Highly viscous silicone oils within a wide range of volumes were left to spread on smooth horizontal substrates to investigate the effects of capillarity on viscous gravity spreadings under the condition of complete wetting. The study was centered on the intermediate asymptotic behavior, where the details of the initial liquid distribution are irrelevant. We detected small but appreciable departures from the well-known solution without surface tension forces (viscous gravity self similar solution, or base solution). Two stages are clearly identified in the spreadings. During the first, which is usually rather brief, capillarity does not play an appreciable role on the dynamics of the spreading, i.e., the base solution is a very good approximation. The head of the current displays a wheel-like profile progressively decreasing in size; when the size becomes on the order of the capillary length, this stage ends. The wheel-like configuration cannot be associated either with the rheological behavior of the fluid used or with the initial conditions. To observe this first stage without the influences due to peculiarities of the initial conditions, a proper release of the spreading is needed.

The second stage is characterized by a spreading rate below the base solution; the slowing is associated with a change of the current head shape, which takes the form of a wedge as a consequence of capillarity. The rate of advance of the front may still be well approximated by the same power law as given by the base solution, but with a smaller prefactor. In this work we measure the parameters that characterize the flow during both stages; besides, for the second stage, we develop a heuristic calculation which shows that the wedge-like shape of the current head gives place to a higher viscous dissipation rate, thus explaining the observed slowing of the spreading.

Key Words: spreading; creeping flows; current front; self-similarity; PDMS.

1. INTRODUCTION

Viscous gravity spreadings have been studied mainly because of the interest in natural flows of geological or geophysical scales (see Refs. (1–4), among others). Thus, they are usually viewed as very slow creeping currents involving huge volumes of highly viscous fluids, for which the rate of variation \( \frac{dE_s}{dt} \) of the free energy \( E_s \) associated with the interfaces (surfaces) is completely negligible with respect to the rate of gravitational energy release \( \frac{dE_G}{dt} \). In these situations, the phenomenology related with capillarity and the wetting of surfaces does not matter as far as global descriptions are concerned; eventually, this phenomenology must be taken into account only if the interest is centered on some small scale feature. For this reason, research on viscous gravity spreadings developed as a branch of fluid mechanics almost completely separated from the vast amount of work addressed to the spreading of droplets [for instance, see Refs. (5–15)], where, instead, capillarity and wettability play a master role in the whole flow. As a matter of fact, the influence of these effects on large volume spreadings has received little attention so far.

Nevertheless, the issue is worth a deeper insight both for practical and theoretical reasons. In fact, some engineering branches deal with viscous gravity spreadings of sizes far larger than droplets although much smaller than geological flows. Moreover, as the evolution of geological and geophysical spreadings can hardly be systematically studied by direct observation, modeling by experiments at laboratory scale is often needed. In these intermediate volume spreadings capillarity effects cannot be neglected a priori. Finally, we believe that it is useful to build up a conceptual bridge between models suitable to describe large spreadings where capillarity is negligible and those for droplets spreadings where, in contrast, gravity is usually neglected. It is an experimental fact (7, 8, 16) that when a small drop (\( \leq 1 \text{ mm}^3 \)) spreads over a rigid and wettable substrate, a first capillary stage is followed by a stage occurring when the drop is quite extended, where the flow behavior is similar in viscous gravity spreadings.

Spreadings of intermediate volumes of viscous liquids have been experimentally studied, for instance, by Britter (17), Didden and Maxworthy (18), Huppert (19), Maxworthy (20), Diez (21), and Diez et al. (22); the common feature was that volumes in the range 10–100 cm\(^3\) of nonvolatile viscous liquids were allowed to spread over rigid, horizontal substrates chosen as to ensure complete wetting. Though none of these experiments included measurements...
specifically addressed to state the influence of capillarity on the overall flow dynamics, the observed behaviors were judged in agreement with models not including capillarity effects. An interesting point is that the lack of apparent interfacial effects in the above experiments is strictly related to the wettability of the substrate and not to the smallness of the interfacial terms in the overall energy balance. Let us consider, for instance, the spreading of a constant volume of a liquid over a horizontal substrate. The rate of variation of the gravitational energy $E_G$ is

$$\frac{dE_G}{dt} = \frac{V \rho g}{2} \frac{dh}{dt},$$

where $\rho$ is the liquid density, $g$ the gravity acceleration, and $\bar{h}$ the averaged liquid thickness. The corresponding rate for the interfacial energy $E_S$ is

$$\frac{dE_S}{dt} = (\gamma_{LS} - \gamma_{SA}) \frac{dA}{dt} + \gamma \frac{dA_F}{dt}.$$ 

Here $A$ is the area of the covered portion of the substrate, $A_F$ is the area of the free upper surface of the liquid, and $\gamma_{LS}$, $\gamma_{SA}$, $\gamma$ are the interfacial energies of the liquid-substrate, air-substrate, and liquid-air interfaces, respectively. By introducing the spreading parameter $S = \gamma_{SA} - \gamma_{LS} - \gamma$, the above relationship may be conveniently written as

$$\frac{dE_S}{dt} = -S \frac{dA}{dt} + \gamma \frac{d}{dt} (A_F - A).$$

The first term represents the energy rate involved in the coverage of the substrate, while the second term accounts for the difference between the upper and lower liquid surfaces. Depending on the sign of $S$, the first term may favor the spreading $(S > 0)$ or counter it $(S < 0)$. Instead, the second term always favors the spreading since $(A_F - A)$ is positive and decreases as $\bar{h}$ decreases.

