Capillary Rise with Velocity-Dependent Dynamic Contact Angle

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The classic description of the rate of capillary rise given by the Washburn equation, which assumes that the contact angle preserves the equilibrium value at all times, has been recently questioned in the light of the known experimental dependence of the dynamic contact angle on the velocity of the contact line. For a number of such proposed functions of velocity for the dynamic contact angle, we analyze the resulting dependences of the contact angle and of the time of rise, respectively, on the height of the capillary rise. By applying our results to the particular cases of a high-viscosity silicone oil and water, respectively, in a glass capillary, we show that, in general, strong similarities arise between the various approaches and the classic theory in what concerns the time dependence of the capillary rise, which explains the lack of consistent experimental evidence for deviations in the rate of capillary rise from the Washburn equation. However, for a strong dependency of the contact angle on the velocity in the range of small velocities, as in the case of water on glass, one of the models predicts significant deviations even for the time dependence of the capillary rise. Moreover, our results show that the time or height dependence of the contact angle during the capillary rise can clearly discriminate between the various models.

1. Introduction

The penetration of a wetting liquid into a narrow tube or slitlike channel in contact with bulk liquid, which is due to the capillary pressure resulting from the interplay between the adhesive wall−liquid interactions and the cohesive liquid−liquid interactions, is a ubiquitous natural phenomenon. The rise of underground water in soil, water transport from the roots to the leaves of a plant, and the spreading of a coffee stain in the table cloth are some of the everyday life examples of capillary-driven wetting.[1] Moreover, a wide variety of technological applications such as oil extraction through porous rocks, or ink-jet printing, are fundamentally dependent on capillary flows. It is thus of no surprise that interest in this subject, from engineering applied science and theoretical perspectives, has repeatedly resurfaced during the time since the Washburn equation (often described as the Lucas−Washburn equation) provided the first theoretical description of such flows[2,3] (note that Washburn references Bell and Cameron[4] for an earlier similar result obtained in the case of a horizontal capillary).

New, advanced fabrication techniques employed in the field of microfluidics (where the large surface-to-volume ratios make the capillary forces dominant), based on sophisticated methods of accurate imprinting of topological and/or chemical patterns on substrates, have revived interest in the dynamics of capillary flows. There is now a need to address new questions, such as that of the influence of varying cross sections or heterogeneous (chemically or/and topographically patterned) walls for the tubes or channels, or that of a dynamic contact angle that is variable and dependent on the velocity of the three-phase contact line (TPCL),[5−10] i.e., generalizations of the problem originally discussed by Washburn.

The issue of the influence of a velocity v-dependent contact angle θ on the rate of the capillary rise has been approached in a number of studies.[11−13] By analogy with the classical case studied by Washburn,[2] the resulting dynamics $h(t)$, where h is the height of the liquid column in the tube at time t, derived under the assumption of a capillary force determined by the dynamic contact angle has been called a "modified" Washburn equation. Joos et al. have used a heuristically derived dependence $\theta(v)$; the resulting $h(t)$ compares favorably with their experimental data for silicon oils in glass capillaries and shows significant deviations from the classical result of Washburn.[11] A similar conclusion has been reported by Martic et al.: the dynamics $h(t)$ derived using the linear approximation of Blakes's theory for $\theta(v)$[8] is significantly different from the classical result and can fit the molecular dynamics (MD) simulations results very well.[13] These interesting results leave, however, a number of issues to be clarified. Both approaches report good agreement with experiments and simulations, although they use rather different expressions for the velocity dependence of the dynamic contact angle, but no critical comparison between the two is provided. Most importantly, none of them comments on, or explains, why such deviations from the classical result of Washburn have not been observed before; e.g., ref 14 reports a very careful testing of the Washburn equation and concludes that it provides an accurate description of the experimental results. [The situation is similar to the case of forced wetting, where it was shown that several distinct theories, emphasizing either hydrodynamic[7,9] or microscopic[8] aspects, can describe the available experimental and numerical results with similar accuracy (see, e.g., ref 10). Justifying a specific choice for $\theta(v)$ in favor of the others seems to be a very difficult task in the absence of high-quality dynamic wetting data over a very wide velocity range].

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In this paper, we address systematically the question of the modified Washburn equation by critically comparing the kinetics of capillary rising in vertical tubes resulting from the most common possible choices $\theta(v)$, i.e., those in refs 7−9 and 11 that from now we will denote by C (Cox), B (Blake), S (Shikhmurzaev), and J (Joos), respectively. The organization of the paper is as follows. Section 2 briefly introduces the classic Washburn equation. In section 3 we discuss the four specific choices for $\theta(v)$, and in section 4 the corresponding dynamics of capillary rising. A summary of the results and the conclusions of this study are presented in section 5.

