Laplace pressure driven drop spreading

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This work concerns the spreading of viscous droplets on a smooth rigid horizontal surface, under the condition of complete wetting (spreading parameter \( S > 0 \)) with the Laplace pressure as the dominant force. Owing to the self-similar character foreseeable for this flow, a self-similar solution is built up by numerical integration from the center of symmetry to the front position to be determined, defined as the point where the free-surface slope becomes zero. Mass and energy conservation are invoked as the only further conditions to determine the flow. The resulting fluid thickness at the front is a small but finite (\( \approx 10^{-7} \)) fraction of the height at the center. By comparison with experimental results, the regime is determined in which the spreading can be described by this solution with good accuracy. Moreover, even within this regime, small but systematic deviations from the predictions of the theory were observed, showing the need to add terms modifying the Laplace pressure force.

I. INTRODUCTION

The spreading of a drop on a solid surface is a problem of considerable interest and difficulty in fluid mechanics, where the basic physical processes are still not completely understood. In this work, we are concerned with the spreading of a nonvolatile liquid drop on a solid plane substrate with a positive value of the spreading parameter \( S = \gamma_{SG} - \gamma_{SL} - \gamma > 0 \) (with \( \gamma_{SG}, \gamma_{SL} \), and \( \gamma \) respectively, the solid–gas, solid–liquid, and liquid–gas interfacial tensions). Therefore, spontaneous spreading occurs and the coverage of the solid by the liquid can be stopped only by the small thickness effects. We restrict ourselves to situations where the gravity force is negligible, i.e., to small Bond numbers. This requires that both the maximum (central) drop thickness \( h_0(t) \) and the drop radius \( x_f(t) \) must be less than the capillary length \( \lambda = (\gamma/\rho g)^{1/2} \) (\( \rho \) is the fluid density and \( g \) the gravity), which is usually of the order of 1 mm. In the spreading of such small drops, the Reynolds number \( R_e = (\rho h_0^2 / \mu)(h_0/x_f)^{3} \), where \( \nu_f = dx_f / dt \), is much less than unity even for a rather low liquid viscosity \( \mu \). Finally, \( h_0 \) becomes promptly much less than \( x_f \), so that the lubrication approximation may be used.

Under these conditions it is known that the spreading displays with good approximation the self-similar behavior foreseeable if the liquid were driven solely by the Laplace pressure force on a "solid" with identical chemical structure, i.e., as if \( S \) were zero. For instance, the front position and the apparent contact angle \( \theta_a \) vary approximately on time as \( x_f \approx t^{0.1} \) and \( \theta_a \approx t^{0.5} \) (Tanner's law) without an appreciable dependence on the actual value of \( S \), and it is easy to show that these power laws may be regarded as direct consequences of the above hypothesis.

The proposed interpretation is that the energy excess associated to \( S \) together with the small thickness effects (not accounted for in the values of the surface tensions) give place only to an almost invisible submicrometer precursor film, which covers the substrate preceding the macroscopic part of the drop. This approach was followed by Starov, who built up a self-similar solution for the macroscopic part of the spreading in terms of successive approximations for the solution of an integral equation. Then he was able to calculate approximate values for the prefactors of the above power laws. However, the values obtained in later experiments differ very much from those given by Starov.

In Sec. II we develop a self-similar solution following a procedure quite different from that used by Starov. The main differences are the particular attention paid to the behavior of the solution as the height become very small and the introduction of the global energy balance as a constraint to determine the solution. As expected, the central part of the drop is like a spherical cap, but towards the front the slope \( \partial h / \partial x \) becomes approximately constant, with a broad maximum at about 0.05 \( h_0(t) \). Finally, very near the drop edge, the slope suddenly decreases; this behavior is shown qualitatively in Fig. 1. A remarkable point is that, as noticed by several authors, \( h(t) \) cannot be made strictly zero: \( \partial h / \partial x \) becomes zero at a certain point \( x = x_f \), where \( h(x_f) = h_f \) is a small but finite constant fraction of \( h_0(t) \) (the precise value given by our calculation is 2.35 \( 10^{-7} \)).

Clearly, this intrinsic limitation of spreading models based on the Laplace pressure is not serious in itself, because in the spreadings here studied \( h_f < 2 \AA \) (\( h_f < 1 \text{ mm} \)), so that the onset of effects not accounted for through the Laplace pressure surely deprives the solution of any phys...
ical meaning for values of $h$ well larger than $h_f$. However, it introduces some arbitrariness in the closure of these models which we solve by identifying the zero slope point $x_f$ as the front position. Of course, there are no reasons for this limit to coincide with a physical realistic limit for the macroscopic part of the drop which indeed should correspond to a liquid thickness considerably larger than $h_f$. This originates discrepancies between the model predictions and the experiments which we shall widely discuss in the work.

In Sec. III, the solution is compared with elsewhere reported and our own experimental results obtained from the spreadings of polydimethilsyloxane (PDMS) fluid drops of different volumes and viscosities on optically polished glass slides. The measurements were performed by using interferometric and refractive techniques. As a first result, the comparison determines the range of parameters in which the solution describes with reasonable accuracy the spreading features. Within this range we observed small but systematic departures between theory and experiments of the order of 10%.