By writing $A = \pi x_i^2 = \pi V/\bar{h}$, we observe that the ratio of the first term of the last equation to $dE_G/dt$ is proportional to $(S/\rho g)/\bar{h}^{\frac{3}{2}}$, which may hardly be kept small enough in laboratory experiments to ensure the negligibility of $dE_S/dt$. This is why spreading of the intermediate volume is soon stopped if $S < 0$. However, the situation is quite different if $S > 0$; in fact, it has long been recognized that in this case the dynamics of a droplet spreading is not influenced by the actual magnitude of $S$, the energy excess related to the positive value of $S$ being to a high degree of accuracy burnt out in the propagation of a thin almost unobservable precursor film. In other words, from a macroscopic point of view, spreadings occur as if the substrate were chemically identical to the liquid, i.e., with $S = 0$, no matter the magnitude of the (positive) value of $S$. Then, in this case, the ratio of the interfacial term to the gravitational term becomes

$$\frac{dE_S}{dt} \approx \gamma \frac{d(A_F - A)}{dt},$$

Under rather general hypothesis (see, for instance, Ref. (23)) $A_F \approx A[1 + \frac{h_0^2}{2x_i^2}]$, where $x_i$ is the extension of the spreading (the radius for axisymmetrical spreadings) and $h_0$ is the height at the current center. Then, we have

$$\frac{dE_S}{dt} \approx 0 \left(\frac{a^2}{x_i^2}\right) = 0 \left(\frac{1}{B}\right).$$

Here $a = (\gamma/\rho g)^{1/2}$ is the capillary length (usually on the order of 1 mm), and the ratio $x_i^2/a^2$ is currently referred to as the Bond number $B$ of the spreading. Therefore, the ‘‘weak’’ condition $B \gg 1$ ensures that the rate of interfacial energy release may be neglected. A fact worth observing is that when a droplet spreads over a wettable substrate, capillarity may be dominant at the beginning (because $B < 1$) but soon, as the spreading proceeds, is overwhelmed by gravity (because $B > 1$).

The mentioned experimental results and the above considerations led to the conclusion that under the condition of complete wetting, capillarity does not contribute appreciably to the overall dynamics of even relatively small volume spreadings. However, some measurements from silicone oil spreadings over Perspex or glass (21, 24) unexpectedly showed that the rate of advance of the current front was systematically a bit slower than predicted by the lubrication approximation theory with gravity as the only driving force. The effect could not have come from the contribution of the term $dE_S/dt$ to the energy balance because of its sign and magnitude. Though it was possible to rule out some trivial explanations, it was clear that the point should be investigated through specifically designed experiments addressed to precise quantitative determinations. With this purpose, we carried out experiments by using highly viscous polydimethylsiloxanes (PDMS), i.e., liquids with a well-known rheology, which can be assumed Newtonian with a good degree of approximation, and glass and Perspex substrates wettable by PDMS. Spreadings were performed at constant volumes and in axisymmetrical geometry. The released volume $V$ was changed from 36.5 to 1500 cm$^3$ with viscosity $\nu \approx 100$ cm$^2$/s. Also, a more viscous PDMS with $\nu \approx 1000$ cm$^2$/s was used to produce very slow spreadings, thus easing the detailed observation of the height profile in the front region. The description of the experiments and their results are given in Section 2. Some additional spreadings, involving other
liquids and, eventually, different geometries were performed in order to test the generality of the observed main features and will be briefly referred to in Section 5.

The experimental results are quantitatively compared with a well-known self-similar analytical solution first obtained by R. E. Pattle (25) for nonlinear diffusion processes (hereinafter referred to as base solution) which can be used to describe viscous gravity spreadings (3, 19, 26–29) if the lubrication theory approximation is valid and capillarity is neglected. A recall of the properties of this solution is given in Section 3; briefly, the base solution gives the radius of an axisymmetrical spreading, the height at the current center, and the height profile by the simple analytical relationships

\[ x_f(t) = 0.894 \left( \frac{gV^3}{3\nu} \right)^{1/8} t^{1/8} \]  \hspace{1cm} [1.1]

\[ h_0(t) = 0.531 \left( \frac{g}{3\nu V} \right)^{-1/4} t^{-1/4} \]  \hspace{1cm} [1.2]

\[ h(x, t) = h_0(t) \left( 1 - \left[ \frac{x}{x_f(t)} \right]^2 \right)^{1/3}. \]  \hspace{1cm} [1.3]

The last relationship determines for the shape factor \( I = V/x_f^2h_0 \) (which is constant because of the self-similar character of the solution) the value \( 3\pi/4 \). Of course, the comparison is significant only for the intermediate asymptotic regime, where features of the initial liquid distribution become irrelevant. Within this limitation, the departures with respect to the base solution provide a good estimate of the magnitude of the effects not accounted for in the theory.

The most noticeable result is that, after a short first stage where the spreading dynamics are fairly approximated by Eq. [1.1], a slowing down of the spreading appears. The change does not practically affect the functional form of [1.1] but only the value of the prefactor, which takes an almost constant value somewhat smaller than in [1.1]. At the same time, the shape of the current head changes from a wheel-like to a wedge-like profile, which is maintained afterward.

A precise determination of these effects needs accurate experimental procedures, described in Section 2: controllable and reproducible initial conditions, high quality spreading substrates, and accurate optical techniques to measure distances and height profiles (global and local) are required. Also the horizontality of the substrates must be carefully controlled. Finally, as capillarity effects are expected to be more apparent in the front region, a technique allowing for detailed observations of the height profile evolution in this zone should be provided.

With regard to the initial conditions, it is worth noting that the observation of the first stage where Eq. [1.1] holds with very good approximation requires rather restrictive conditions to be fulfilled for the spreading release. An axisymmetrical initial configuration involving all the liquid volume should be settled up on the liquid substrate in a short time. If this is not the case, experimental data independent of the initial conditions can be obtained only after the spreading is quite extended, which results in the loss of the first mentioned stage.

We show in Section 4 that the transition between the two observed stages is consistently explained in terms of the irruption of the interfacial effects in the spreading phenomenology. During the first stage these effects are irrelevant. Afterward, in spite of the fact that, thanks to wettability, the direct contribution of the interfacial terms to the energy balance is still negligible (for \( x_f^2 \gg a^2 \)), the size of the current head becomes so small that capillarity acts as a constraint locally important there. Hence, the current head is forced to take a wedge-like shape, which is considerably more dissipative than the previous wheel-like shape. As far as the overall dynamics are concerned, the effect is equivalent to an increase in the viscosity in Eq. [1.1]. In Section 4, on the basis of known ideas on the front region of large Bond number spreadings, we develop a heuristic estimate of the slowing effects which agrees very well with observation. In Section 5 we give additional evidences on why the PDMS rheology and the release procedure should be discarded as possible causes of the observed behavior.

2. EXPERIMENTS

(a) Experimental Procedures

The intermediate asymptotic regime is reached when the flow ceases to be appreciably influenced by the way the liquid is released. Though it seems difficult to state general criteria to predetermine when a given particular spreading will reach the intermediate asymptotic regime, the choice of a suitable releasing technique is clearly a major factor in ensuring a quick approach to this regime.

