Late stage kinetics for various wicking and spreading problems

Patrick B. Warren
Unilever R&D Port Sunlight, Bebington, Wirral, CH63 3JW, United Kingdom
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The kinetics of spreading of a liquid drop in a wedge or V-shaped groove, in a network of such grooves, and on a hydrophilic strip, is reexamined. The length of a droplet of volume Ω spreading in a wedge after a time t is predicted to scale as $\Omega^{1/5}t^{2/5}$, and the height profile is predicted to be a parabola in the distance along the wedge. If the droplet is spreading radially in a sparse network of V-shaped grooves on a surface, the radius is predicted to scale as $\Omega^{1/6}t^{1/3}$, provided the liquid is completely contained within the grooves. A number of other results are also obtained.

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I. INTRODUCTION

Wetting in complex geometries and on rough surfaces provides a wealth of fascinating nonlinear hydrodynamics problems, as well as being of commercial importance in numerous industrial sectors. Perhaps the first kind of problem to be considered was the penetration of liquid into porous materials, where Washburn in 1921 demonstrated that the distance attained by the wetting front follows a $t^{1/2}$ law where t is time [1]. Much later the spreading of droplets on flat surfaces was addressed by various workers, such as Tanner [2] and Lopez *et al.* [3], although it took some time for the subtleties of the physics at the wetting front to be resolved [4–7]. Generally, the wetting front advances with a t^{α} law where α is a small exponent which depends on the geometry of spreading and the origin of the driving force. For example, $\alpha=1/10$ for a drop spreading radially driven by surface tension (Tanner's law) and $\alpha=1/8$ for a droplet spreading radially driven by gravity (see Oron *et al.* [7] for a summary of results).

The kinetics of wetting on rough surfaces has also been investigated experimentally and theoretically [8–10]. A paradigm for this problem is the spreading of a liquid in a wedge or V-shaped groove [11–13]; indeed wetting in a network of V-shaped grooves has been invoked recently for oil spreading on skin [14]. Another kind of problem that has been considered is the wetting of hydrophilic strips [15], as an example of wetting in a controlled microstructure that might be contemplated in a microfluidic device. In all these problems, a $t^{1/2}$ spreading law has been observed, but in the cases considered thus far, there has been a reservoir which provides liquid at essentially a constant pressure. In the present paper, the problems of spreading in a wedge, in a network of V-shaped grooves, and on a hydrophilic strip are revisited. It is found that in the absence of a reservoir, the spreading law changes to t^{α} with $\alpha<1/2$, similar to Tanner's law and related problems.

These problems are first approached by scaling arguments developed in the following section. The *bona fides* of the scaling arguments is established by rederiving some known results for spreading on flat surfaces. In a further section, the scaling exponents are recovered by similarity analysis on the underlying partial differential equations which govern spreading. This also allows the scaling shape of the spreading drops to be computed.

II. SCALING ARGUMENTS

The Washburn problem of a liquid being drawn into a capillary tube of internal dimension d shown in Fig. 1(a) is considered first [1]. This is a model for penetration of liquid into a porous material for which d interpreted as a mean pore size. The arguments here are very familiar, but form the basis for the more complex problems considered below.

Once the liquid has penetrated a sufficient distance $L \gg d$, a Poiseuille law obtains for the liquid velocity and the penetration rate, thus

$$\frac{dL}{dt} \sim \frac{d^2}{\eta}\frac{\Delta p}{L}, \tag{1}$$

where η is viscosity, and the pressure drop

$$\Delta p \sim \sigma/d \tag{2}$$

is due to the surface tension σ of the curved surface at the wetting front, at a mean curvature $\sim 1/d$. All geometric factors associated with the shape of the tube and a finite contact

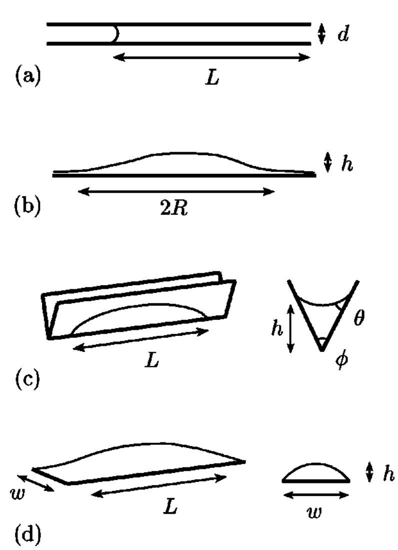

FIG. 1. Various wetting problems: (a) wicking into a capillary, (b) spreading on a flat substrate, (c) spreading in a wedge, and (d) spreading along a hydrophilic strip.