2. Washburn Equation

We commence with a simple derivation of the Washburn equation, closely following ref 2. Consider a uniform cross section capillary of radius r, with chemically homogeneous, inert walls, inserted vertically in a bath filled with an incompressible Newtonian liquid of density ρ and viscosity η. (N.B. While we restrict the discussion to the case of vertical insertion, the results are easily generalized to an inclined capillary.)[2] The surface tension of the liquid−vapor interface is σ, and the equilibrium contact angle (determined by the Young's equation) is θ_e (Figure 1).

If $h := h(t)$ is the liquid rise in the capillary at time t and dh is the change in height during the time interval dt, the mass conservation, the incompressibility of the liquid, and the assumption that the meniscus does not change its shape (or that any such change is negligibly small) imply that the flow rate (volume per unit time) should equal $\pi r^2\, dh/dt$. In order to determine the hydrodynamic flow and the corresponding flow rate, one has to use additional assumptions:[2] that at any time t the relaxation of the velocity profile toward a Poiseuille−Hagen flow (steady-state viscous laminar flow in a very long cylinder under a fixed pressure drop) corresponding to the pressure drop at t between the advancing meniscus and the bottom of the capillary can be considered as almost instantaneous; that the contact angle θ has the constant value θ_e during the rise; that the vapor phase has negligible hydraulic resistance; that any end effects associated with the finite length of the tube and the presence of a meniscus are negligible;[2,15] and, finally, that the transient regime after the contact between the capillary and the liquid bath is very short compared with the time scale of the capillary rise.[1,15] Within the confines of these assumptions, one finds that the flow rate is proportional to the pressure gradient and is given by
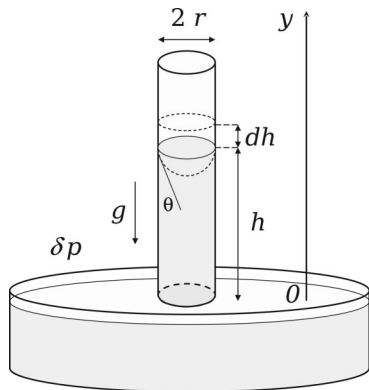

Figure 1. Schematic drawing of liquid rising along the y-direction in a capillary of radius r vertically inserted in the liquid bath. The liquid column in the capillary has height h at time t (measured from the level of the liquid in the bath). δp denotes the fixed pressure difference between the outside and the inside of the capillary, and g denotes the gravitational acceleration. The contact angle θ, between the wall and the tangent to the meniscus, is measured through the liquid.

$$\frac{\pi r^4}{8\eta}\,\frac{\delta p + \dfrac{2\sigma}{r}\cos\theta_e - \rho g h}{h} \tag{1}$$

where δp is the pressure difference between the outside and the inside of the tube. δp is zero for an open tube, but can be nonzero if, e.g., the upper end of the tube is connected to a pressure reservoir. For completeness, we will consider this latter case. Requiring that the expression above equals $\pi r^2\, dh/dt$, one obtains the following dimensionless differential equation describing the rate of capillary rise:

$$y\frac{dy}{d\tau} = \zeta + \cos\theta_e - y \tag{2}$$

where

$$y = h/L, \quad \tau = t/T, \quad \text{and} \quad \zeta = \delta p/P \tag{3}$$

are the capillary rise, the time of rise, and the external pressure drop measured, respectively, in the following units:

$$L = \frac{2\sigma}{\rho g r}, \quad T = \frac{16\sigma\eta}{\rho^2 g^2 r^3}, \quad \text{and} \quad P = \frac{2\sigma}{r} \tag{4}$$

Note that L and P have a simple intuitive interpretation: L is the equilibrium rise at zero external pressure drop for a complete wetting case ($\theta_e = 0$) and P is the Young−Laplace capillary pressure. Additionally, L/T defines a characteristic velocity

$$V = L/T = \frac{\rho g r^2}{8\eta} \tag{5}$$

which will be used as velocity scale.

For typical liquids such as water ($\rho = 10^3$ kg/m^3, $\eta = 10^{-3}$ Pa s, $\sigma = 72 \times 10^{-3}$ N/m) or high-viscosity silicon oils ($\eta = 10$ Pa s, $\rho = 10^3$ kg/m^3, $\sigma = 21.7 \times 10^{-3}$ N/m, see refs 5 and 10), which we will use to exemplify the theoretical results (see section 3), and a capillary with radius $r \simeq 10^{-4}$ m, the length, time, pressure, and velocity scales defined in eqs 4 and 5 have the following values: water $L \simeq 1.5 \times 10^{-1}$ m, $T \simeq 18$ s, $P \simeq 1.4 \times 10^3$ Pa, and $V \simeq 8 \times 10^{-3}$ m/s; silicone oil $L \simeq 4.5 \times 10^{-2}$ m, $T \simeq 3.7 \times 10^4$ s, $P \simeq 4.4 \times 10^2$ Pa, and $V \simeq 1.22 \times 10^{-6}$ m/s.

In both cases, the equilibrium contact angle is $\theta_e \simeq 0$.