The flow was initiated by using the technique schematically shown in Fig. 1. The liquid, initially stored in a cylindrical container with radius \( r_p \) below the level of the spreading surface, was allowed to spread by a fast rising of the piston which constitutes the container’s bottom. The radii \( r_p \) of the cylindrical containers for small (\( V \lesssim 250 \text{ cm}^3 \)) and large spreadings, were 3.5 and 7.3 cm, respectively. Figure 2a is an example of a spreading release obtained with this technique. For comparison, we show in Fig. 2b a spreading release obtained by the sudden rising of a cylindrical dam, as was made in virtually all the previously reported works (19, 21, 22). Clearly, the piston rising technique not only leads to a more precise determination of the spreading vol-
Capillarity Effects on Viscous Gravity Spreading

Table 1

Data of the Two Liquids (PDMS) Used for $T = 25^\circ C$

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\nu_0$ (cm$^2$/s)$^a$</th>
<th>$\nu$ (cm$^2$/s)$^b$</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$\gamma$ (dyn/cm)</th>
<th>$\Delta\nu/\Delta T$ (cm$^2$/s$^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
<td>109.6</td>
<td>0.96</td>
<td>20.9</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>1200</td>
<td>0.971</td>
<td>21.2</td>
<td>24.3</td>
</tr>
</tbody>
</table>

$^a$ The notation $\nu_0$ corresponds to the value of viscosity given by the manufacturer (Dow Corning).

$^b$ $\nu$ is the viscosity value obtained by using standard methods of measurements.

The rheology of high molecular weight PDMS is worth a brief comment. Rahalker et al. (30) (see also Ref. (31)) reported the existence of entanglements between molecules for $M_w > M_c$ ($M_c \approx 2.1 \times 10^4$ is a critical value corresponding to a viscosity $\nu \approx 10$ cm$^2$/s), thus implying a non-Newtonian behavior. However, the entanglement appears only for relatively high values of the shear rate, i.e., larger than $10^2$ s$^{-1}$ for $\nu < 1000$ cm$^2$/s. This practically excludes the possibility of relevant effects associated to a non-Newtonian rheology in our experiments.

As interactions between molecules are weak, the PDMS surface tension $\gamma$ is low (about 21 dyn/cm) and almost independent of the molecular mass. The substrates were a Perspex sheet 40 $\times$ 40 cm and a glass sheet 100 $\times$ 100 cm for small ($V \approx 250$ cm$^3$) and large spreadings, respectively. Horizontality of the spreading surface was controlled by means of the reflection of a laser beam. The departures with respect to a horizontal average ideal plane were reduced to less than $10^{-2}$ mm for the case of the Perspex substrate and $10^{-1}$ mm for the glass plate. The complete wetting condition was largely fulfilled because the values of the critical surface tension $\gamma_c$ for Perspex and glass are about 40 dyn/cm (6, 32, 33).

Global liquid profiles $h(x)$ and detailed profiles near the

FIG. 1. Schematic representation of the device used to release the spreadings.

FIG. 2. Sequence of profiles during a spreading release by using (a) the rising piston technique ($V = 229$ cm$^3$, $\nu = 109.6$ cm$^2$/s at $25^\circ C$, $r_p = 3.5$ cm, $t_p = 0.2$ s) and (b) the rising dam technique ($r_{inside} = 1.67$ cm, $V = 20$ cm$^3$, $x_f = 4$ cm, $\nu = 109.6$ cm$^2$/s at $25^\circ C$). Observe the noticeable initial narrowness of the fluid column when falling and the formation of bubbles, thus delaying the formation of a smooth profile.
front were recorded by using a zoom $\times 100$ video camera focused on a vertical plane containing the axis of symmetry (see Fig. 3). In order to keep the front region centered, the camera was manually displaced along a rail. On the same plane, we formed the virtual image of a fixed scale of reference, which therefore appears superposed to the liquid profile image in the video screen. The recorded images were digitized and the liquid contours were determined by standard software. From these images we determined the position of the front $x_f$ as a function of time. A resolution less than 0.1 mm was possible. Indeterminacy in $x_f$ depends on the magnification, which must be manually changed as the spreading proceeds; therefore, the full potentiality of the method was available only for low spreading rates ($\leq 0.01$ cm/s).

To determine the thickness $h_0$ of the liquid near the center of symmetry, the free liquid surface was probed by a He–Ne focused laser beam (see Fig. 4). Due to the virtual absence of diffused light, the side observation of the incidence point $P_i$ ($i = 1, 2, \cdots$), at a given time $t_i$, of a vertical beam was impossible. Therefore, both the incident beam and the axis of the objective which formed the image of $P_i$ on a graduated screen were at 45° with respect to the vertical. In this way, the image of $P_i$ was kept always focused on the screen whatever the height of $P_i$. Besides, the position $Q_i$ of the image of $P_i$ did not depend on the slope of the surface, but only on the height of $P_i$ (34). The radial displacement of $P_i$ for different heights introduced a very small error, because the profile is almost horizontal near the center.

The scale on the screen was calibrated before each spreading and indeterminacy in the liquid heights was about 0.01 mm.

(b) Results

Hereinafter we give the results excluding a brief initial stage which is strongly influenced by the initial conditions; that is, we exclude the experimental points for which either $\text{Re} \geq 0.1$ or $\phi = h_0/x_f \geq 0.15$ or $x_f \leq 2 r_p$; this last condition is related to the entrance in the intermediate asymptotic regime, a point which will be briefly discussed in Section 4.

Figure 5 is a log–log representation of the experimental front position $x_{\text{exp}}$ as function of time $t$ for a wide range of volumes (from 36.5 to 1504 cm$^3$) together with the corresponding base solutions $x_i(t; V)$ given by Eq. [1.1] (continuous lines). Initially, $x_{\text{exp}} \approx x_i$; but, subsequently, the $x_{\text{exp}}$ points approach asymptotically lines with slope 0.125, a little below the corresponding base solutions. Even though the displacements are small, it is clear that the effect is more evident for smaller volumes. Note that if the observations were limited only to advanced stages, the departures might well be attributed to uncertainties in the values of $V$ or $\nu$ affecting the prefactor of Eqs. [1.1] and [1.2].