The limits of validity of the theory are given by gravity effects for large drops (Ref. 3) and by small thickness effects for very thin drops (Ref. 2-4). These limits are not deeply studied here. Instead, Sec. IV is devoted to a detailed discussion on the above-mentioned small discrepancies within the validity range of the theory. It is shown that, as said above, they are due to the physically nonrealistic limit introduced in the theory to separate the macroscopic part of the drop dominated by the Laplace pressure from the border region where the small thickness effects are relevant. The sensitivity of the macroscopic spreading quantities to this limit may offer an interesting possibility for experimental studies.

II. THEORY

A. Basic equations

We shall begin with a brief recall of the standard lubrication approximation for this flow. With the notation of Fig. 1, the Navier–Stokes equations for the onedimensional ($\partial h/\partial x \ll 1$) slow viscous flow reduce to

$$\frac{\partial p}{\partial x} = \mu \frac{\partial^2 v_x}{\partial z^2},$$

where $\mu$ is the viscosity and $p$ is Laplace pressure given by $p = -\gamma c$, being $\gamma$ the surface tension and $c$ the curvature of the free-surface profile $h(x)$; for $\partial h/\partial x \ll 1$ the curvature may be written as

$$c = \frac{1}{R_1 + \frac{1}{R_2}} = \frac{\alpha h}{x \partial x} = x^{-\alpha} \frac{\partial}{\partial x} \left( x^{\alpha} \frac{\partial h}{\partial x} \right),$$

where $R_1, R_2$ are the principal curvature radii and $\alpha = 0.1$ for plane (ribbon), axisymmetric (drop) geometry, respectively.

By integrating Eq. (1) twice with respect to $z$, with the assumption of zero velocity at $z=0$ and zero shear stress ($\partial v_x/\partial z = 0$) at $z=h$, a parabolic velocity distribution is obtained. An averaging over the drop thickness gives the mean horizontal velocity $v$ as

$$v = \gamma \frac{\partial c}{3 \mu h^2 \partial x}.$$

This equation must be used together with the mass conservation equation,

$$\frac{\partial h}{\partial t} = x^{-\alpha} \frac{\partial}{\partial x} (x^{\alpha} \partial h) = 0.$$

B. Similarity transformation

We shall build up a self-similar solution for the system of Eqs. (3) and (4) subject to the constrains of mass conservation and energy balance, which will be conveniently expressed through shape factors.

According to self-similarity, the drop thickness can be written as

$$h(x,t) = h_0(t) H(q) \text{ with } q = x/x_f,$$

where $h_0(t)$ is the thickness at the center ($x=0$), $H$ is a nondimensional function of $q$, and $x_f$ is the front position. Both $h_0(t)$ and $x_f(t)$ must be power laws on time, of the form

$$h_0(t) = \lambda_0 t^\beta, \quad x_f(t) = \xi_f t^\delta,$$

where the coefficients have been separated for convenience in dimensional ($\lambda_0, \xi_f$) and nondimensional ($\beta, \delta$) constants. In view of the $x_f(t)$ dependence, the velocity $v(x,t)$ can be expressed as

$$v(x,t) = \frac{\delta x}{t} U(\eta),$$

where $U(0) = 0$ and $U(1) = 1$.

We shall see that the exponents $\beta, \delta$, and the constants $k, b$ can be obtained simply from the mass and energy conservation, while the calculation of the nondimensional constants $\lambda_0, \xi_f$ requires the complete solution of the equations. In fact, the mass (or volume) conservation can be written as

$$V = \int_0^{x_f} (2\pi x)^{a/h(x,t)} dx.$$
where \( V \) is the drop volume; by replacing Eq. (5) we get

\[
V = I \theta_0 \pi x_f^{\alpha+1},
\]

where

\[
I = \int_0^1 (2 \pi \eta)^{\alpha} H(\eta) d\eta
\]

is the shape factor for the “distribution” of \( V \) over \( x \). As \( V \) and \( I \) are constants, substitution of Eq. (6) into Eq. (9) gives

\[
\beta = -(\alpha + 1) \delta
\]

and

\[
V = I (\lambda_0 k) (\xi_f b)^{\alpha+1}.
\]

Without loss of generality we may separate the dimensional part from the nondimensional part in Eq. (12) in the following way:

\[
V = k b^{\alpha+1} \quad \text{and} \quad 1 = l \lambda_0 k^{\alpha+1}.
\]

These expressions are two of the four equations needed to calculate the four constants \( k, b, \lambda_0, \) and \( \xi_f \). The other two equations will come from the energy balance.

To obtain a useful expression for the energy balance, we notice that all the energy released from the surface tension must be dissipated at the same rate by the viscous forces, as the kinetic energy is always negligible. The rate of the surface energy variation can be calculated as

\[
\frac{dE_s}{dt} = \gamma \frac{d}{dt} \left( A - \pi x_f^{\alpha+1} \right),
\]

where \( A \) is the area of the free surface, given by

\[
A = \int_0^{x_f} (2 \pi x)^{\alpha} \left[ 1 + \left( \frac{\partial h}{\partial x} \right)^2 \right] dx.
\]

In Eq. (14) the difference between \( A \) and the area of the covered surface \( \pi x_f^{\alpha+1} \) appears because no energy is supposed to be spent in wetting the surface. This difference gives rise to the potential energy which drives the spreading. This assumption is based on the hypothesis that the small-scale effects lock to zero the spreading parameter \( S \), just as if the substrate were chemically identical to the liquid.