Using the initial condition $y(0) = 0$, eq 2 is solved for τ:

$$\tau(y) = -y - (\zeta + \cos\theta_e)\ln\left(1 - \frac{y}{\zeta + \cos\theta_e}\right) \tag{6}$$

which is the classical Washburn equation. For $y/(\zeta + \cos\theta_e) \ll 1$, a series expansion of eq 6 up to second order in y leads to the better known (and most used) form

$$y^2 = 2(\zeta + \cos\theta_e)\tau \iff$$

$$h^2 = \frac{r^2}{4\eta}\left(\delta P + \frac{2\sigma}{r}\cos\theta_e\right)t \tag{7}$$

i.e, the square of the capillary rise is proportional to time, and, for $\delta P = 0$, the proportionality constant contains the product between the surface tension and the contact angle. Equation 7 has thus been extensively used as a simple way of extracting from the slope of the experimental h^2 vs t data either σ or θ_e, while knowing the other (see, e.g., refs 1, 14, and 16 and the references therein).

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3. Velocity-Dependent Dynamic Contact Angle

A moving TPCL is associated with a dynamic (advancing or receding) contact angle that depends on its velocity.[5,8] A number of theoretical[7−9] or empirical[11] expressions have been proposed for this dependence. Since the exact form of the dependence $\theta(v)$ is still a question of debate (see, e.g, ref 16 and the references therein), here we discuss the most common choices for $\theta(v)$, including those two used in refs 11 and 13.

The molecular kinetic theory of the moving contact line proposed by Blake[8] considers the energy dissipation at the triple line to occur through effective free-energy barriers for the displacement away or toward the TPCL of the fluid molecules. The dependence of the dynamic contact angle on the velocity v (N.B.: here and below v is positive (negative) for an advancing (receding) contact line, respectively), which we denote by (B), is given by

$$\cos \theta = \cos \theta_e - \frac{\sigma_0}{\sigma} \sinh^{-1} \frac{v}{v_0} \qquad (8)$$

where σ_0 is proportional to the thermal energy and has units of surface tension and v_0 is a velocity determined by some molecular quantities (average frequency of displacement and distance between minima of the effective free energy). Although σ_0 and v_0 cannot be directly computed or experimentally measured, significant progress has been made in improving the accuracy of determining them from experimental data by fitting with eq 8; relatively good estimates (at least the order of magnitude) of these parameters are now available for a number of systems, including aqueous glycerol solutions and silicone oils on glass substrates.[10] In this work, we will use the following values: water $\sigma_0 = 1.7 \times 10^{-2}$ N/m, $v_0 = 5 \times 10^{-3}$ m/s; oil $\sigma_0 = 10^{-2}$ N/m, $v_0 = 1.35 \times 10^{-5}$ m/s, in both cases the value v_0 (which fixes the velocity scale) being chosen such that it leads to a velocity range that is similar to the choices (J) and (C) (which are determined solely by the a priori known viscosity and surface tension of the liquid). These values are compatible with the ranges reported in ref 10 (see Figures 18 and 21): $\sigma_0 \simeq 10^{-2}$ N/m for oil and water, and $10^{-6} \lesssim v_0 \lesssim 10^{-4}$ m/s for silicone oil, $10^{-5} \lesssim v_0 \lesssim 10^{-3}$ for the aqueous glycerol (depending on their viscosity).

The dependence of the advancing dynamic contact angle on the velocity suggested empirically by Joos et al.,[11] which we will denote by (J), is given by

$$\cos \theta = \cos \theta_e - 2(1 + \cos \theta_e)\sqrt{\frac{\eta v}{\sigma}} \qquad (9)$$

Although this expression has no theoretical basis and thus cannot be considered as more than an (eventually good) fit to the experimental data, for completeness we will include it in the discussion below.

The hydrodynamic theory of the moving contact line proposed by Cox[7] emphasizes the viscous energy dissipation in the bulk and removes the singularities at the triple line by using a microscopic slip boundary condition. Assuming the viscosity of the vapor phase to be negligible, the dependence of the dynamic contact angle on the velocity, which we denote by (C), is given by the implicit relation:

$$G_c(\theta) = G_c(\theta_e) + \chi \frac{\eta v}{\sigma} \qquad (10)$$

where

$$G_c(x) = \int_0^x d\alpha \, \frac{\alpha - \sin \alpha \cos \alpha}{2 \sin \alpha}$$

and $\chi \sim 16$ is a constant defined by the natural logarithm of the ratio between the macroscopic ($\sim 10^{-2}$ m) and the microscopic ($\sim 10^{-9}$ m) length scales. [For $\theta < 3\pi/4$, one can use the approximation $G_c(\theta) \simeq \theta^3/9$, and eq 10 simplifies to $\theta^3 = \theta_e^3 + 9\xi(\eta v/\sigma)$.[7]] Note that (i) the velocity dependence given in eq 10 is just the leading term in an asymptotic expansion in both the capillary number $\eta v/\sigma$ and the ratio χ,[7,9] and (ii) using θ_e as the argument of the function G_c in the right-hand side of eq 10 is an additional approximation.[7] Because eq 10 has been shown to be in good qualitative (and even quantitative) agreement with experimental results,[5] here we simply assume these approximations to hold.

The last choice we will discuss is that due to Shikhmurzaev.[9] In the limit of small Reynolds and capillary numbers, the proposed velocity dependence of the contact angle, which we will refer to as choice (S), is given by the implicit formula

$$\cos \theta = \cos \theta_e - \frac{2u(a_1 + a_2 u_0)}{(1 - a_2)[(a_1 + u^2)^{1/2} + u]} \qquad (11)$$

where

$$u = a_3 \frac{\eta}{\sigma} v, \quad u_0 = \frac{\sin \theta - \theta \cos \theta}{\sin \theta \cos \theta - \theta},$$
$$a_1 = 1 + (1 - a_2)(\cos \theta_e - a_4) \quad (12)$$

and a_2, a_3, and a_4 are some phenomenological constants. Similarly with the proposal of Cox, this velocity dependence arises from a theory that emphasizes the viscous energy dissipation in the bulk. It removes the singularities at the triple line by assuming that the solid−liquid and the liquid−vapor interfaces have distinct thermodynamic properties (thus they behave like true thermodynamic phases), and the motion occurs as a result of mass exchange between these two "phases" (note that such an assumption has been criticized for apparent theoretical inconsistencies).[18]

Following ref 17, for aqueous solutions typical values of these are $a_2 \simeq 0.54$ and $a_4 \simeq -0.07$; we will use them for the case of the silicone oil, too. For a_3, which simply fixes the velocity scale, we use $a_3 = 12.5$ (for water) and $a_3 = 13$ (for silicone oil) such that $v(\theta)$ covers a similar range to the other three choices. As pointed out by ref 17, one notices that, although the overall agreement with the experimental results for the glycerol solutions is good, the fitting is clearly underestimating the low-velocity range of the data, which may have an influence on the results for the dynamics of capillary rise (since this proceeds at low velocities). We shall return to this point in section 4.

In Figure 2 we show all four expressions $\theta(\omega)$, where $\omega = v/V$, for both a high-viscosity silicone oil (panel a) and water (panel b) on glass. The results $\theta(\omega)$ are qualitatively very similar in spite of the quite different analytical expressions, with the notable exception of choice (B) in the case of water, which shows a much more steep increase of the contact angle at low velocity than the other three choices. Quantitatively, the choices (B), (C), and (S) seem similar (as discussed, this is expected since they have been shown to provide reasonably good fits to the available experimental data) while the choice (J) in both cases gives significantly lower dynamic contact angle than the other three. The quantitative differences are not sufficient to discriminate

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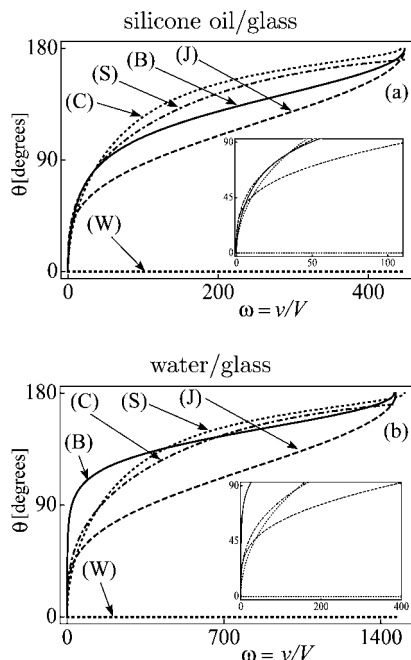
Figure 2. Dynamic contact angle θ as a function of the scaled velocity $\omega = v/V$ of the TPCL from eqs 8–12, respectively, for (a) high-viscosity silicone oil and (b) water on glass (for the values of the parameters given in the main text). The insets detail the range $\theta_e \leq \theta \leq \pi/2$ relevant for the capillary rise (see section 4).

between the models (B), (C), and (S); this is so not only because the models (B) and (S) depend on fitting parameters that cannot be independently determined but also because experimentally it is difficult to measure the dynamic contact angles with the required high accuracy over a sufficiently wide velocity range (see, e.g., the discussion in ref 16).

In all four cases, the velocity ω is finite for all angles $0 \leq \theta \leq \pi$, and thus in principle any value of the dynamic contact angle can be experimentally realized by adjusting the driving velocity. Note that not only is the velocity scale V much smaller (μm/s compared to cm/s, see section 2) but also the scaled velocity range is significantly smaller in the case of the silicone oil. Therefore, the two cases we discuss cover both slow and fast dynamics, as well as weak and strong velocity dependences, and thus are expected to provide a representative view of the dynamic contact angle effects in capillary rising.