A representation emphasizing the effect is shown in Fig. 6, where the relative departures from Eq. [1.1] $\Delta = (x_t - x_{\text{exp}})/x_{\text{exp}}$ are reported as functions of $x_{\text{exp}}$. All the curves exhibit essentially the same behavior, i.e., they start from very small values, increase up to a maximum $\Delta_{\text{max}}$, and then slowly decrease. Two main quantitative parameters related to the slowing effect may be defined:
FIG. 4. Optical system for measuring $h_0(t)$. The ray $r_0$ is the reflected ray without fluid; the rays $r_1$ and $r_2$ are the rays reflected on the liquid free surface for $t_1$ and $t_2$, respectively.

FIG. 5. Log–log representation of $x_f$ vs $t$ together with the lines corresponding to the base solution (continuous line) for $\nu = 109.6 \text{ cm}^2/\text{s}$ (25°C) and different volumes (*, 36.5 cm$^3$; □, 82.7 cm$^3$; △, 152 cm$^3$; ◊, 229 cm$^3$; ☆, 350 cm$^3$; +, 493 cm$^3$; ×, 992 cm$^3$; ★, 1494 cm$^3$).
FIG. 6. Relative differences $\Delta$ between experimental and theoretical $x_f$ values as a function of measured $x_f$, for the same cases as in the legend to Fig. 5. The vertical dashed lines correspond to the critical front positions $x_{fc}$.

(i) the value of $\Delta_{max}$, which is representative of the magnitude of the effect, and
(ii) a critical front position $x_{fc}$ defined by the relationship $\Delta(x_{fc}) = \Delta_{max}/2$, representative of its appearance. The $x_{fc}$ values are indicated with vertical dashed lines in Fig. 6.

Figures 7a and 7b are log–log representations of $x_{fc}$ and $\Delta_{max}$ as a function of $V$ for $\nu = 109.6 \text{ cm}^2/\text{s (25°C)}$ (asterisks), respectively, together with the best fit lines

\[
x_{fc}(V) = 1.112 V^{0.4259} \quad [2.1]
\]

\[
\Delta_{max}(V) = 0.368 V^{-0.4230} \quad [2.2]
\]

The fact that the results for $\Delta_{max}$ corresponding to $\nu = 1200 \text{ cm}^2/\text{s (25°C)}$ (squares) do not agree quite well with Eq. [2.2] will be discussed in Section 4.

The height $h_0$ at the center of symmetry is shown in Fig. 8 as function of time for the three largest volumes. The points lie very close to the corresponding base solution, but for advanced times the experimental height becomes a little smaller. This departure implies that the slowing of the spreading dynamics is accompanied by a change in the form of the profile; if the volumetric shape factor $I = V/h_0 x_f^2$ were constant, higher values of $h_0$ should be expected. For this reason it is convenient to center the attention on the
evolution of $I$, which is shown in Fig. 9. Initially $I$ approaches the base solution value $3\pi/4$ within a small range of front positions $x_f < x_{fc}$. In our experiments this range is rather short and increases slightly with the volume. For instance, it goes from $x_f \approx 14$ cm to $x_f \approx 17$ and 19 cm for $V = 992$ cm$^3$ and $V = 1504$ cm$^3$, respectively. Instead, as we shall discuss in Section 4, this range is not present for the case $V = 493$ cm$^3$. As it is mentioned above, for $x_f > x_{fc}, I > I_{base}$, thus indicating that after the slowing the whole profile becomes flatter than in the base solution. This is confirmed by direct observations of the global profile. Figure 10 shows a sequence of profiles of a typical spreading for $x_f \leq x_{fc}$; the profiles corresponding to Eq. [1.3] (base solution) are given for comparison. It can be seen that for $x_f \approx 2 r_p$, the experimental profiles are very close to the base solution, except within a peripheral region whose size decreases as the spreading proceeds. Figure 11 shows a typical global profile for an advanced stage of the same spreading. Here, the measured heights are affected by a considerable dispersion due to the smallness of the values. The dashed line is the base solution profile for the same $x_f$; the base solution is still a good approximation, but the experimental profile is a little flatter, in agreement with a value of $I$ a bit larger than the base solution value $3\pi/4$.

In order to have detailed information on the flow near the front, we observed the shape of the current head by employing the technique described in Section 2(a). An important and general result was that the shape of the current
FIG. 9. Volumetric shape factor $I$ as function of the front position $x_f$ for $\phi = 493 \text{ cm}^3$, $992 \text{ cm}^3$, $1504 \text{ cm}^3$ for $\nu = 1200 \text{ cm}^2/\text{s}$ (25°C).

The evolution of the current head shape for $x_f \leq x_{fc}$ corresponding to the largest volume case is shown in Fig. 12a. Each curve corresponds to a different position of the current front (i.e., to a different time), indicated by a different ratio $x_f/x_{fc}$. To characterize quantitatively the wheel-like profile of the current head, we define two parameters: $x^*$ and $h^*$ (see Fig. 12a); $x^*$ is the distance along the $x$ axis between the most advanced point of the current (or current front $x_f$), and the contact line $x_{cl} = x_f - x^*$, while $h^*$ is the height of the liquid at $x_{cl}$. Note that the shape remains invariant as long as $x_f < x_{fc}$ in spite of the strong scale contraction. This is more evident in Fig. 12b where the same four profiles of Fig. 12a were superposed by a proper scaling. Thus, the aspect ratio $\phi^* = h^*/x^*$ of the wheel-like configuration should retain a constant value. In fact, $\phi^* \approx 4$ (see Fig. 13) until $h^*$ becomes close to 1–2 mm. When $x_f \approx x_{fc}$, $\phi^*$ is not a constant anymore, as the current head evolves toward the wedge-like form and $x^* \to 0$. Regarding the variation of $h^*$, we noticed that a representation of $h^*/h_0$ as a function of the spreading aspect ratio $\phi = h_0/x_f$ resumes to a unique curve for $x_f \leq x_{fc}$ (see Fig. 14). The best fit line is

$$h^*/h_0 = 0.686 \phi^{1/2}. \quad [2.3]$$

The dispersion of the experimental points in the region of low $\phi$ is due to the fact that $x_f$ approaches $x_{fc}$ at different values of $\phi$ according to the value of the volume. From Eq. [2.3], $h^* \sim h_0^{1/2} x_f^{-1/2} \sim x_f^{-7/2}$, i.e., the size of the wheel-like configuration is a strong inverse function of $x_f$.