By using the self-similar transformation, Eqs. (5)-(7), we get

\[
\frac{dE_s}{dt} = -\delta (\alpha + 3) (\lambda_0 k)^2 (\xi_f b)^{\alpha-1} x_f^{-(\alpha+3)\delta-1} (\xi_f b)^{\alpha+3} I_s,
\]

where

\[
I_s = \int_0^1 (2 \pi \eta)^{\alpha} \left( \frac{dH}{d\eta} \right)^2 d\eta
\]

is the shape factor for the distribution of the surface energy variation rate.

On the other hand, the viscous dissipation rate may be calculated as

\[
\frac{dE_v}{dt} = \mu \int_0^1 \left( \frac{\partial v}{\partial x} \right)^2 dV = 3 \mu \int_0^{x_f} (2 \pi x)^{\alpha} \frac{v^2}{h} dx
\]

which in the self-similar variables becomes

\[
\frac{dE_v}{dt} = 3 \mu \delta^2 (\lambda_0 k)^{-1} (\xi_f b)^{\alpha+3} \delta (\alpha+2) - 2 I_v,
\]

where

\[
I_v = \int_0^1 (2 \pi \eta)^{\alpha} \frac{\eta^2}{H(\eta)} U(\eta)^2 d\eta
\]

is the corresponding shape factor for the distribution of the viscous dissipation energy rate. Note that in principle \( I_v \) may diverge as \( H \rightarrow 0 \), while there are no divergence problems with \( I \) or \( I_s \). The existence of the solution requires a finite value for \( I_v \); this is the reason why the thickness cannot be made zero at the front.

By equating the absolute value of both rates, from Eqs. (16) and (19) we get

\[
\delta = (7 + 3 \alpha)^{-1}
\]

and

\[
\frac{I_v}{I_s} = \frac{\alpha + 3}{28} \left( \lambda_0 k \right)^3 (\xi_f b)^{-4}.
\]

A remarkable fact is that the value of the similarity exponent \( \delta \) is a direct consequence of the mass and energy conservation, no matter the values of the shape factors. However, as we shall see, the values of the coefficients in Eq. (22) depend on these factors. By separating the dimensional part from the nondimensional part in Eq. (22), we obtain

\[
\frac{I_v}{I_s} = \frac{\alpha + 3}{28} \left( \lambda_0 k \right)^3 (\xi_f b)^{-4}
\]

which are the other two necessary relations to calculate the four constants \( k, b, \lambda_0, \) and \( \xi_f \). Then, from Eqs. (13) and (23) we get

\[
k = V^{\alpha+3} (\gamma/3 \mu)^{-(\alpha+1)\delta}, \quad b = V^{\alpha+3} (\gamma/3 \mu)^{\delta}
\]

and,

\[
\lambda_0 = I - \delta (\alpha+3) I_s^{-(\alpha+1)\delta}, \quad \xi_f = I - \delta (\alpha+3) I_s^{\delta}.
\]

It is clear that the nondimensional constants \( \lambda_0 \) and \( \xi_f \) can be obtained only if the complete solutions \( H(\eta) \) and \( U(\eta) \) are known, thus determining the shape factors.

The equations for the nondimensional functions \( H(\eta) \) and \( U(\eta) \) must be obtained by replacing the self-similar transformation given by Eqs. (5)-(7) into Eqs. (3) and (4); after some algebra, we have

\[
\omega \delta U = H^2 C', \quad U'' - \eta U' + (\eta U U)' + \alpha H U = 0.
\]
where we have defined the nondimensional curvature as

\[ C = \eta^{-\alpha} (\eta^\alpha H')' \]

(27)

and the primes denote derivation with respect to \( \eta \).

It can be easily seen that Eq. (26b) admits an exact analytical solution,

\[ \eta^{\alpha+1} H(U-1) = \text{const.} \]

(28)

As this equation must be satisfied for \( \eta = 0 \), then the constant must be zero; therefore, Eq. (28) simply determines the solution \( U = 1 \). Then, with this value of \( U \) Eq. (26a) must be solved together with the energy balance condition, which we rewrite as [see Eq. (23)],

\[ \frac{I_s}{I_\eta} = \frac{\omega}{2\delta(1+I_\eta)}, \quad \omega = 2\xi_f \]

(29)

An obvious difficulty for solving Eq. (26a) is that \( \omega \) is not known a priori. This problem may be overcome by defining

\[ \tilde{\eta} = \omega^{1/4} \eta \]

(30)

which transforms Eq. (26a) with \( U = 1 \) into

\[ \delta\tilde{\eta} = H^2 \frac{d\tilde{C}}{d\tilde{\eta}}, \]

(31)

where \( \tilde{C} \) is given by Eq. (27) with \( \tilde{\eta} \) instead of \( \eta \). Under this transformation, the shape factors are related as

\[ \tilde{I} = \omega^{(\alpha+1)/4} I_s, \quad \tilde{I}_s = \omega^{(\alpha-1)/4} I_s, \quad \tilde{I}_6 = \omega^{(\alpha+3)/4} I_6. \]

(32)

So, the condition given by Eq. (29) becomes

\[ \frac{\tilde{I}_s}{I_s} = \frac{\alpha+3}{2\delta} \]

(33)

and then the unknown constant is not involved neither in the differential equation (31), nor in the condition equation (33).

