Spreading of a Droplet on a Solid Surface

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SYNOPSIS

The spontaneous spreading of small liquid droplets on solid surfaces is examined with the objective of developing closed-form expressions for the spreading dynamics, both for the case in which there is complete equilibrium spreading, that is the equilibrium contact angle is 0°, and for the case in which equilibrium spreading is incomplete. Such solutions are obtained using a simple hydrodynamic model. The results are consistent with the format of the *universal* Hoffman–Voinov–Tanner law (for complete spreading) and the modified Hoffman–Voinov–Tanner law for incomplete spreading. In the latter case, concurrence is found only when the dynamic contact angle is close to the equilibrium angle throughout the spreading process.

INTRODUCTION

The kinetics of the spreading of liquid droplets on solid substrates is important from a practical point of view because the process is central to many spray coating operations and from a fundamental point of view because its description yields valuable information concerning the nature of solid–liquid interactions. Numerous studies of the phenomenon have been made, as reviewed, for example, by Marmur,[1] de Gennes,[2] Cazabat,[3] and most recently and thoroughly by Kistler.[4] The process has been found to depend in the most general case on many factors, including the liquid surface tension, viscosity (or other rheological parameters if non-Newtonian), density and volatility, solid surface roughness, texture and chemical heterogeneity, and drop size. The spreading behavior also depends critically on whether the equilibrium contact angle is effectively 0° (complete spreading) or if it is finite. Surface tension gradients that may develop during spreading, as caused by uneven evaporative cooling or asymmetric mass transfer in multicomponent droplets, may also play an important role. If consideration is limited, however, to completely spreading, single-component, nonvolatile, Newtonian liquids spreading on smooth, homogeneous solid surfaces, the relevant data of most investigators may be fit to a simple power law giving the spreading radius, R, as a function of time, t:

$$R(t) \propto t^n \tag{1}$$

in which the empirical constant n generally lies in the range $0.1 \le n \le 0.14$, and the proportionality factor depends on the drop volume and fluid properties. For droplets sufficiently small that the effects of gravity may be neglected, experimental results suggest $n \approx 0.1$. The spreading law may also be expressed in terms of the time dependence of the apparent dynamic contact angle, θ, as pictured in Figure 1(a). Under the conditions stated above, the droplet will take the form of a spherical cap, and if in addition the contact angle is small ($\theta \ll \pi/2$), the linear spreading rate consistent with Eq. (1) is given by[2]

$$U(t) \equiv \frac{dR(t)}{dt} \propto \theta^{(1-n)/3n} = \theta^3 \tag{2}$$

Equation (2) is consistent with the well-known result obtained by Tanner[5] and by Voinov[6] from the hydrodynamic analysis of steady-state *forced* spreading, as well as the well-known data of Hoffman[7] for the steady forced movement of silicone oils in glass capillaries, viz.

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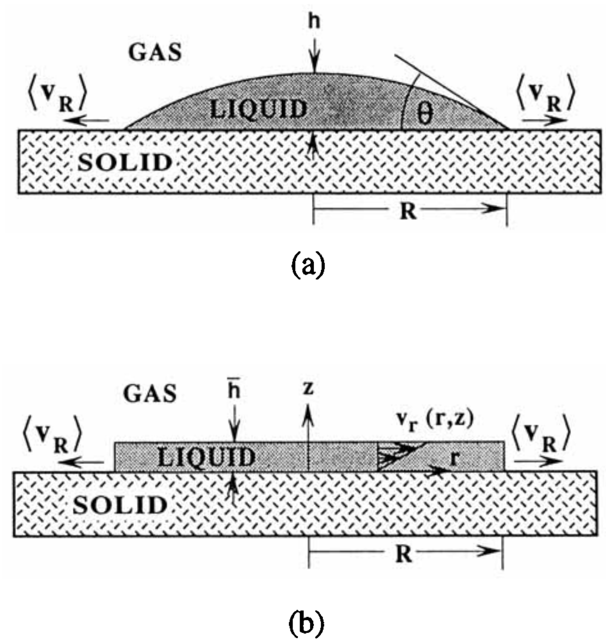

Figure 1 A small, thin droplet spreading on a solid: (a) the spherical cap approximation, (b) the cylindrical disk approximation.

$$\theta^3 \approx c_T\text{Ca} \equiv c_T\left(\frac{\mu U}{\sigma}\right) \tag{3}$$

where c_T is a numerical constant, and Ca is the capillary number, as defined above, with μ = viscosity and σ = surface tension.