For $x_f \approx x_{fc}$, the evolution of the profile of the current head is shown in Fig. 15. The shape is like a wedge with the wedge angle decreasing progressively.

In summary, the evolution of the spreads may be separated in a first brief stage for $x_f < x_{fc}$ and a second prolonged stage for $x_f > x_{fc}$. During the first stage the front position $x_f$ and the shape factor $I$ are very near the base solution, while the current head exhibits a wheel-like shape. In many cases this stage is rather short and eventually may not be present. During the second stage spreads advance approximately with the same functional form of Eq. [1.1] too, however, the prefactor is a bit smaller; at the same time, the current head takes a wedge-like shape. The value of the volume influences both the magnitude of the slowing and the radius at which the transition occurs ($x_{fc} \sim V^{3/7}$).
We shall show that the transition cannot be interpreted as a trivial evolution from the initial conditions toward an asymptotic intermediate configuration; neither can it be addressed to specific rheological properties of the PDMS. Rather, it seems attributable to the irruption in the physical scenario of a phenomenology related to capillarity, which is practically absent during the first stage.

3. RECALL OF THE PROPERTIES OF THE BASE SOLUTION

The self-similar solution for axisymmetrical viscous spreadings without capillarity has been widely studied; see, for instance, Refs. (22, 29, and 35) (also, see Refs. (4, 26–28, 36)). Nevertheless, to emphasize the role of the overall energy balance it will be useful to introduce here a formalism previously used by Diez et al. (23, 37) for the spreading of droplets driven by Laplace pressure.

As usual, we simplify the Navier–Stokes equations by employing the lubrication approximation (Reynolds number \( \text{Re} \ll 1 \) and one directional horizontal flow). Thus, the vertically averaged horizontal velocity \( \dot{x} \) is given by:

\[
\dot{x} = \frac{g}{3\nu} \frac{h^3}{h^2} \frac{\partial h}{\partial x} \quad [3.1]
\]

The velocity \( \dot{x} \) and the fluid thickness \( h \) must also satisfy the continuity equation

\[
\frac{\partial h}{\partial t} + x^{-\alpha} \frac{\partial (x^\alpha h \dot{x})}{\partial x} = 0, \quad [3.2]
\]

where the coefficient \( \alpha = 0, 1 \) stands for plane and axisymmetric geometry, respectively.

Eqs. [3.1] and [3.2] must be solved subject to certain conditions, namely that the volume remains constant during the spreading and that the energy released by gravity must be completely dissipated by viscosity at the same rate, as the flow is assumed to have negligible inertia. In general, appropriate boundary conditions for the contact line must also be used, but we shall return to this point later. The above conditions are expressed as

\[
\phi^* = h^* x^* \quad [\text{of the current head as function of } h^* \text{ for the largest volumes (*, 493 cm}^3; \Box, 992 \text{ cm}^3; \triangle, 1504 \text{ cm}^3) \].
\]

Observe that the ratio \( \phi^* \approx 4 \) until \( h^* \approx a \).
Here, the primes denote derivative with respect to $\eta$ and $h$ and

$$\beta = \frac{3\rho \nu}{\gamma} \frac{x_f}{h_0} \left( \frac{x_f}{h_0} \right)^3, \quad \omega = \frac{x_f}{v_f h_0} \frac{dh_0}{dt}. \tag{3.9}$$

In the variables defined by Eqs. [3.7], the constant volume condition given by Eq. [3.3] reduces to

$$V = h_0 x_f^{a+1} = \text{constant}, \tag{3.10}$$

where

$$I = \int_0^1 (2\pi \eta)^a H(\eta) d\eta \tag{3.11}$$

is the volumetric shape factor. In virtue of Eq. [3.10], it can be easily seen that

$$\omega = -(\alpha + 1). \tag{3.12}$$

As a result, Eq. [3.8b] admits the exact analytical solution
\[ \eta^a H(U - \eta) = \text{constant}. \quad [3.13] \]

As \( U(0) = 0 \), the constant is zero and then the solution of Eq. [3.13] is simply \( U = \eta \), i.e., the velocity profile is linear. Thus, Eq. [3.8a] can be integrated with the normalization condition \( H(0) = 1 \), giving

\[ H(\eta) = \left(1 - \frac{3}{2} \beta \eta^2\right)^{1/3}. \quad [3.14] \]

Now, the value of \( \beta \) is usually determined by posing the boundary condition at the front \( H(1) = 0 \), thus \( \beta = \frac{1}{5} \) and Eq. [1.3] is recovered. However, due to the circumstance that the self-similar profile loses physical meaning near the front (where the small slope hypothesis of lubrication approximation fails, in particular \( H'(1) = \infty \)) it seems preferable to determine \( \beta \) by using instead the global energy balance, Eq. [3.4]. With the definitions of Eqs. [3.7], Eq. [3.5] is

\[ \frac{dE_v}{dt} = 3 \rho \nu \frac{I}{V} x_t^{3(a+1)} v_t^2 I_v, \quad [3.15] \]

where

\[ I_v = \int_0^1 (2\pi \eta)^a \frac{U^2(\eta)}{H(\eta)} d\eta \quad [3.16] \]

is the viscous dissipation shape factor. Analogously, from Eq. [3.6] we obtain

\[ \frac{dE_g}{dt} = -\frac{(\alpha + 1)}{2} \rho g \left(\frac{V}{I}\right)^2 x_t^{-(\alpha+2)} v_t I_v, \quad [3.17] \]

where we have defined the gravity shape factor as

\[ I_v = \int_0^1 (2\pi \eta)^a H^2(\eta) d\eta. \quad [3.18] \]

By substituting Eqs. [3.15] and [3.17] into Eq. [3.4], we find that the energy balance can be expressed as

\[ x_t^{(3\alpha+4)} v_t = \frac{(\alpha + 1)}{2} \frac{g}{3\nu} V^3 \frac{I_v}{I_v}, \quad [3.19] \]

which, compared with Eq. [3.9] gives

\[ \beta = \frac{(\alpha + 1)}{2} \frac{I_v}{I_v}. \quad [3.20] \]

Finally, by introducing Eq. [3.14] into the integrals \( I_v \) and \( I_v \), given by Eqs. [3.16] and [3.18], from Eq. [3.20] we obtain \( \beta = \frac{1}{5} \) as before.