Note that when integrating Eq. (31) the variable \( \tilde{\eta} \) will take some value \( \tilde{\eta}_f \approx 1 \) at the front, defined by \( dH/d\tilde{\eta}=0 \). However, by definition \( \eta_f = 1 \) and then from Eq. (30), we have

\[ \omega^{1/4} = \tilde{\eta}_f \]

(34)

thus determining the ratio \( \xi_f^2 / \lambda_0^2 \) in Eq. (29). In consequence, the nondimensional constants \( \xi_f \) and \( \lambda_0 \) can be calculated after the integration by using Eqs. (25) and (32):

\[ \xi_f = \tilde{\eta}_f^{1/2}, \quad \lambda_0 = 1/\tilde{\eta}_f^{3/2}. \]

(35)

It must be noted that within this treatment the requirement for the energy balance determines the value of \( \tilde{\eta}_f \) which, as can be seen from Eq. (35), has a direct consequence on the values of the prefactors \( \xi_f \) and \( \lambda_0 \).

C. The phase plane \( Z-F \)

A first attempt to solve Eq. (31) was made by Starov\(^{10} \) who by integrating three times was able to reduce it to an integral equation for \( H(\tilde{\eta}) \):

\[ H(\tilde{\eta}) = 1 - \frac{A}{4} \tilde{\eta}^2 + \frac{\delta}{4} \int_0^\tilde{\eta} \left( \tilde{\eta}^2 - y^2 \right) - 2y^2 \ln \left( \frac{\tilde{\eta}}{y} \right) \frac{dy}{H(y)^{1/2}} \]

(36)

where \( A \) is an integration constant. This relationship shows that the profile is basically of the parabolic type plus a correction term which produces an inflection point in the periphery. The parabolic shape profile corresponds to a quasisteady solution.\(^{13,17} \)

Starov solved Eq. (36) by successive approximations up to the first order without considering the energy balance and by defining the drop radius as coincident with the inflection point. He obtained values for the prefactors \( \xi_f \) and \( \lambda_0 \), which are considerably different from those determined from the experiments,\(^{11,12} \) therefore, it is evident that the theory needs a substantial improvement.

A direct numerical integration of Eq. (31) is hard to be handled near the front, where \( H \) becomes very small and \( C' \) very large. Fortunately, thanks to a convenient transformation, the equation may be written in such a way that its numerical treatment becomes quite simple and the general behavior of the solution can be studied in a phase plane.

By using the variable transformation suggested by Joanny,\(^{4} \) we define

\[ F = -\frac{dH}{d\tilde{\eta}}, \quad G = -\frac{dF}{d\tilde{\eta}} \frac{d^2H}{d\tilde{\eta}^2}. \]

(37)

So, for the slope we have \( F = G = dH/dF \) and from Eq. (28) we get \( dC/dF = -\delta\tilde{\eta}/(GH^2) \). If we use the variable

\[ Z = HC \]

(38)

which is proportional to the thickness times the curvature of the profile, Eq. (31) can be expressed in the new variables as

\[ \frac{dZ}{dF} = \left( F - \frac{\delta\tilde{\eta}}{Z} \right) \left( 1 + \frac{\alpha HF}{\tilde{\eta}Z} \right) \]

(39)

This equation is particularly useful to study the flow near the front; in that region \( \tilde{\eta} \sim \tilde{\eta}_f = \text{const} \) and Eq. (39) becomes an autonomous equation (for \( \alpha = 1 \), the denominator is almost one as both \( H \ll 1 \) and \( F \to 0 \)) that is

\[ \frac{dZ}{dF} \approx F - \frac{\delta\tilde{\eta}_f}{Z}. \]

(40)

This fact is interesting because any Laplace pressure driven flow (no matter if the volume is constant or not) can be represented by the solutions of Eq. (40) near the front. In fact, the approximation \( U = 1 \) and \( \eta = \tilde{\eta}_f \) would hold in that zone whatever be the flow far from the front.

In Fig. 2 we show the topography of the phase plane \( Z-F \), which is a good approximation to what must be expected in the nonapproximated problem. In our case, we are interested only in the half-plane \( F > 0 \), as the height \( H \) monotonically decreases with \( \tilde{\eta} \). The point representing the center of symmetry (\( \tilde{\eta} = 0 \), point O) is located on the Z
FIG. 2. Integral curves (solid lines) in the phase plane for Eq. (40). Point O corresponds to \( \eta = 0 \); point I, to the inflection point at the profile \( H(\eta) \); point B, to the inflection point of the integral curve \( Z(F) \), and point A to the front \( (F = 0) \). The dashed curve between the \( dZ/dF = 0 \) and \( d^2Z/dF^2 = 0 \) curves is the separatrix curve.

axis and so should be the case for the point representing the front \( (\bar{\eta} = \bar{\eta}_f, \text{point A}) \) if one wants here to make the slope zero.