4. Capillary Rise with a Velocity-Dependent Dynamic Contact Angle

Recently, the question of the effects of a velocity dependence of the contact angle, such as that proposed in refs 8 and 11 on the rate of capillary rise has been raised.[13] In the following we present a complete description of the resulting dependence of the dynamic contact angle on the height of the capillary rise and of the modified Washburn equations resulting from each of the possible dependencies $\theta(\omega)$ introduced in section 3.

The starting point is to assume that the rate of capillary rise still obeys eq 2, but with the static contact angle θ_e being replaced by the dynamic value θ (see also ref 11). This also assumes that the capillary pressure driving the liquid rise is still given by the Young–Laplace expression, corresponding to a spherical meniscus touching the tube at the instantaneous dynamic contact angle θ. Further assuming that v and dh/dt are identical,[13] one obtains the following (dimensionless) equation for the rate of capillary rise:

$$y\omega = \zeta + \cos[\theta(\omega)] - y, \quad \omega = \mathrm{d}y/\mathrm{d}\tau \quad (13)$$

Equation 13 can be combined with each of eqs 8, 9, 10, and 11, respectively, to eliminate ω and obtain the dependence $y = y(\theta)$ of the height on the dynamic contact angle during the capillary rise. Combining $y(\theta)$ with the corresponding $\omega(\theta)$ allows one to determine the time dependence $\theta(\tau)$ of the dynamic contact angle during the capillary rise; then the time dependence of the height is obtained as $y(\tau) = y(\theta(\tau))$. Note that the initial condition $y(0) = 0$ together with eq 13 and the fact that $\omega(\theta)$ is a bounded function (see the discussion at the end of previous section) imply that for an open capillary ($\zeta = 0$) one has $\cos \theta(\tau{=}0) = 0$, and thus $\theta(\tau{=}0) = \pi/2$. According to each of the eqs 8, 9, 10, and 11, this will determine the initial velocity $\omega(0)$ of the TPCL. In the numerical analysis below, we will focus on the case $\zeta = 0$; the case $\zeta \neq 0$ is treated similarly, the only difference being that the initial contact angle will be determined by solving $\cos \theta(\tau{=}0) = \zeta$.

Before proceeding with the analysis of the four theoretical models, we note that eq 13 can be used to predict the modified dynamics without requiring a specific model for the velocity dependency of the contact angle if experimental data is available. This is because a numerical approximation for the function $\theta(\omega)$ can be obtained, e.g., by a smooth spline interpolation, from the experimental data, and the result can then be used in the algorithmic approach described above. Therefore, for a given liquid-capillary system, accurate experimental data for $\theta(v)$ is enough information to determine if the modified capillary rise dynamics, eq 13, predicts deviations from the classic Washburn result.

Choice (B). Eliminating $\cos \theta$ from eqs 8 and 13, the rate ω of the capillary rise in this case is described by

$$y(\omega + 1) + \frac{\sigma_0}{\sigma}\sinh^{-1}\!\left(\frac{V}{v_0}\omega\right) - \cos \theta_e - \zeta = 0 \quad (14)$$

Although (14) cannot be solved analytically, it can be easily integrated numerically; the resulting capillary rise $y^2(\tau)$ for silicone oil and for water, respectively, are shown in Figures 3a and 4a, respectively.

While in the case of oil the result is practically identical to the classical prediction of Washburn, quantitative (but not qualitative) deviations (*in scaled variables*) are observed in the case of water. The maximum deviation in y^2, occurs near $\tau = 2$, where $y^2_{(W)} \simeq 0.9$ and $y^2_{(B)} \simeq 0.8$; remembering that the length scale in the case of water is $L = 10^{-1}$ m, this deviation translates into a (dimensional) difference between the capillary rise in the two cases of $h_{(W)} - h_{(B)} \simeq 5$ mm, which is well within the experimental resolution. Therefore, we conclude that the dynamic contact angle effects as described by the Blake's model should lead to observable deviations from the Washburn's equation in the case of water in the glass capillary, but not in the case of oil.

Once $y(\tau)$ is known, eq 13 determines the time dependence $\theta(\tau)$ of the dynamic contact angle, shown in the insets in Figures 3a and 4a, respectively. Combining eq 13 and 8 directly gives $y(\theta)$:

$$y = \frac{\zeta + \cos \theta}{1 + \dfrac{v_0}{V}\sinh\!\left[\dfrac{\sigma}{\sigma_0}(\cos \theta_e - \cos \theta)\right]} \quad (15)$$

which is shown in Figures 3b and 4b. (Note that this can be recast in dimensional form by simply replacing $y \rightarrow h/L$, $\tau \rightarrow t/T$, and $\zeta \rightarrow \delta p/P$.) It can be seen that in the case of silicone oil (Figure 3) there is a significant drop in the value of the dynamic contact angle at early times followed by a slow relaxation toward the
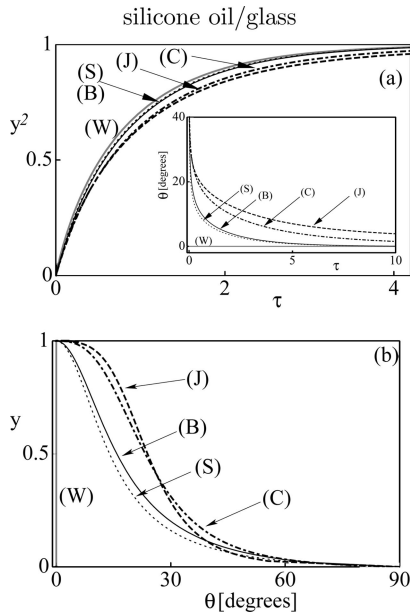
silicone oil/glass

water/glass

Figure 3. (a) Square of the capillary rise, y^2, and (inset) dynamic contact angle θ as a function of time τ, and (b) meniscus height y as a function of the dynamic contact angle θ during the capillary rise for the case of silicone oil in a glass capillary (the parameters have those values quoted in the main text, and $\zeta = 0$). The results shown correspond to the classical Washburn equation (W) and to the $\theta(\omega)$ dependencies given by eqs 8, 9, 10, and 11, respectively.
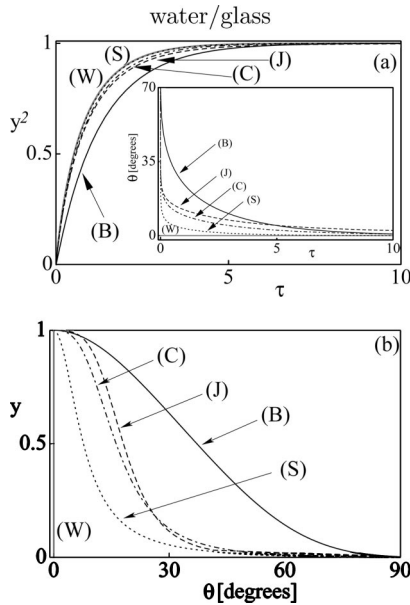
Figure 4. (a) Square of the capillary rise, y^2, and (inset) dynamic contact angle θ as a function of time τ, and (b) meniscus height y as a function of the dynamic contact angle θ during the capillary rise for the case of water in a glass capillary (the parameters have those values quoted in the main text, and $\zeta = 0$). The results shown correspond to the classical Washburn equation (W) and to the $\theta(\omega)$ dependencies given by eqs 8, 9, 10, and 11, respectively.

equilibrium value; for water (Figure 4) the initial drop in the value of θ is much smaller, but the relaxation time is similar. In both cases, the predicted variations in the contact angle during the relaxation part are significant (more than 30° and 60° for oil and water, respectively) and thus experimentally measurable.

The somewhat surprising result that the velocity dependence $\theta(\omega)$ has almost insignificant influence on the modified Washburn equation in the case of oil but leads to measurable deviations
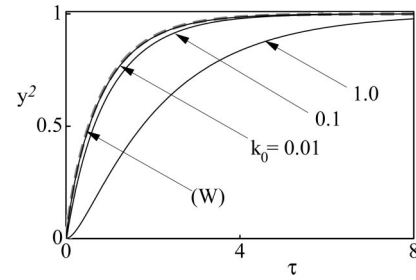

Figure 5. Square of the meniscus height, y^2, as a function of time τ for the linearized model (B). The results correspond to the classical Washburn equation (W) and to eq 18 with $k_0 = 10^{-2}$, 10^{-1}, and 1.0, respectively, for $\theta_e = 0$ and $\zeta = 0$.

from the classic description in the case of water can be intuitively understood by analyzing the behavior of the model under the assumption that the capillary rise proceeds at very low speeds; equivalently, that $(\sigma/\sigma_0)(\cos \theta_e - \cos \theta) \ll 1$. Within the confines of this assumption, eq 8 can be replaced by the linear approximation

$$k_0 \omega = \cos \theta_e - \cos \theta, \quad \text{where} \quad k_0 = \frac{V}{v_0}\frac{\sigma_0}{\sigma} \quad (16)$$

This equation can be solved analytically (see also ref 13) and leads to the $y(\theta)$ dependence

$$y = \frac{k_0(\zeta + \cos \theta)}{k_0 + \cos \theta_e - \cos \theta} \quad (17)$$

The corresponding modified Washburn equation is

$$\tau(y) = \tau_{cl}(y) - k_0 \ln\left(1 - \frac{y}{\zeta + \cos \theta_e}\right) \geq \tau_{cl}(y) \quad (18)$$

where $\tau_{cl}(y)$ denotes the solution of eq 6 and the last inequality holds for $\zeta + \cos \theta_e > 0$, i.e., for liquid rising in the capillary. Therefore, the modified dynamics in the linear approximation is slower than that corresponding to the classical case by an amount proportional to k_0. For $k_0 \ll 1$, the deviations from Washburn's equation are expected to be negligible, while for $k_0 \gg 1$ such deviations are significant, as shown in Figure 5. This is equivalent to a strong dependence of the contact angle on the velocity *in the low-velocity range*, which provides a simple criterion for selecting liquid−solid systems in the search for deviations from the classic results of Washburn. This rationalizes the numerical findings shown in Figures 3a and 4a: the case of oil corresponds to $k_0 \simeq 0.04$, and thus the resulting $y(\tau)$ should be close to the classic result of Washburn, while for water $k_0 \simeq 0.4$, and thus deviations are expected to occur. Note that, as we pointed out, this argument explains the qualitative trends observed, but it cannot be made quantitative: the deviations seen in Figure 4a are clearly larger than the predictions of the linearized model because in both cases (water and oil) σ/σ_0 is of the order of unity, and thus the linear approximation holds only in the late stages of the capillary rise, when $\theta \simeq \theta_e$.

Choice (J). After eliminating $\cos \theta$ from eqs 9 and 13, one finds that the rate ω of capillary rise in this case is described by

$$y(\omega + 1) + 2(1 + \cos \theta_e)\sqrt{\frac{\eta V}{\sigma}}\omega - \cos \theta_e - \zeta = 0 \quad (19)$$

The results $y^2(\tau)$ from the numerical integration of eq 19 for $\zeta = 0$ (the other parameters being fixed to the values discussed in the previous section) are shown in Figures 3a and 4a. It can be seen that in both cases the qualitative behavior is the same as that of the classic Washburn result. Quantitatively, in the case

of oil the capillary rise is somewhat slower than that predicated by Washburn (the maximum deviations, in real units, correspond roughly to a difference in height of about 0.3 mm over a capillary rise of 1 cm in a capillary of radius 0.1 mm, and thus may be detected), while in the case of water it is almost indistinguishable from it. Although the differences we obtain are somewhat smaller than those reported in ref 11 (this may be due to slightly different parameters employed in the present study), they show a similar trend: a slower capillary rise than the classic Washburn result.

Once $y(\tau)$ is known, (13) is used to determine $\theta(\tau)$, shown in the insets in Figures 3a and 4a, and the resulting $y(\theta)$

$$y = \frac{\zeta + \cos\theta}{1 + \frac{\sigma}{\eta V}\left[\frac{\cos\theta_e - \cos\theta}{2(1 + \cos\theta_e)}\right]^2} \quad (20)$$

which is shown in Figures 3b and 4b. The behavior is similar to the one shown by the model (B) in that a sharp drop in the contact angle at early stages is followed by a slow relaxation toward the equilibrium value, but it is seen that the quantitative differences from the model (B) are significant in both cases. Moreover, there are qualitative differences between the two cases analyzed in that for oil the decrease in the contact angle predicted by (B) is slower than that predicted by (J), while the opposite is true for the case of water. These differences should allow discrimination between the two models based on experimental data.

Choice (C). Following similar steps as above, the equation of the $y(\theta)$ dependence is found to be

$$y = \frac{\zeta + \cos\theta}{1 + \frac{\sigma}{\eta V\chi}[G_c(\theta) - G_c(\theta_e)]} \quad (21)$$

Taking the time derivative and combining with (9) leads to a differential equation for $\theta(\tau)$, which is solved numerically using the initial condition $\theta(\tau{=}0) = \pi/2$. The time dependence $y(\tau)$ of the capillary rise then follows from eq 21 evaluated at $\theta(\tau)$. As shown in Figures 3 and 4, the results for the dynamics of the capillary rise are very similar to the predictions of model (J), and thus the same conclusions as for that case apply here.

Choice (S). As for the case (C), once the $y(\theta)$ dependence

$$y = \frac{\zeta + \cos\theta}{1 + \frac{\eta V}{a_3\sigma}G_s(\theta, \theta_e)\sqrt{\frac{a_1}{1 - 2S_s(\theta, \theta_e)}}} \quad (22)$$

where

$$G_s(\theta, \theta_e) = \frac{(1 - a_2)(\cos\theta_e - \cos\theta)}{2(a_1 + a_2 u_0)}$$

is found from eqs 13 and 11, one takes the time derivative and combines with (11) and $\theta(\tau{=}0) = \pi/2$ to obtain $\theta(\tau)$. Then $y(\tau)$ follows from eq 22 evaluated at $\theta(\tau)$. The results for oil and water are shown in Figures 3 and 4, respectively. In both cases, the predictions of the corresponding modified Washburn equation for $y^2(\tau)$ are practically identical with the classic result. Somewhat surprisingly, while $\theta(\omega)$ in the both cases is rather similar to the one corresponding to (C) (see Figure 2), the resulting $\theta(\tau)$ and $y(\theta)$ are different from this one in both cases. In the case of oil, the predicted dependencies are actually very similar to the ones of model (B), but for water the predicted decrease of the contact angle toward the equilibrium value is much faster than in any of the other cases. It is tempting to conclude that this would allow discrimination of model (S) from experimental data. However, we noted that the details of the velocity dependence

of the dynamic contact angle seem to influence in a subtle way the resulting capillary rise dynamics; i.e., the similarities with model (C) at the level of $\omega(\theta)$ for the two cases considered are not reflected at the level of $\theta(\tau)$. This cautions against a hasty conclusion and indicates the need for a thorough analysis to determine if the differences noted above are intrinsically due to the model or if they are consequences of a not enough accurate determination of the parameters a_2, a_3, and a_4 via the fitting of experimental $\theta(v)$ data.