It is now well known that the advancing front of a completely spreading liquid is preceded by a thin precursor *foot,* whose presence may be verified in a number of ways but which is generally invisible to the naked eye.[8] The dynamic contact angle in Eqs. (2) and (3) refers to the angle that is macroscopically observable and not to that which is made between the leading edge of the precursor foot and the dry solid surface.

There are very few published data for the dynamics of spreading of liquid droplets that *incompletely* wet the solid, that is, for which the equilibrium contact angle, θ_e, is finite, and only a relatively small database for forced wetting under these conditions. Hoffman[7] suggests that the universality of Eq. (3) may be preserved by making use of a *shift factor* accounting for the nonzero nature of the equilibrium angle, such that

$$\theta^3 - \theta_e^3 \approx c_T\text{Ca} \tag{4}$$

The success in fitting data for forced spreading to Eq. (4) has been rather limited. Recent experiments on the steady forced wetting of partially wet surfaces by liquids capable of different types of molecular interaction (van der Waals, acid-base) with the solid suggest that no parameter beyond an appropriate value of θ_e is needed to fit the results in each case.[9] The main difficulty in using a relationship of the type of Eq. (4) may be in not knowing what *equilibrium contact angle,* θ_e, to use. Effectively all real surfaces have roughness at least at the microscopic level so that considerable hysteresis exists between the measured static advanced and receded angles. Even when θ_e is treated as an adjustable parameter, however, there is sometimes difficulty in fitting data to the format of Eq. (4).

Whether equilibrium spreading is complete or incomplete, what the current literature appears to lack is a convenient closed-form relationship, free of adjustable parameters, which can be used to predict the spontaneous spreading behavior of droplets on horizontal solid surfaces. A simple hydrodynamic model, whose results are consistent with the Hoffman–Voinov–Tanner law, Eq. (3), or its modified version, Eq. (4), is proposed below for this purpose.

THEORY

We examine the spreading of a small, thin, nonvolatile Newtonian droplet as pictured in Figure 1(a). It will take the form of a spherical cap of constant volume V_d. Its central height h is much smaller than its spreading radius R because its contact angle θ is assumed small ($\theta \ll \pi/2$). Under these assumptions,

$$V_d = \frac{\pi}{2} hR^2 \tag{5}$$

$$h = \tfrac{1}{2} R\theta \tag{6}$$

To calculate the spreading, consider first the analogous situation of a spreading cylindrical disk, as shown in Figure 1(b). We choose both the volume and the radius to be equal in the two figures. Then from Eq. (5) we note, if the volume of the spherical cap is equivalent to the volume of the cylindrical disk, $V_d = \pi R^2\bar{h}$, and $\bar{h} = h/2$. Thus the spreading will cause a similar decrease in the height of the liquid in both figures. We assume, to a first approximation, that the fluid dynamics of the spreading spherical cap approximates that of a spreading cylindrical disk. We examine the disk spreading in quasi-steady laminar Couette flow driven by an effective radial surface tension gradient at the upper surface given by

$$\frac{d\sigma}{dr} = \frac{S_{\text{eff}}}{r} \tag{7}$$

where S_{eff} is the effective instantaneous spreading coefficient. We further assume $R \gg \bar{h}$, so from (5)

$$v_z = \frac{d\bar{h}}{dt} \ll v_r \tag{8}$$

and in the flow analysis we set $v_z \approx 0$ in evaluating $v_r(r, z)$. For this model the continuity and r-momentum equations for the cylindrical disk are, respectively,[10]

$$\frac{\partial(rv_r)}{\partial r} = 0 \tag{9}$$

$$\mu\left[\frac{\partial}{\partial r}\left(\frac{1}{r}\frac{\partial(rv_r)}{\partial r}\right) + \frac{\partial^2 v_r}{\partial z^2}\right] = 0 \tag{10}$$