As the curvature at \( \eta = 0 \) must be negative, we have \( Z_0 - H_0 C_0 < 0 (H_0 - 1) \). Therefore, the solution curve starts at a point on the negative \( Z \) axis and ends at \( Z_f = H_f C_f > 0 \), where \( C_n, H_f, C_f, \) and \( \bar{\eta}_f \) are not known a priori. Besides, as the curve must reach the \( Z \) axis, it cannot cut the hyperbola \( FZ = \delta \bar{\eta}_f = \text{const} \), because \( dZ/dF \) must remain negative for \( Z > 0 \). Moreover, it must remain below the separatrix shown in Fig. 2 (dotted line), which divides the curves that cross the hyperbola with \( dZ/dF = 0 \) from the curves that cut the \( F \) axis with \( dZ/dF = -\infty \) after an inflection point (defined by \( d^2Z/dF^2 = 0 \), point B) on the curve,

\[
P - \delta \bar{\eta}_f/Z - Z^2/\delta \bar{\eta}_f
\]

which is also represented in Fig. 2.

Due to the change of sign of \( Z \), there will be a point where \( Z = 0 \) for \( H \neq 0 \); for the case \( \alpha = 0 \), this coincides with an inflection point of the height profile, as this corresponds to \( G = 0 \). Instead, for \( \alpha = 1 \), the inflection point of the height profile will not coincide with \( Z = 0 \), but with \( Z = -FH/\bar{\eta} \), that is before the solution curve cuts the \( F \) axis.

D. Numerical integration

Summarizing, the system of equations to be solved numerically (for instance, by means of a Runge-Kutta algorithm) is

\[
\begin{align*}
\frac{dF}{dZ} &= Z + \alpha HF/\bar{\eta}, \\
\frac{d\bar{\eta}}{dZ} &= -H, \\
\frac{dH}{dZ} &= FH \\
\frac{dF}{dZ} &= FZ - \delta \bar{\eta}
\end{align*}
\]

with the initial conditions: \( F = 0, \bar{\eta} = 0, H = 1 \) at \( Z = Z_0 \) (unknown).

The value of \( Z_0 \) must be changed until determining the unique curve which fulfills the energy requirement, Eq. (33). In Fig. 3 we give this curve for \( \alpha = 0 \) and 1, while the most remarkable figures of the solution are presented in Table I. Note that most of the flow corresponds to the portion of the curve going from point O \( (\eta = 0) \) to point I \( (\eta = \eta_f, \alpha = 0, \eta = \eta_f, \alpha = 1) \), which the fluid thickness is two orders of magnitude less than the thickness at the center of symmetry. The other portion of the curve, from I to A, passing through B \( (\eta = \eta_f, \alpha = 0, \eta = \eta_f, \alpha = 1) \), represents the flow near the front. The solution \( H(\eta) \) and its derivatives are shown in Fig. 4 for \( \alpha = 0,1 \). Note that the curves \( H(\eta) \) are coincident for \( \alpha = 0 \) and 1, and that an increasing difference between both cases appears for higher derivatives. This is because the equations for \( H \) and \( \eta \) as a function of \( Z, F \) are the same for \( \alpha = 0,1 \), while only the equation for \( dF/dZ \) is dependent on \( \alpha \) [see Eq. (42)].

The approximate constancy of \( G \) in the bulk shows that the profile is like a parabola. However, it should be noted that when expressed in the physical variables \( (h, x) \) with \( h_0 < x_f \), the shape of the free surface is indistinguishable from a spherical cap, which is the shape that many authors have previously suggested.

A special feature of the solution is that the height does not strictly vanish when \( F = 0 \), but tends to a well-defined value \( H_f \approx 10^{-7} \) (see Table I). It can be shown that this value has not a numerical origin, but it is a result of the theory. In fact, from Eq. (42), we can obtain

\[
H = e^{-\varphi}, \quad \varphi = - \int_{Z_0}^{Z} \frac{F}{FZ - \delta \bar{\eta}} \, dZ.
\]
It can be clearly seen that \( \varphi \) will not diverge for \( Z \rightarrow Z_f \) (as it would be necessary for \( H_f \rightarrow 0 \)), because the denominator of the integrand does not vanish in this interval. Thus the value of \( H_f \) is not strictly zero and its value depends only on \( Z_0 \), which at the same time is fixed by the energy balance, Eq. (33). However, it is so small that the theory becomes certainly invalid much before and then it has not a physical meaning. The fact that in this and similar problems the height cannot be led to zero has been noted by several authors, though reliable values for \( H_f \) (i.e., the height at the zero slope point) have not been given insofar to our knowledge. In fact, the value of \( H_f \) we obtain is strictly related to the integral energy balance constrain, and to zero slope condition imposed at the border, which fix a particular solution curve in the phase plane. If this constrain would be released, other curves might be chosen as hypothetical solutions for the leading part of the spreading, each one giving place to a different value of \( H_f \); this value decreases as the hypothetical solutions approach the separatrix on Fig. 2. Conversely, as we shall show in Sec. IV, the energy constrain may be maintained but other conditions may be stated at the border (for instance, by defining the front with a given value of \( H \), which should be greater than \( H_f \)).