angle have been dropped, although a contact angle $\theta < \pi/2$ is required for imbibition to take place. Combining Eqs. (1) and (2) gives

$$\frac{dL}{dt} \sim \frac{\sigma}{\eta}\frac{d}{L}, \tag{3}$$

which integrates to

$$L \sim (\sigma t d/\eta)^{1/2}. \tag{4}$$

This is the simplest form of the Washburn equation [1]. The result arises from a constant pressure drop acting over an increasing length of liquid, which responds by flowing according to the Poiseuille law. As we shall see below, this can be the case for many situations where a reservoir of liquid is present, but if a reservoir is absent, the rate of spreading can be much slower.

Next, the problem of a drop of liquid spreading on a flat surface is considered, as shown in Fig. 1(b). Usually the problem is approached by an appeal to the hydrodynamics in the vicinity of the moving contact line [4,5], but it can be analyzed using similar concepts to the Washburn problem. Whilst only previously known results are recovered, the approach serves to illustrate further the arguments that will be used for the other problems.

Consider a drop of liquid spreading on a flat surface, in the case of complete wetting. Let a measure of the radius of the spreading drop be R and the height in the center be h. In the lubrication approximation, assuming a scaling shape of the droplet, all velocities will be proportional to $(h^2/\eta)(\Delta p/R)$ (compare Poiseuille law above) where Δp is the pressure drop between the center and the radius R. In particular the drop radius is expanding at a rate

$$\frac{dR}{dt} \sim \frac{h^2}{\eta}\frac{\Delta p}{R}. \tag{5}$$

First consider the capillary spreading case where the pressure gradient is due to surface tension σ. Simple geometry shows that the mean curvature at the center of the droplet for $h \ll R$ is $\sim h/R^2$ therefore the pressure drop is

$$\Delta p \sim \sigma h/R^2, \tag{6}$$

and hence

$$\frac{dR}{dt} \sim \frac{\sigma}{\eta}\frac{h^3}{R^3}. \tag{7}$$

If h were to be constant, as in the Washburn problem, this would be enough to determine the spreading rate. Here, though, a second relation connecting R and h must be sought. The desired relation follows from the conservation of drop volume Ω,

$$hR^2 \sim \Omega. \tag{8}$$

Thus

$$\frac{dR}{dt} \sim \frac{\sigma}{\eta}\frac{\Omega^3}{R^9}, \tag{9}$$

which integrates to

$$R \sim (\sigma t \Omega^3/\eta)^{1/10}. \tag{10}$$

This result is Tanner's law [2]. The basic scaling $R \sim \Omega^{3/10}\, t^{1/10}$ is well documented and has been experimentally verified [4].

For the case where the spreading is driven by gravity, one has $\Delta p \sim \rho g h$ where ρ is the mass density and g is the acceleration due to gravity. Following the same line of argument as above, one obtains $R \sim (\rho g t \Omega^3/\eta)^{1/8}$ [3]. The behavior crosses over from capillary spreading to gravity spreading when the Bond number $\rho g R^2/\sigma$ increases. Since R is increasing, this means that capillary spreading always crosses over to gravity spreading if one waits long enough. The weak increase in spreading rate has been observed experimentally [8].

Another case that can be considered is planar or one-dimensional spreading. The only thing which changes is the volume conservation law which becomes $hL \sim \Omega$ where L replaces R as the measure of extent of spreading, and Ω is a volume per unit length. This yields $L \sim (\sigma t \Omega^3/\eta)^{1/7}$ and $L \sim (\rho g t \Omega^3/\eta)^{1/5}$ for capillary [2] and gravity [3] spreading, respectively.

In the next problem, exactly analogous arguments are applied to the case of spreading in a wedge, shown in Fig. 1(c). In the case of spreading from a reservoir, this problem has been addressed by Romero and Yost [12]. The basic idea is that one has scale invariance, with the depth h of fluid being the only relevant length scale. Hence the transverse curvature of the interface $\propto 1/h$. Thus, provided the droplet has become sufficiently extended so that the contribution of the longitudinal curvature to the mean curvature can be neglected, the pressure $p \propto (-)\sigma/h$ where the negative sign obtains if the surface is convex into the liquid. This is the case if $2\theta + \phi < \pi$ where θ is the contact angle and ϕ is the wedge angle as in Fig. 1(c). In this case, the pressure becomes more negative as the amount of fluid in the wedge gets smaller. This provides a pressure gradient which drives the liquid from regions of high loading to low loading.