Even though both procedures lead to the same results, we believe that the energy balance procedure followed here is more in accord with the physical hierarchy of the conditions; the boundary condition \( H(1) = 0 \) and its consequence \( H'(1) = \infty \) are required to satisfy the more general constraint of the global energy balance, rather than being suggested by a physical treatment of the contact line region, which is left free of constraints because the interface phenomenology is simply ignored. Besides, the energy balance is also sufficient to determine the solution due to the order of Eqs. [3.8a].

The front position and the thickness at the center can now be calculated from Eqs. [1.3], [3.10], and [3.20] as

\[ x_f = \xi_g \left(\frac{gV^3 t}{3\nu}\right)^{\delta_g}, \]

\[ h_0 = \lambda_g \left(\frac{gV^2 t^{(a+1)}}{3\nu}\right)^{-(a+1)\delta_g}, \quad [3.21] \]

where \( \delta = 1/(5 + 3\alpha) \) is the similarity exponent and the prefactors are given by

\[ \xi_g = I^{-3\delta} \left(\frac{(\alpha + 1)}{2\delta} \frac{I_v}{I_v}\right)^{\delta_g}, \]

\[ \lambda_g = I^{-2\delta} \left(\frac{(\alpha + 1)}{2\delta} \frac{I_v}{I_v}\right)^{-(a+1)\delta_g}. \quad [3.22] \]

In particular, for axial symmetry \((\alpha = 1)\)

\[ I = \frac{3\pi}{4}, \quad I_v = \frac{3\pi}{5}, \quad I_v = \frac{9\pi}{10} \quad [3.23] \]

so that

\[ \xi_g = 0.89391, \lambda_g = 0.53113 \]

thus leading to Eqs. [1.1] and [1.2].

The above formalism emphasizes an important point: the actual values of the shape factors \( I, I_v, \) and \( I_v \) are needed to calculate the prefactors of Eqs. [1.1] and [1.2], whereas only their constancy (related to self similarity) is required to determine the functional form of these relationships. Should it be possible through some artifice to keep fixed the values of the shape factors to different values without introducing or subtracting a significant amount of energy, the prefactors of Eqs. [1.1] and [1.2]
would change, but their functional form would not. Equations [3.19] or [3.21] and [3.22] show that, in what concerns the spreading advance, such a change would be formally equivalent to give different values to \( \nu, \rho, g, \) or \( V, \) and that a discrimination between this possibility and the previous one might come only from profile measurements. Now, due to the form of Eq. [3.16], \( I \) may be considerably affected by changes of the profile in the region where \( H \ll 1 \) (i.e., near the front), eventually so small that the energy directly involved to produce them might be negligible in the overall balance. This circumstance is the basis of the interpretation for the experimental results.

4. INTERPRETATION OF THE EXPERIMENTAL RESULTS

(a) First Stage: Determination of the Critical Parameters

In Section 2(a) we have shown that, due to a suitable choice of the initial conditions, it is possible to generate spreadings displaying a brief stage during which the values of \( x_i, h_0, \) and \( I \) are in agreement with the base solution, albeit the current head would require a more general description in view of its characteristic wheel-like shape.

In particular, the fact that \( I = \text{constant} \approx 3\pi/4 \) indicates that the base solution holds from the center of symmetry up to a radius very close to \( x_i. \) Figure 10 confirms that for a typical spreading it holds with very good approximation since \( x_i \) becomes about the double of the radius of the piston \( x_p \) or even somewhat less. During this first stage, the viscous dissipation should be a bit below the value given by the base solution, because in Stokes’ flows the viscous dissipation takes always the minimum value compatible with the constraints, and the lubrication approximation poses a constraint which does not exist in the actual flow. However, our experiments suggest that the difference is too small to affect noticeably the spreading dynamics, which therefore may be safely calculated by using the base solution.

However, this pure viscous gravity regime cannot go on much farther: the experiments show clearly that when the rapidly decreasing size \( h^* \) of the characteristic wheel-like configuration of the current head becomes on the order of 1 or 2 mm, there appears a deep change in the flow regime and the first stage ends. Our guess is that the transition, whose typical parameters we call critical parameters, occurs when \( h^* \) becomes on the order of the capillary length \( a, \) and so, the Laplace pressure, up to this moment practically negligible everywhere, causes a strong modification of the current head shape.

As we saw in Section 2(b), the experimental data showed that \( h^* = Z h_0^{3/2} x_i^{-1/2} \) (see Eq. [2.3]), with the coefficient \( Z \) close to 1.5. Therefore, by posing \( h^* = \psi a, \) it results that

\[
X_{ic} = \left( \frac{Z}{\psi a} \right)^{2/7} \left( \frac{V}{I} \right)^{3/7},
\]

This relationship agrees very well with the experimental dependence reported in Eq. [2.1]. Also the numerical coefficient agrees, \( \psi \) being on the order of unity. Regarding the critical thickness \( h_{ic}, \) the resulting relationship is

\[
h_{ic} = \left( \frac{\psi a}{Z} \right)^{4/7} \left( \frac{V}{I} \right)^{1/7},
\]

that is, \( h_{ic} \) depends on the volume so slightly that the departure from the base solution is supposed to take place when the central height (or the averaged height) passes a fixed limiting value.

Though the full consistency between the determinations of \( x_{ic} \) from the spreading dynamics and from the condition \( h^* \approx a \) is a remarkable fact by itself, the experimental dependence of Eq. [2.3] merits some comments. A complete interpretation would probably require a full two-dimensional treatment of the flow, which is beyond the scope of the present work. However, we may advance some heuristic argument which makes Eq. [2.3] plausible. To begin with, it seems reasonable to assume that the rolling structure affects the lubrication profile given by Eq. [1.3] below a certain height, which may be identified with \( h^* \), where the slope \( \partial h/\partial x \) goes beyond a certain fixed limiting value \( (\partial h/\partial x)_l \); a simple calculation shows that this condition leads to Eq. [2.3] with the coefficient \( Z = [2/3(\partial h/\partial x)_l]^{1/2}. \) Also, the same functional dependence results by assuming that \( h^* \) is on the order of the minimum radius of curvature of the profile given by Eq. [1.3]. Therefore, Eq. [2.3] gives the expectable size of the region where the free surface is characterized by a strong curvature.