In order to compare the theoretical results with the experiments for \( \alpha = 1 \) (see Sec. III), it is convenient to write Eq. (6) in a nondimensional form as

\[
\frac{h_0}{x_c} = \lambda_0 \left( \frac{t}{t_c} \right)^{\left( \alpha + 1 \right) \delta} = \lambda_0 \left( \frac{t}{t_c} \right)^{-0.2} \quad (\alpha = 1),
\]

\[
x_f/x_c = \xi_f \left( \frac{t}{t_c} \right)^{0.1} \quad (\alpha = 1),
\]

where \( x_c = \sqrt{A} \) and \( t_c = 3\mu \sqrt{A} / \gamma \) are the characteristic length and time, respectively, and \( \lambda_0 = 0.718 \), \( \xi_f = 0.944 \) (see Table I).

Another measurable quantity is the apparent contact angle \( \theta_\alpha \); by assuming that \( t g \theta_\alpha \) can be identified as the slope of the thickness profile at the inflection point, from Eqs. (5), (6), (24), (30), and (34) we get

\[
t g \theta_\alpha = \phi_1 \left( \frac{t}{t_c} \right)^{0.3} \quad (\alpha = 1),
\]

where \( \phi_1 = \lambda_0 \xi_f / \xi_f = 1.412 \) (see Table I). The prefactors \( \xi_f \), \( \lambda_0 \), and \( \phi_1 \) strongly differ from those obtained by Starov (see also Ref. 11) as he obtained \( \xi_f = 1.35 \), \( \lambda_0 = 0.372 \), and \( \phi_1 = 0.442 \).

In uniform approaches, where the whole drop is considered including the contact line, it is usual to define an angle-versus speed characteristic relationship given by \( \nu_f = K_3^m \) (for zero static contact angle), where \( K \) and the mobility exponent \( m \) are empirical constants. From the present approach the mobility results \( m = 3 \), while from Eqs. (44b) and (45) we get

\[
K = \left( \frac{\xi_f}{\phi_1} \right)^{\gamma} \frac{\gamma}{\mu} = 0.0901 \frac{\gamma}{\mu} \quad (\alpha = 1)
\]

which agrees reasonably well with the indirect findings of \( K \) reported by Ehrhard.12

### III. COMPARISON WITH EXPERIMENTS

There are many reported experimental data concerning the functional forms of Eqs. (44) and (45). For instance, Tanner\(^4\) reported values for the exponent in the \( \theta_\alpha \) law between 0.317 and 0.335, while in Ref. 8 we found the exponent \( \delta = 0.1 \pm 0.01 \) for Eq. (44b) and 0.3 \pm 0.015 for Eq. (45).

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**TABLE I. Values obtained from the solution curve in the phase plane.**

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<tr>
<th>( \alpha = 0 )</th>
<th>( \alpha = 1 )</th>
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<td>( \xi_f )</td>
<td>1.265 67</td>
</tr>
<tr>
<td>( \lambda_0 )</td>
<td>1.192 89</td>
</tr>
<tr>
<td>( \phi_1 )</td>
<td>1.747 98</td>
</tr>
<tr>
<td>( F_c )</td>
<td>1.672 57</td>
</tr>
<tr>
<td>( H_f )</td>
<td>1.108 85</td>
</tr>
<tr>
<td>( H_f )</td>
<td>5.14 ( 10^{-2} )</td>
</tr>
<tr>
<td>( H_f )</td>
<td>3.22 ( 10^{-7} )</td>
</tr>
</tbody>
</table>
However, there are only a few which allow a suitable comparison of the prefactors of these laws. Chen reported $\tau_f(t)$, $h_0(t)$, and $\delta_0(t)$ for PDMS volumes between 0.305 and 0.034 mm$^3$. He obtained enlarged photographs of the silhouette of the drops through a microscope. The values of $\tau_f$ and $h_0$ were measured by using a micrometer, while for the angle $\delta_0$ he used a protractor. In practice, he measured $2h_0$ and $2\delta_0$ because the silhouettes appear together with their mirror images produced by the glass substrate. The volumes were obtained from $\tau_f$ and $h_0$ by assuming that the drop shape is a spherical cap.

We performed a set of experiments with the same kind of liquid and substrata, but with different techniques. First, we obtained enlarged drop interferograms from which we obtain $\tau_f(t)$, $h_0(t)$, the drop profile and by integration, the drop volume. Second, we simultaneously obtained the maximum slope $\delta_0$ from the refracted far field when using the drop as a plano-convex lens. This method allows a simultaneous measurement of the border radius on the whole periphery and not just for a particular cross section, as it is usually done. Then, the magnified refracted field allows an easy detection of circular shape distortions.

A spatially filtered parallel He-Ne laser beam was sent upward through the substrate. As the beam section was much larger than the drop sizes, only a small part was refracted by the drop, the rest remaining unperturbed. Just after the drop, we place a beam splitter made by a relatively thick (6 mm) glass parallel plate at about 45° with respect to the beam axis. From the far field pattern given by the transmitted beam, we determined the maximum deflection angle $(n-1)\theta_\alpha$. On the other hand, the two almost equal intense reflected beams were collected by a good quality 18 cm focal length $f/2.5$ objective to produce a magnified shear interferogram on a screen placed 3.00 m apart. Here, the first face reflection formed a focused drop image (a very slight defocusing was eventually introduced to enhance by shadowgraphy the visibility of the drop edge), while the second face reflection, which gave a shifted image due to the beam splitter thickness, worked as a reference field.