Substitution of (9) into (10) gives

$$\frac{\partial^2 v_r}{\partial z^2} = 0 \tag{11}$$

We note from Eq. (9) that the function $\phi = rv_r$ is a function of z only, so that its substitution into (11), followed by two integrations, yields

$$\phi = Az + B \tag{12}$$

from which

$$v_r = \frac{1}{r}(Az + B) \tag{13}$$

Applying to (13) the no-slip boundary condition: at $z = 0$, $v_r = 0$ for all $r > 0$ gives $B = 0$. Balancing the radial shear stress at $z = \bar{h}$ gives (for $v_z \approx 0$)

$$-\mu\frac{\partial v_r}{\partial z} + \frac{d\sigma}{dr} = 0 \tag{14}$$

Applying (7) and (13) to (14) with $B = 0$ gives $A = S_{\text{eff}}/\mu$, from which (13) becomes

$$v_r = \frac{S_{\text{eff}} z}{\mu r} \tag{15}$$

The surface velocity is given by (15) with $z = \bar{h}$, and the *average* radial velocity at the outer edge $r = R$ is

$$\langle v_R \rangle = \frac{S_{\text{eff}}\bar{h}}{2\mu R} \tag{16}$$

which we take as the rate of spreading, that is,

$$\langle v_R \rangle = \frac{dR}{dt} \tag{17}$$

where we note in (16) that $\bar{h}$, R, and S_{eff} are all functions of time t.

Although (16) and (17) give the rate of spreading for the cylindrical disk of Figure 1(b), we want to apply the result to the spherical cap of Figure 1(a). To do this we recall that Figures 1(a) and 1(b) were chosen to have equal volumes and an equal base radius R, which gave $\bar{h} = h/2$. Therefore, setting $\bar{h} = h/2$ gives the rate of spreading for a thin spherical cap droplet as

$$\frac{dR}{dt} = \frac{S_{\text{eff}} h}{4\mu R} \tag{18}$$

If at $t = 0$, $h = h_0$, $R = R_0$, Eq. (4) gives

$$hR^2 = h_0 R_0^2 = \frac{2V_d}{\pi} \tag{19}$$

and (19) into (18) gives

$$\frac{dR}{dt} = \frac{S_{\text{eff}} V_d}{2\pi\mu R^3} \tag{20}$$

At equilibrium, Young's equation[11] gives the balance of forces on a unit length of the front as

$$\sigma \cos\theta_e = \sigma_{\text{SG}} - \sigma_{\text{SL}} \tag{21}$$

where θ_e is the equilibrium contact angle, and σ_{SG} and σ_{SL} are the surface energies of the solid against the gas and the liquid, respectively. When the droplet is not in equilibrium with its surroundings, the forces are not balanced, and the driving force on a unit length of front is given by the effective spreading coefficient,

$$S_{\text{eff}} = \sigma_{\text{SG}} - \sigma_{\text{SL}} - \sigma\cos\theta \tag{22}$$

Substituting Young's equation into (22) gives

$$S_{\text{eff}} = \sigma(\cos\theta_e - \cos\theta) \tag{23}$$

We are assuming that $\theta_e = \theta_\infty$, the contact angle observed at infinite time. For small θ, $\cos\theta \approx 1$

$-\theta^2/2$, and (23) becomes

$$S_{\text{eff}} = \sigma\left(\frac{\theta^2}{2} - \beta\right) \tag{24}$$

where $\beta = 1 - \cos\theta_e$.

In the next two sections we apply these equations to complete and partial spreading, respectively.

COMPLETE SPREADING

For complete spreading $\theta_e = 0$, $\beta = 0$, and

$$S_{\text{eff}} = \frac{\sigma\theta^2}{2} \tag{25}$$

Combining (5) and (6) gives

$$\theta = \frac{4V_d}{\pi R^3} \tag{26}$$

which with (25) gives

$$S_{\text{eff}} = \frac{8\sigma V_d^2}{\pi^2 R^6} \tag{27}$$

as the instantaneous effective spreading coefficient for complete wetting. Combining (20) and (27) gives

$$\frac{dR}{dt} = \frac{4\sigma V_d^3}{\pi^3\mu R^9} \tag{28}$$

Integrating (28) from time $t = 0$, $R = R_0$ to a general time t at $R = R(t)$ gives*

$$R = R_0\left(1 + \frac{40\sigma V_d^3}{\pi^3\mu R_0^{10}}\,t\right)^{1/10} \tag{29}$$

Equation (29) is the closed-form relationship sought for the case of complete equilibrium spreading. We may examine its concurrence with the Hoffman–Voinov–Tanner law by considering the variation of $\theta(t)$ it predicts. Combining (17), (26), and (28) gives

$$\theta^3 = 16\left(\frac{\mu\langle v_R\rangle}{\sigma}\right) \equiv 16\ \text{Ca} \tag{30}$$

consistent with Eq. (3), as required.