Even though the liquid has a free surface, a Poiseuille-like law obtains

$$\frac{dL}{dt} \sim \frac{h^2}{\eta}\frac{\Delta p}{L}, \tag{11}$$

where L is a measure of the extent of spread of the liquid drop. The pressure drop follows from the above arguments, $\Delta p \sim \sigma/h$, and therefore

$$\frac{dL}{dt} \sim \frac{\sigma}{\eta}\frac{h}{L} \tag{12}$$

in perfect analogy to Eq. (3) in the Washburn problem. The difference here is that h is a dynamic variable which, similar to the Tanner's law derivation above, is found by a volume conservation law. In this case $AL \sim \Omega$ where $A \sim h^2$ is the cross section area occupied by the liquid, and Ω is the volume of liquid. Thus $h \sim (\Omega/L)^{1/2}$. Substituting into Eq. (12) results in

$$\frac{dL}{dt} \sim \frac{\sigma}{\eta}\frac{\Omega^{1/2}}{L^{3/2}}, \tag{13}$$

which integrates to

$$L \sim (\sigma t \Omega^{1/2}/\eta)^{2/5}. \tag{14}$$

This spreading law, $L \sim \Omega^{1/5} t^{2/5}$, is a prediction. It can also be recovered by a more detailed analysis of the underlying partial differential equations which will be given in a later section.

Note that if the liquid had been spreading along the wedge from a reservoir, this would correspond to $h \sim$ constant. This leads to the Washburn result $L \sim t^{1/2}$ and is the origin of the scaling law obtained by previous workers [11,12].

The next case to be considered is the problem of a droplet spreading into a network of grooves. This has also been considered by various groups [8,9,14]. If spreading occurs from a reservoir, then the front advances with a $t^{1/2}$ Washburn-like law. However the case where the liquid is completely confined in the grooves is different. The scaling law in this case follows from arguments similar to those already applied to a drop spreading in a wedge. The analysis assumes that the grooves are rather sparse on the surface, in particular that the volume of liquid in the junction zones can be neglected compared to the volume contained in the grooves.

Consider therefore a drop of liquid spreading in a sparse random network of grooves. It will spread essentially radially. Suppose that the groove cross section is a V shape, so that both the capillary pressure and the Poiseuille scaling laws can be taken over from the case of spreading in a wedge. The fact that the grooves are randomly inclined with respect to the radial pressure gradient only introduces an additional numerical prefactor [14]. Thus Eq. (12) above still holds (with L replaced by R). What changes is the volume conservation law: as R increases, more grooves become filled. If the length of grooves per unit area is l^{-1}, where l is a characteristic groove spacing on the surface, the total length of grooves occupied by the liquid $\sim R^2/l$ and the volume $\Omega \sim h^2 R^2/l$. Eliminating h between this and Eq. (12) (with L replaced by R) gives $dR/dt \sim (\sigma/\eta)(l\Omega)^{1/2}/R^2$. This integrates to

$$R \sim [\sigma t (l\Omega)^{1/2}/\eta]^{1/3}. \tag{15}$$

The basic prediction therefore is that the spreading rate should slow from the $t^{1/2}$ Washburn-like law for spreading from a reservoir, to an $R \sim \Omega^{1/6} t^{1/3}$ law as the liquid becomes confined to the grooves. The result is confirmed by a more detailed analysis of the underlying partial differential equations given later.

The final problem that is considered is spreading along a hydrophilic strip, shown in Fig. 1(d). The case where spreading occurs from a reservoir has been investigated both theoretically and experimentally, and it is found that the spreading front advances with a Washburn-like $t^{1/2}$ law [15]. The situation in the absence of a reservoir was not investigated though. Once again, the absence of a reservoir leads to a slower rate of spreading, and the scaling law can be determined using analogous arguments to those applied above.

Consider a drop of liquid which is completely wetting on a hydrophilic strip of width w. In the late stages, let the height of the liquid above the surface be $h \ll w$, and a measure of the extent of spreading be $L \gg w$. The capillary pressure which drives the spreading is due to the transverse curvature of the interface, which for $h \ll w$ is $\sim h/w^2$. The pressure gradient is thus $\Delta p/L \sim \sigma h/w^2 L$. In the lubrication approximation with $h \ll w$, a Poiseuille-like law obtains for the fluid velocity with h being the relevant length scale. Hence the rate of extension of the droplet obeys $dL/dt \sim (h^2/\eta)(\Delta p/L) \sim (\sigma/\eta)h^3/w^2 L$. Volume conservation indicates $hwL \sim \Omega$ and eliminating h between this and the above spreading rate finds $dL/dt \sim (\sigma/\eta)\Omega^3/w^5 L^4$. This integrates to $L \sim (\sigma t \Omega^3/\eta w^5)^{1/5}$. This is the predicted scaling law for the late stages of spreading in this problem, in the absence of a reservoir.