A typical interferogram is shown in Fig. 5; the parallel fringes are produced by a small angle between the beam splitter faces. The difference of the liquid height between the position of two circular consecutive fringes (along the parallel fringes direction) is $\Delta h = \lambda/(n - 1)$ with $\lambda=0.6328 \, \mu \text{m}$. The pattern evolution was recorded to obtain by direct observation $\tau_f$ vs $t$ and to improve the determination of $h_0$ vs $t$ through the counting of successive central fringe vanishing. Besides, the height profile $h$ vs $x$ was obtained from the interferograms several times during each spreading (often, direct photographs of the screen were used for this purpose), thus allowing an accurate determination of the drop volume.

Some results for $\tau_f/\tau_c$ vs $t/\tau_c$ in the Laplace pressure driven regime (defined as it will be shown below by $\tau_f<2 \, \text{mm}$ and $h_0>35 \, \mu \text{m}$) are shown in Fig. 6 and compared with the theoretical solution (solid line), Eq. (44b). We have also included the Starov's solution (long dashes) and an average of the experimental results by Chen (short dashes) within our volume range. As reported previously, the best fitting exponent is near 0.1, our actual value being 0.1086, while Chen obtained 0.108-0.123. Note that both experimental data are much better approximated with $\xi_f=0.944$ (this work) than with the value given by Starov, $\xi_f=1.35$.

In addition, we may also see that the experimental points are systematically a little above the theoretical curve. Although these differences do not exceed a few percent, we believe that they are physically significant, as it will be discussed later.

In Figs. 7 and 8 we give, respectively, the measured values of $tg\theta_\alpha$ vs $t/\tau_c$ and $h_0/x_c$ vs $t/\tau_c$ together with the corresponding theoretical curves (solid lines), Eqs. (44a) and (45). The long dashes correspond to Starov's solution, while the short dashes correspond to Chen's experimental
FIG. 7. Apparent contact angles for the cases of Fig. 6. The solid line corresponds to the theoretical curve Eq. (44b), the long dashes to Starov's solution (Ref. 10) and the short dashes to an average of the runs 1–9 reported by Chen (Ref. 11).

data. In both figures the agreement between his and our results is not so good as for the measurements of $x_f$. This may be due to his estimation of $h_0$ and $\theta$ including the mirror image, while we measured these values from more accurate optical techniques, which reduce the dispersion due to incidental errors.

All of the experimental points are systematically below the theoretical curves, the best fitting exponents for our data being $-0.332$ and $-0.215$, for $\theta_+(t)$ and $h_0(t)$, respectively. The differences have opposite sense and are somewhat larger than those observed for the case of the $x_f$ vs $t$ dependence. We shall show later that all these relatively small discrepancies may be explained in a consistent way.

As reported elsewhere, we have observed that the measurements of $x_f$ vs $t$ show a transition from the Laplace pressure to the gravity driven regime, characterized by $x_f \approx t^{0.125}$. This transition always appeared at $x_f \approx 2$ mm in our experimental conditions. On the other hand, we also observed a breakup of the theory for very thin drops when $h_0$ became less than about 35 $\mu$m; however, we cannot assure that this value would be the same with different liquids and substrata, i.e., for different spreading parameters $S$.

Finally, in Fig. 9 we show three typical drop profiles with $h$ normalized to $h_0$ and $x$ to $x_f$; we also report (solid line) the profile given by the theory. The higher profile corresponds to a drop well within the gravity dominated regime ($x_f=4$ mm), the lower to a drop within the “thin drop” regime ($h_0=25$ $\mu$m) and the central one to a drop within the Laplace pressure driven regime ($x_f=1.5$ mm, $h_0=50$ $\mu$m). The qualitative differences between the three experimental profiles shown in the figure confirm that the theory can be used only within rather restrictive conditions.

IV. DISCUSSION AND CONCLUSIONS

We shall restrict ourselves to the spreading within the regime driven by the Laplace pressure; for our experimental conditions this means $x_f < 2$ mm, $h_0 > 35$ $\mu$m. The general behavior of these spreadings and the measured values are closer enough to the predictions of the solution to substantially validate the underlying assumptions. Basically, the separation of the energy balance in two particular balances: The energy liberated in the thin border region is exactly dissipated in the precursor film (through processes not described by the theory), while the dissipation in the macroscopic part of the drop exactly compensates the Laplace pressure work.

Now, according to the calculations, the integrals involved in the macroscopic balance are extended just up to the front position $x_f$, defined by the condition $\partial h/\partial x=0$; the corresponding liquid thickness is $h_f=2.35 \times 10^{-7} h_0$, of the order of a few angstrom in usual experiments. However, as said in Sec. I, there is no doubt that the small thickness effects become relevant far before, thus determining a border region much thicker than $h_f$ where the solution is meaningless. Therefore, in order to exclude the border region when calculating the macroscopic energy balance, these integrals should be truncated at some physically significant limit defined on a completely different basis. We shall show that the small but quantitatively well-determined discrepancies between the theory and the experimental results reported in the previous section are very likely a consequence of the definition of $x_f$ used in the calculations.