Jiang et al.'s correlation[12] of Hoffman's data for forced wetting inside capillary tubes gives a constant closer to 90 than the value of 16 found here for spontaneous droplet spreading. However, de Gennes[2] points out that for forced wetting in capillaries, the constant might be dependent on the capillary diameter.

INCOMPLETE SPREADING

For the case of incomplete spreading, putting Eqs. (24) and (26) into Eq. (20) gives

$$\frac{dR}{dt} = \frac{4\sigma V_d^3}{\pi^3\mu R^9} - \frac{\sigma\beta V_d}{2\pi\mu R^3} \tag{31}$$

which integrates to the somewhat unwieldy form

$$t = \frac{\pi^3\mu}{40\sigma V_d^3}(R^{10} - R_0^{10}) + \frac{\pi^5\mu\beta}{512\sigma V_d^5}(R^{16} - R_0^{16}) + \frac{\pi^7\mu\beta^2}{5632\sigma V_d^7}(R^{22} - R_0^{22}) + \cdots \tag{32}$$

Equation (32) gives the leading terms of a series expansion, which should be sufficient if $\beta \ll 1$, that is, for cases in which the equilibrium contact angle is small.

To check consistency with the modified Hoffman–Voinov–Tanner law, we substitute Eq. (26) into (31) yielding

$$\frac{dR}{dt} \equiv \langle v_R\rangle = \frac{\sigma\theta^3}{16\mu} - \frac{\sigma\beta\theta}{8\mu} \tag{33}$$

which, upon rearrangement gives

$$\frac{\theta^3}{16} - \frac{\beta\theta}{8} = \text{Ca} \tag{34}$$

For small θ_e, $\cos\theta_e \approx 1 - \theta_e^2/2$, so $\beta \approx \theta_e^2/2$, and (34) becomes

$$\frac{\theta^3}{16} - \frac{\theta_e^2\theta}{16} = \text{Ca} \tag{35}$$

* The corresponding formula in terms of $\theta(t)$ is

$$\theta = \frac{4V_d}{\pi R_0^3}\left(1 + \frac{40\sigma V_d^3}{\pi^3\mu R_0^{10}}\,t\right)^{-3/10}$$

which is the same form as Eq. (4), but only when $\theta_e \approx \theta$. This may provide a partial explanation for the only limited success that has been achieved for the fitting of forced spreading data for incompletely wetting liquids.

CONCLUSIONS

Closed-form expressions free of adjustable parameters have been obtained for the spontaneous spreading of small droplets on solid surfaces using a hydrodynamic model of a flat circular cylinder in quasi-steady Couette flow driven by an effective surface tension gradient. The result obtained for the case of complete equilibrium spreading, Eq. (29), is consistent with the functional form of the Hoffman–Voinov–Tanner law for forced spreading. For the case of incomplete equilibrium spreading, the result obtained is consistent with the modified Hoffman–Voinov–Tanner law only when the dynamic contact angle is close to that of the equilibrium angle throughout the spreading process.

The result obtained for completely spreading liquids, Eq. (29), should be particularly useful for the quantitative analysis of data for spontaneous droplet spreading.

NOTATION

A	constant in Eq. (12)
B	constant in Eq. (12)
R	spreading radius
R_0	initial droplet radius
S_{eff}	effective spreading coefficient
V_d	droplet volume
h	spherical cap height
h_0	initial droplet height
$\bar{h}$	cylindrical disk height
r	radial coordinate
t	time
v_r	radial velocity of liquid
$\langle v_r \rangle$	interline velocity
v_z	axial velocity of liquid
z	axial coordinate
β	constant in Eq. (24), $1 - \cos \theta_e$
σ	droplet surface tension
σ_{SG}	surface energy of solid
σ_{SL}	solid–liquid interfacial energy
θ	dynamic contact angle
θ_e	equilibrium contact angle

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