III. SIMILARITY METHODS

The results obtained above can also be derived by using similarity methods to analyze the underlying partial differential equations (see for example Ref. [6]). Focus first on the problem of spreading in a wedge shown in Fig. 1(c). An equation which expresses local conservation of liquid in the wedge is

$$\frac{\partial A}{\partial t} + \frac{\partial (A\overline{v})}{\partial x} = 0, \tag{16}$$

where $A \sim h^2$ is the local cross section area occupied by liquid, $\overline{v}$ the mean velocity of the liquid, and x is distance along the wedge. The Poiseuille law indicates that the mean velocity follows

$$\overline{v} \propto -\frac{h^2}{\eta}\frac{\partial p}{\partial x}. \tag{17}$$

The arguments above show that $p \propto -\sigma/h$ thus

$$\frac{\partial p}{\partial x} \propto \frac{\sigma}{h^2}\frac{\partial h}{\partial x}. \tag{18}$$

Combining Eqs. (16)–(18) gives the following equation for the time evolution of the depth of liquid in the groove [compare Eqs. (8a)–(8c) of Romero and Yost [12]]

$$\frac{\partial (h^2)}{\partial t} = K\frac{\sigma}{\eta}\frac{\partial}{\partial x}\left(h^2 \frac{\partial h}{\partial x}\right). \tag{19}$$

The dimensionless coefficient $K(\theta, \phi)$ is given by Eq. (8c) in Romero and Yost [12] in terms of the static contact angle θ and the wedge angle ϕ. For spreading to occur, $K > 0$ is required. This corresponds to $2\theta + \phi < \pi$, or a liquid interface which is convex into the liquid. For the remainder of the discussion, the factor $K\sigma/\eta$ and other trivial numerical prefactors can be adsorbed into the units of time and will be omitted.

Equation (19) is basically a nonlinear diffusion equation and one can seek similarity solutions of the form

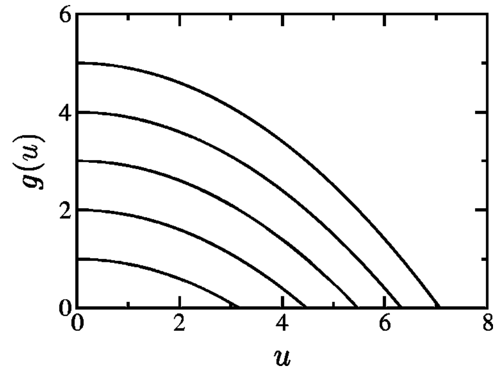

FIG. 2. Shape of a droplet spreading in a wedge. These are similarity solutions $g(u)$ found by integrating Eq. (22) with boundary conditions $g=A$ and $g'=0$ at $u=0$, for $A=1(1)5$, where u is a scaled distance: the shape is a parabola given by Eq. (25).

$$h(x,t) \sim t^{-\beta} g(xt^{-\alpha}), \tag{20}$$

where $u=xt^{-\alpha}$ is the similarity variable and α is the exponent in the spreading law. Substituting this in Eq. (19) obtains both an exponent relation

$$2\alpha + \beta = 1, \tag{21}$$

which must be satisfied for the similarity solution to hold, and an ordinary differential equation (ODE) for the similarity function

$$gg'' + 2(g')^2 + \alpha u g' + \beta g = 0. \tag{22}$$

This is a nonlinear second-order ODE with boundary conditions $g(0)=A$ (which is set by the drop volume) and $g'(0)=0$ (required by symmetry).

A second exponent relation follows from the integrated conservation law. Volume conservation dictates that $\Omega \propto \int_{-\infty}^{\infty} h^2 dx$ is constant. Inserting the similarity solution in this shows that $\Omega \sim t^{\alpha-2\beta} \times \int_{-\infty}^{\infty} g^2 du$ is constant, and therefore

$$\alpha = 2\beta. \tag{23}$$

Solving Eqs. (21) and (23) gives

$$\alpha = 2/5, \quad \beta = 1/5. \tag{24}$$

Thus the spreading law $L \sim t^{2/5}$ of the preceding section is recovered. The dependence on Ω and σ/η can be determined by dimensional analysis.