It is accepted that the small thickness effects are relevant when the liquid thickness is of some hundred $\AA$ or less. In our experiments, this is about $10^{-3} - 10^{-4} h_0$, so that only a very small fraction of the drop volume should be excluded to correct the energy balance and, in conse-
FIG. 9. Comparison between the theoretical profile (solid line) and the experimental results: stars: results reported in Ref. 5; squares: $V=0.12 \text{ mm}^2$, $v=10.3 \text{ cm}^2/\text{s}$ for $x_f=1.40 \text{ mm}$ and $h_0=38 \mu\text{m}$; triangles: $V=4.04 \text{ mm}^2$, $v=1.0 \text{ cm}^2/\text{s}$ for $x_f=4.67 \text{ mm}$ and $h_0=103 \mu\text{m}$; crosses: $V=0.05 \text{ mm}^2$, $v=0.1 \text{ cm}^2/\text{s}$ for $x_f=1.20 \text{ mm}$ and $h_0=12.7 \mu\text{m}$.

sequence, the expected effect would be small. Nevertheless, the point requires a careful analysis because of the strongly nonuniform distribution of the viscous dissipation rate.

Let us return to the shape factors defined in Sec. II, which, as said there, determine the nondimensional coefficient of the power law giving $x_f$, $\theta_a$, $h_0$. In Fig. 10 we show the radial cumulative distribution of the shape factors $I_1$ and $I_2$, that is the integrals given by Eqs. (17) and (20) with $\eta$ as the (variable) upper limit of integration; the insert shows in detail the same functions near the front ($\eta \to 1$). Clearly, a considerable reduction of $I_2$ would result if even a very small region near the front were excluded, while the value of $I_1$ (and so the value of $I_2$, which is not represented in the figure) would not practically vary. Therefore, the nondimensional coefficient $\xi_f$, for instance, is sensitive to even small changes of the truncation limit.

Unfortunately, the fully consistent introduction of a truncation limit in the model developed here cannot be made in a general way. This is because self-similarity requires the time invariance of the shape factors, so that the thickness at the truncation point must be a constant fraction of $h_0(t)$. Clearly, this condition would hardly be fulfilled for physically realistic truncation criteria, which, consequently, are expected to introduce deviations from self-similarity.

In Fig. 11 we give the nondimensional coefficients corresponding to a family of self-similar solutions, each one characterized by a different value of $h_f^2/h_0$ at the truncation, instead of the zero slope condition used to determine the solution in Sec. II. The values are normalized to the case of minimum value of $h_f$, i.e., $h_f^2/h_0=2.35 \times 10^{-7}$ in order to put in evidence the corrections. Each solution

FIG. 10. Spatial distribution of the surface energy and viscous dissipation rates, $I_1(\eta)$ and $I_2(\eta)$, respectively, for $\alpha=1$. The energy balance, Eq. (33), gives $I_2=20I_1$, for $\eta=1$.

FIG. 11. Correction factors for $\xi_f$, $\lambda_0$, and $\phi_i$ versus the cutoff thickness $h_f^2/h_0$.
corresponds to a different curve in the phase plane, so that the radial cumulative distribution of the shape factors differs from case to case. However, the values of the shape factors are close to those obtained simply by evaluating the functions of Fig. 10 at different values of η corresponding to some value of $h_T/\eta_0$.

The results reported in Fig. 11 explain quantitatively why the spreadings display an almost self-similar behavior. In fact, let us suppose that the truncation is determined by a fixed value of the thickness ($h_T^* = \text{const}$); therefore, during the observation of the spreadings, $h_T^*/\eta_0(t)$ varies over a range determined by the variation of $\eta_0$ along the observation period. As this range rarely exceeds one order of magnitude, $\xi_T$ may be treated as a constant within a few percent; though $H_0$ and $\phi_t$ are somewhat more sensitive, the same consideration basically holds thereon.

Therefore, it seems reasonable to assume that the evolution of a given spreading is well described by a time succession of self-similar solutions, each one corresponding to a properly renormalized truncation limit. The suitable succession of self-similar solutions, each one corresponding to $\eta_0$, slightly increases as the spreading goes on. This last front position $c_f$ is somewhat larger than 0.944 and, being the observation of the spreadings, $\eta_0/\eta_0(t)$ varies over a range determined by the variation of $\eta_0$ along the observation period. As this range rarely exceeds one order of magnitude, $\xi_T$ may be treated as a constant within a few percent; though $H_0$ and $\phi_t$ are somewhat more sensitive, the same consideration basically holds thereon.

All the discrepancies reported in the previous section are in qualitative agreement with this interpretation. From a quantitative point of view, they suggest that the truncation should be introduced at a liquid thickness of some hundred Å, which looks as a very reasonable value. Clearly, the above interpretation opens an interesting way to obtain data on the border region starting from the measurement of macroscopic spreading features; for instance, a systematic study might establish whether the thickness is the only relevant parameter to fix the truncation limit or, instead, other magnitudes such as $\phi_t$, the velocity, the spreading parameter $S$, etc., should be accounted for.

References: