purpose of this approximate treatment. Equation 30 can be integrated along with the initial condition

$$U(0) = 0 \tag{31}$$

to yield

$$U = \frac{F_{\mathrm{driving}}}{\beta}\left[1 - \exp\left(-\frac{\beta t}{m}\right)\right] \tag{32}$$

Therefore, for fixed driving and resisting forces, the time scale in which the drop is accelerated from rest to its steady velocity is given by m/β. Using a drop of water of footprint radius 1 mm and a contact angle of 90° as an example, we obtain $m = 2.09 \times 10^{-6}$ kg. The resistance coefficient β, which can be evaluated approximately from eq 27, is 1.89×10^{-5} N·s/m, so that the transient time scale is roughly 0.11 s. We must also consider the viscous relaxation time scale R^2/ν, where ν is the kinematic viscosity of the liquid, because for a given driving force the flow must develop from rest, leading to unsteady evolution of the resistance over that time scale. For a length scale of 1 mm and a kinematic viscosity for water, which is 10^{-6} m^2/s, this viscous time scale is approximately 1.0 s. Therefore, in the above example, if it takes several seconds for the drop to move appreciably, it is reasonable to use the quasi-steady approximation. If the contact angle is 40° and the liquid is ethylene glycol, the transient time scale decreases to 1.2×10^{-4} s and the viscous relaxation time is 0.069 s, so that, even if the drop moves appreciably in 1 s, the quasi-steady approximation can be used.

Discussion

Sample results for the magnitude of the dimensionless drag from the wedge model and lubrication theory, defined as $-F_{\mathrm{h}}/\mu UR$, are displayed against the dynamic contact angle in the range $(0, \pi/2)$ in Figure 3 for a representative set of values of ϵ. These results do not include the contribution from the slip region near the contact line because as noted earlier that contribution would depend on the model chosen for the slip region. The asymptotic approximation given in eq 27 also is shown so that the reader can gauge when it can be safely used instead of the

(13) Huh, C.; Mason, S. G. *J. Fluid Mech.* **1977**, *81*, 401.

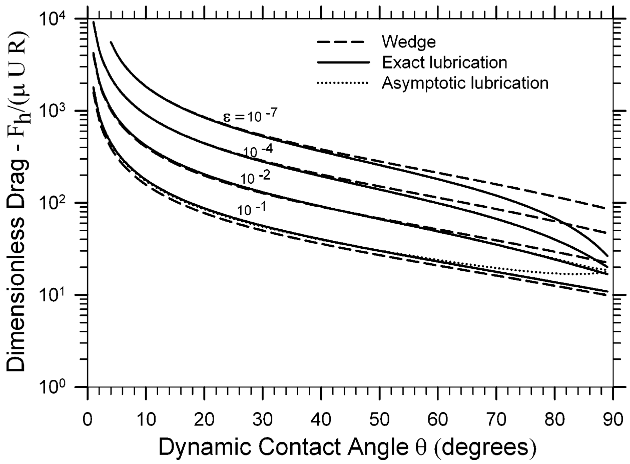

Figure 3. Dimensionless hydrodynamic force (drag) $-F_h/\mu UR$ plotted against the dynamic contact angle θ for a set of representative values of ϵ. Shown are the results from the wedge solution, the lubrication solution, and the asymptotic approximation for small ϵ given in eq 27.

exact result from lubrication theory. To avoid clutter in the drawing, we have not displayed the results from the small-contact-angle approximations given in eqs 12 and 26, which can be shown to be truncated versions of the small-angle expansion of eq 27.

The lubrication approximation should be good for relatively small contact angles but can be expected to become increasingly poor as the contact angle is increased. Results from the lubrication approximation are practically indistinguishable from those obtained using the wedge solution at small contact angles up to approximately 30° for $\epsilon \leq 10^{-2}$. Even at contact angles as large as 40°, the difference between the two results is small and likely no larger than the approximations inherent in these solutions. At larger contact angles, however, the differences become clear, with the wedge approximation predicting a larger drag on the drop for $\epsilon \leq 10^{-2}$. Only in the case of nanodrops, for which ϵ is likely to be as large as 10^{-1}, is the trend reversed, with lubrication theory predicting a larger drag than the wedge approximation. We note that the wedge approximation provides a lower bound on the hydrodynamic resistance because the actual height of the liquid in any given slice of the spherical cap is smaller than that of the wedge used to approximate that slice; therefore, the shear stress calculated from an exact solution should be larger than that from the wedge solution.