The range of the front positions where self-similar viscous gravity behavior may be expected is also worth a special comment since it is related with the appearance of the first stage. If \( r_p \) is the piston radius and \( h_p \) is the initial liquid thickness before the spreading release, it is reasonable to suppose that self similarity holds since the front passes a radius \( x_i = f(\phi_p)r_p, \) with \( \phi_p = h_p/r_p. \) For a series of experiments with identical \( \phi_p, \) \( f \) takes the same value and then \( x_i \sim V^{1/3}; \) thus giving \( x_{ic}/x_i \sim V^{3/7}/V^{1/3} \sim V^{2/7}, \) which increases very slowly with volume. However, the magnitude which is kept fixed for a series of experiments is not \( \phi_p, \) but \( r_p. \) From the spreadings in which this first stage is clearly observed, we had \( x_{ic}/x_i \approx 1.5 \) for \( \phi_p = 1, 1.5, \) and 1.7 (\( V \approx 1000, 1500, \) and 229 \( \text{cm}^3, \) respectively); and we expect this value should change only a bit for \( V \) between 10 and \( 10^3 \) \( \text{cm}^3. \) On the
other hand, in the spreading of 500 cm$^3$ ($\phi_p = 0.5$), the first stage was not observed as shown in Fig. 9. Even if these results cannot be accepted as conclusive, they indicate that in laboratory experiments a first stage is present only if $\phi_p \geq 1$ and that it starts since $x_t \approx 2x_p$.

Of course, some other more trivial conditions should also be satisfied. The Reynolds number must be small since the beginning and the perturbations related to the releasing technique should cease as soon as possible. Clearly, if reliable measurements were limited only to an advanced stage of spreading, i.e., for $x_t > x_{tc}$, the first stage could not be observed. The entire set of conditions is hardly fulfilled in nonspecified designed experiments. For instance, in Huppert’s experiments (19), all the reported values of $x_t$ were larger than the corresponding values of $x_{tc}$. In our opinion, this is why the transition at $x_{tc}$ has not been previously reported.

(b) Second Stage: Estimate of the Increase of the Viscous Dissipation

The second long stage, clearly observed in every spreading, begins when the characteristic size of the wheel-like head becomes on the order of $a$; then the profile of the peripheral zone acquires a wedge-like shape which produces an increase of the viscous dissipation. Though the energy involved in this change is negligible, the shape factor $I_c$ is increased enough to appreciably slow the spreading dynamics.

Strictly speaking, it is known (6, 41) that $I_c$ tends to infinity as $h \to 0$ (see Eq. [3.16]) for a wedge-like shape and therefore, the spreading should be stopped. However, due to the wettability of the substrate and like the spreading of droplets driven by the Laplace pressure, the energy inventory can be separated into two parts: a macroscopic balance between the released energy (virtually only gravitational in our case) and the viscous dissipation, which extends up to a radius corresponding to a cutoff thickness $h_c$; and a microscopic balance, which takes place below $h_c$, between the energy excess associated with the spreading parameter $S$ and the viscous dissipation in a thin precursor film (see for instance, (6, 9, 37)). Following Diez et al. (37), $h_c \approx 10^{-5}$ cm. An important point is that the actual value of the cutoff height $h_c$ affects very slightly the macroscopic balance (as we shall see, through the logarithm of a large number).

Other ways to overcome this difficulty have been proposed and largely discussed; for instance, those based on slip conditions (42). However, for the purpose of the present work the simple introduction of the cutoff height is well suited.

In the following, we shall be concerned with obtaining $\Delta(x_t/x_{tc})$ and an analytical scaling law for the maximum departure $\Delta_{max}$. To start with, we need an analytical expression for the height profile; the experimental results show that the profile given by the base solution approximately holds from the current center up to a peripheral region where a wedge-like profile appears and whose size is related to the capillary length. Therefore, we assume that the height profile may be approximated by

$$H(\eta) = \begin{cases} (1 - \eta^2)^{1/3} & \text{for } 0 \leq \eta < \eta_1, \\ (H_1 - H_c)(1 - \eta) \frac{x_c}{a} + H_c & \text{for } \eta_1 < \eta \leq 1, \end{cases}$$

[4.3]

where $\eta_1 = (1 - a/x_t)$ and $H_1 = h_1/h_0$ are on the order of unity and $H_c = h_c/h_0 \ll 1$ as we assume the cutoff height $h_c \approx 10^{-5}$ cm (37).

Numerical profiles with similar features to those of Eq. [4.3] were reported by Brochard-Wyart et al. (41) for the spreadings of axisymmetrical heavy liquid droplets on flat solid surfaces driven by both gravity and capillary forces. They solved the corresponding differential equations by starting from a finite height at $x_t$, and found that in the central region the profile is approximately given by an equation for $h(x)$ similar to Eq. [1.3], which vanishes beyond $x_t$, say $x_2 > x_t$. In a peripheral zone near the actual front position $x_t$, their results show that the profile acquires a wedge-like shape with size on the order of the capillary length. These basic properties are also contained in the simplified analytical profile proposed in Eq. [4.3]. The underlying assumption $x_2 = x_t$ seems reasonable in view of the spreading extension considered here ($x_t \gg a$).

Although the current is not strictly self-similar, the shape factors vary so little and so slowly that, at first approximation, we can consider them as constants; namely, we have an approximate self similarity. Among the three shape factors defined in the Section 4(a), $I_c$ is by far the most sensitive to changes in the height profile near the front. Therefore, we only take into account the variation of $I_c$ and neglect the variations of $I$ and $I_p$. By using Eq. [3.16] we calculate $I_c$ for the profile given by Eq. [4.3] and, at first approximation, we have:

$$I_c = \frac{9\pi}{10} \left[ 1 + \frac{N}{x_t} \right],$$

[4.4]

where, we have defined $N = 20aL/9H_1$ and $L = \ln(H_1/H_c)$ with $H_1/H_c \gg 1$.

By introducing Eq. [4.4] into Eq. [3.19] and integrating, we obtain for $x_t \gg x_{tc}$

$$x_t(t) = \xi \left( \frac{gV^4 t}{3L} \right)^{1/8} \left[ 1 + \frac{(N\xi^2 t)/(7At)}{1 + (8N/7x_t)} \right]^{1/8},$$

[4.5]
where we give $\Delta(x_i/x_{fc})$ vs $x_i/x_{fc}$ for two representative cases of Fig. 6.