5. Summary and Conclusions

In summary, we have discussed the dynamics of capillary rise with the main assumption that the driving force is determined by the velocity-dependent dynamic contact angle rather than by the static one. Four proposed dependencies $\theta(v)$, shown in Figure 2, have been used and we have focused on the question of discriminating between them using as an example the cases of a high-viscosity silicone oil and of water, respectively, in glass capillaries.

Our results for the relationship $y^2(\tau)$, shown in Figures 3a and 4a, indicate that only for the model (B) in the case of water in glass capillaries significant deviations from the classical Washburn equation are predicted. The findings can be qualitatively understood within a linear approximation of model (B), as shown in Figure 5.

It is, however, somewhat puzzling that such deviations may have been missed by the thorough investigation of Fisher and Lark.[14] A careful look at ref 14 actually reveals that deviations have been observed (and only in the case of water), but they have been attributed either to uncertainties in determining the radius of the capillary or to formation of gas bubbles in the case of very narrow capillaries. While both are possible causes, they do not refute the possibility that actually the deviations observed are due to the dynamic contact angle effects, and clarification of this point will require further investigation.

The results for water in glass capillaries indicate that the occurrence of such deviations is connected with a strong dependence of the dynamic contact angle on the velocity in the range of (very) low velocities, and this may well explain the lack of experimental evidence for systematic deviations from Washburn's equation: unless there is such a strong velocity dependence of the contact angle, any deviations in the capillary rise are predicted to be below (or very near) to the reported limits of experimental accuracy and one would conclude, as in ref 14, that the Washburn equation provides an accurate description of the experimental results. In all the other cases, the results are very similar to (and in some cases almost identical with) it, although the dynamic contact angle varies significantly during the capillary rise. These results qualitatively agree with the findings reported in ref 11, except that we observe smaller deviations (which can be due to somewhat different parameters employed in the present study). In what concerns the results reported in ref 13, a direct comparison is difficult because of the not so well-defined connection between the parameters in MD simulations and the macroscopic ones, σ and η; we can just infer that the deviations reported there are compatible with a strong $\theta(\omega)$ dependency at low velocities.

As discussed in section 4, within the confines of the assumption that the driving force for capillary rise is given by the equilibrium expression evaluated at the dynamic value of the contact angle, the question of whether or not the capillary rise in a particular liquid-capillary system may exhibit deviations from Washburn's equation can be answered using solely the experimentally determined $\theta(\omega)$. Comparing such predictions against actual

capillary rise experiments offers the possibility of testing the validity of this basic assumption about the expression for the driving force in a nonequilibrium process. It also provides a simple qualitative way of discriminating between the four models by simply checking if their outcomes for $y^2(\tau)$ are similar or different from the classic result. This is a more stringent test on the models than the fitting of the $\theta(\omega)$ data because, as we have shown in section 4, such deviations from the classic result would require that the model captures specific details of the dynamic contact angle dependence on velocity.

Finally, we emphasize that the predicted dependencies of the dynamic contact angle on the height of the capillary rise (shown in Figures 3b and 4b) and on the time of rise (insets in Figures 3a and 4a) are experimentally accessible and would clearly allow discrimination between the models (B), (S), and (C) [or (J), whose predictions are very similar to the ones of (C)].

Glossary

ρ = density of the liquid

η = viscosity of the liquid

θ = dynamic contact angle

θ_e = equilibrium contact angle

σ = liquid−vapor surface tension

r = radius of capillary

g = gravitational constant

h = capillary rise (dimensional)

t = time (dimensional)

v = velocity of the contact line (dimensional)

δP = pressure difference (dimensional) between the outside and the inside of the capillary

L = unit of length

T = unit of time

P = unit of pressure

V = unit of velocity

y = (dimensionless) capillary rise in units L

τ = (dimensionless) time in units T

ω = (dimensionless) velocity of the contact line in units V

ζ = (dimensionless) pressure difference between the outside and the inside of the capillary in units P

σ_0, v_0, k_0 = parameters in Blake's model

$G_c(\cdot)$ = auxiliary function in Cox's model

$u_0(\cdot)$ = auxiliary function in Shikhmurzaev's model

u = auxiliary dimensionless velocity in Shikhmurzaev's model

$a_1,..., a_4$ = parameters in Shikhmurzaev's model

$G_s(\cdot,\cdot)$ = auxiliary function in Shikhmurzaev's model