To complete the discussion, the ODE for the similarity function $g(u)$ can be solved. Inserting Eq. (24) into Eq. (22) results in $gg''+2(g')^2+2ug'/5+g/5=0$, with $g(0)=A$ and $g'(0)=0$. Remarkably, this equation has an extremely simple closed form solution,

$$g = A - u^2/10. \tag{25}$$

Note that $g \to 0$ for $u \to u_0 = \sqrt{10A}$, so the spreading drop in the groove has a finite extent. Some examples of the shape for different values of A are shown in Fig. 2. The basic prediction is that the height profile of the liquid surface for a droplet spreading in wedge is a parabola in the distance along the wedge. To be specific, from Eqs. (20), (24), and (25),

$$h(x,t) = h_0[1 - (x/x_0)^2], \quad (|x| < x_0) \tag{26}$$

where the height $h_0 \sim t^{-1/5}$ and the maximum extent of spreading $x_0 \sim t^{2/5}$.

For the case of spreading in a network of grooves, a radial version of Eq. (19) should be used (there may be an additional numerical factor from the orientation distribution of the grooves [14]). Substituting the similarity solution obtains again the exponent relation Eq. (21), and the following ODE:

$$ugg'' + 2u(g')^2 + gg' + \alpha u^2 g' + \beta u g = 0. \tag{27}$$

The integrated conservation law is now $\Omega \propto \int_0^{\infty} h^2\, 2\pi r\, dr/l$. Substituting the similarity solution shows that $\alpha=\beta$ must hold in this case. Combining this with Eq. (21) gives $\alpha=\beta=1/3$, thus the previous scaling exponent is recovered. Again, the ODE solves exactly for these exponent values to obtain $g=A-u^2/6$ and again one predicts a parabolic height profile.

Finally, the problem of a liquid spreading along a hydrophilic strip shown in Fig. 1(d) is discussed. The governing partial differential equation has been obtained by Darhuber *et al.* for this problem [15]. It is $\partial h/\partial t \sim \partial[h^3(\partial h/\partial x)]/\partial x$ where the prefactor can be found from Eq. (7) in Ref. [15]. Substituting the similarity trial solution Eq. (20) in this yields an ODE $g^3g''+3g^2(g')^2+\alpha ug'+\beta g=0$ with $g(0)=A$ and $g'(0)=0$ being initial conditions, and an exponent relation $2\alpha+3\beta=1$. It follows from $\Omega \propto \int_{-\infty}^{\infty} wh\, dx$ that $\alpha=\beta$. Solving this together with the preceding exponent relation gives $\alpha=\beta=1/5$, thus recovering the exponent of the preceding section. The ODE in this case must be solved numerically. The resulting shapes again have $g \to 0$ as $u \to u_0$ for some $u_0 > 0$ (which depends on the drop volume) but this time there is a singularity $g \sim (u_0-u)^{1/3}$ as $u \to u_0$ from below (compare Fig. 3 of Ref. [15]).

In all these cases, the fact that $g \to 0$ for $u \to u_0$ stands in contrast to the similarity solution for Tanner's law for which there is no point where $g \to 0$ [6]. In that case one has to invoke an additional microscopic mechanism to account for the shape of the edge of the drop.

The case of spreading from a reservoir can also be treated with variant of the above analysis; in fact the essential arguments are already given by Romero and Yost [12] and Darhuber *et al.* [15]. In the case of a reservoir, h is constant at the reservoir edge which we define to be the point $x=0$. In terms of the similarity solution, Eq. (20), this forces $\beta=0$. Combining this with the exponent relation in Eq. (21) or the analogous exponent relation for the strip problem shows $\alpha=1/2$ for all cases. Thus the Washburn-like spreading law is recovered for spreading from a reservoir, independent of whether spreading takes place in a wedge, in a network of grooves, or along a strip.

IV. DISCUSSION

The main results concern the kinetics of spreading in various geometries. New predictions are made for the scaling laws governing the rate at which a droplet spreads in a wedge or V-shaped groove, in a network of such grooves, and on a hydrophilic strip. These are established both by simple scaling arguments and by similarity solutions of the underlying partial differential equations. The asymptotic shapes of the spreading droplets have also been considered.

Previous work on these problems has assumed the presence of a reservoir which supplies liquid at constant pressure. This results in spreading laws which are essentially the same as the Washburn law for penetration of a liquid into a porous material or into a capillary. The analysis here complements this previous work by considering the problems in the absence of a reservoir. This will apply in the late stages of wetting when the reservoir becomes exhausted or if there is only a small amount of liquid present.

These predictions could be tested by simulation or in experiments. The case of a droplet in a wedge would seem to be particularly simple, for instance a drop will spread in a right-angled corner provided the contact angle is less than 45°. The prediction that the scaling shape of the droplet should be a parabola should also be tested.

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