As the value of ϵ is decreased, most of the contribution to the hydrodynamic resistance comes from a region in the vicinity of the contact line where the flow has to turn around in a liquid region of small height, leading to large shear stresses near the contact line. This is why the asymptotic approximation to the lubrication theory result for $\epsilon \ll 1$ given in eq 27 is indistinguishable from the complete lubrication theory result in eq 24 for values of $\epsilon \leq 10^{-4}$ and nearly so even at $\epsilon = 10^{-2}$. As noted earlier, for small contact angles, both the wedge approximation and lubrication theory predict results that are indistinguishable. Therefore, for macroscopic drops for which ϵ should typically be smaller than 10^{-4}, the asymptotic result in eq 27, which is simple to calculate, can be used as a first approximation for contact angles up to approximately 40°. For larger contact angles, it would be best to calculate the wedge result numerically for predicting the drag.

It is useful to estimate a typical order of magnitude for the quasi-steady velocity of a drop from the wedge approximation in eq 13 and the lubrication approximation in eq 28 using the conditions of the experiments of Daniel and Chaudhury;[4] however, direct comparison with the experimental results is not possible because one of the parameters needed for that purpose is not available from ref 4 and also, as noted in ref 4, hysteresis effects reduce the velocities of the drops in the experiments. At 25 °C, the wedge approximation predicts that an ethylene glycol drop of footprint radius 1.0 mm should move at a velocity of 2.7 mm/s in a wettability gradient of $S = 0.06$ mm^{-1} (from Figure 3 of ref 4) if the dynamic contact angle is 60°, whereas the lubrication approximation predicts a velocity of 3.2 mm/s; the predictions from the wedge and lubrication approximations are 1.5 and 1.6 mm/s, respectively, if the dynamic contact angle is 40°. The velocity reported in Figure 3 of ref 4 for a drop of this approximate size is roughly 1.2 mm/s. The value of the dynamic contact angle is not known.

The calculation of the hydrodynamic resistance is independent of the type of driving force used. Therefore, when a drop slides down an incline under the action of gravity, its sliding speed can be predicted using our results, provided the drop assumes the shape of a spherical cap, with a dynamic contact angle θ that is uniform around the footprint of the drop. If the surface is inclined at an angle α from the vertical, the prediction from the wedge approximation is

$$U = -\frac{\pi R^2 \rho g \cos \alpha (2 - 2\cos\theta - \cos\theta \sin^2\theta)}{24\mu \sin^3\theta f(\theta,\epsilon)} \qquad (33)$$

and that from the lubrication theory approximation is

$$U = \frac{R^2 \rho g \cos \alpha (2 - 2\cos\theta - \cos\theta \sin^2\theta)}{18\mu \sin^3\theta [g(\theta,1-\epsilon) - g(\theta,0)]} \qquad (34)$$

with an asymptotic approximation for small ϵ

$$U = \frac{R^2 \rho g \cos \alpha (2 - 2\cos\theta - \cos\theta \sin^2\theta)}{18\mu \sin^3\theta \left[-\cot\theta \ln\epsilon + \cot\theta \ln\left(\frac{\cos\theta}{1+\cos\theta}\right) + \tan\frac{\theta}{2} + O(\epsilon)\right]} \qquad (35)$$

Concluding Remarks

A simple set of approximate results has been obtained for the hydrodynamic resistance experienced by a spherical-cap drop moving on a solid surface. One approximation involves modeling of the geometry as a wedge; the resistance calculated from this model is given in eq 10. The other approximation uses lubrication theory while retaining the exact shape of the drop; the resistance from this model is reported in eq 24. We find that the results from the wedge approximation and lubrication theory are indistinguishable at small contact angles (≤30°) for drops whose length scale is at least 2 orders of magnitude larger than the slip length. When the cosine of the equilibrium contact angle varies linearly with position, it is possible to evaluate the driving force analytically. In this case, the quasi-steady velocity of the drop from the wedge approximation is reported in eq 13, and the corresponding result from lubrication theory is given in eq 28. We also have obtained asymptotic analytical results useful for small values of the contact angle, as well as an asymptotic result for small values of the slip length relative to the size of the drop, useful for any value of the contact angle.

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