Note that in Fig. 7 the points corresponding to $\nu = 1200$ cm$^2$/s (25°C) lie a little below the points with $\nu = 109.6$ cm$^2$/s (25°C) as if the coefficient in Eq. [4.7] were smaller. We may assign this effect both to a difference in $H_1$ or to a difference in $L = \ln(H_1/H_c)$ resulting from the different fluids used. From a macroscopic point of view, there are no reasons to expect different values for $H_1$, and therefore, the difference should be related to a microscopic effect, i.e., to the molecular forces.

In conclusion, our work is basically a description of the macroscopic behavior standing on experimental data and on an heuristic approach which assumes that the long range molecular forces as well as other effects relevant in the edge are roughly considered through a unique parameter, namely $h_c$. We think that experimental and theoretical studies about how the microscopic mechanisms determine $h_c$ should be the subject of specifically addressed works.

5. ADDITIONAL OBSERVATIONS AND FINAL REMARKS

Additional experiments were carried out in order to verify the generality of some of the above reported features. We shall briefly describe here some observations mainly concerning the first stage; they involve other liquids as well as different initial configurations and geometries.

Axisymmetrical spreadings of moderate volume ($\approx 64$ cm$^3$) of relatively low viscosity PDMS ($\nu \approx 10$ cm$^2$/s) and standard engine oils ($\nu \approx 4.7$ cm$^2$/s) of well-stated Newtonian rheology were performed by removing a circular dam. The substrate was a glass disk of 14 cm in diameter. Reliable quantitative measurements were possible only for $x_i > x_{fc}$ because of perturbations following the release procedure; nevertheless the wheel-like configuration was clearly visible for $x_i < x_{fc}$. Regarding the slowing effect, the main difficulty for a precise determination of the prefactor in Eq. [1.1] came from the uncertainty in the spreading volume, caused by the considerable amount of liquid which remained attached to the dam wall. Only by the very unpractical procedure of...
weighing the clean substrate before the spreading and the substrate plus the liquid after the spreading, it was possible to obtain reliable values for \( V \) (clearly, this technique is not suitable for larger spreadings). Though incomplete, the results agreed fairly well with those here reported.

We also observed spreadings of silicone putty Gomme GSIR mixed with clay, both in axisymmetrical and linear (channels) geometries. The rheology of this fluid is strongly non-Newtonian; however, for relatively high shear rates \( (>10^{-3} \text{ s}^{-1}) \) the behavior is like that of a Newtonian fluid with \( \nu \approx 1.1 \times 10^3 \text{ cm}^2/\text{s} \) and \( \gamma = 16 \text{ dyn/cm}^2 \). Thanks to its high viscosity, the initial configuration can be settled up quite arbitrarily by molding. The wheel-like configuration characteristic of the first stage and the fast decrease of its size was always observed. Of special interest was a series of linear spreadings where the initial configurations consisted of long slabs with a wedge profile whose angle was varied between 0.264 and 0.983 rad. The initial stage of this spreading was always an evolution of the current head from the wedge shape to the wheel-like configuration virtually without movement of the contact line; at the same time, the overall profile tended to that of Eq. [1.3] (see Fig. 17). Afterwards, the spreadings proceeded qualitatively as in the first stage described here; unfortunately, quantitative measurements were of scarce reliability because the shear rates are too low. Thus, these observations are additional evidence to show that the first stage described in this work cannot be addressed either to non-Newtonian rheologies or to specific initial conditions.

For completeness, we may try to relate the spreading regime arising after the slowing with the regime developed by small drops after the crossover between the stages driven by capillarity and gravity. In both cases the final regimes are physically similar: gravity dominates the flow except in the region near the front. However, the initial flow and also the range of the nondimensional parameters are quite different. In fact, for the large volumes \( x_f/x_{ic} \approx 1 \) and the Bond number \( B \approx 10^{3–10^5} \gg 1 \), while for droplets \( x_f/x_{ic} \gg 1 \) and \( B \approx 1–10 \). Besides, in the case of small drops, the critical front position \( x_{ic} \) loses physical sense because there is not an initial pure viscous gravity regime and \( x_f = x_{ic} \) should correspond to a drop with \( h_0 \approx a \) and \( x_f \leq h_0 \), i.e., out of the range of the lubrication approximation. For these reasons, it is also impossible to determine the maximum departure \( \Delta_{max} \) from the pure gravity regime as in large volume spreadings. Nevertheless, we can still define a relative difference \( \delta \) between the base solution and the solution \( x_f \propto x_{1.25} \) by fitting the droplet experimental points after the crossover (note that \( \delta \) is constant for a given spreading as both laws have the same exponent). A plot of the so-calculated \( \delta \) vs \( V \) for the experimental data reported in Refs. (7 and 37) shows \( 0.1 < \delta < 0.2 \) with a strong dispersion and a nondefinite relation between both magnitudes.

Even though the model introduced in Section 4(b) is valid only for large volumes, we can try to use the resulting scaling laws to determine the final regime of small drops. The \( \delta \) parameter may be thought of as an average of the \( \Delta(x_f) \) values over a given range of front positions; then from Eq. [4.6] \( \Delta \propto a/x_f \) for \( x_f \gg x_{ic} \).
(here, $\Delta$ does not depend on $V$). Since $x_t$ takes values within the restricted range of the experiments, we have $\delta \propto a/\langle x_t \rangle$, where $\langle x_t \rangle$ is the average front position. In conclusion, an extrapolation of the results obtained here predicts that there should be a slowing in the extended spreading of droplets, and that this slowing would depend on $\langle x_t \rangle$. In principle, the above mentioned experimental data are in qualitative agreement with these extrapolations.

To conclude, we think it convenient to explain why the effects described in this work have not been reported before. In our opinion, this is due to two circumstances: (i) Previous observations dealt mainly with the time dependence $x_t(t)$; the discrepancy on the value of the pre-factor was masked because the theoretical value given by Eq. [1.1] has a considerable degree of indeterminacy, due to the character of the experiments or to uncertainty about the values of $\nu$, $V$, etc. (ii) Quantitative measurements along the full evolution of the spreadings, involving the first stage and the transition, lack because early measurements were not reliable as they were exceedingly affected by perturbations following the release procedure.

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