Rapid Communications

Capillary as a liquid diode

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We present a theoretical investigation of liquid imbibition into capillaries with axially varying geometry. We show that using appropriate geometry and wettability, converging capillaries, in principle, can act as a liquid diode. We explain the underlying mechanics and conditions that make a converging capillary a liquid diode. Further, we describe a methodology to enhance the rate of liquid imbibition into the proposed diode. We mathematically show that creating a wettability gradient along the axial length of the capillary diode enhances the rate of liquid imbibition compared to a capillary diode with uniform wettability. Our mathematical model predicts that using a wettability gradient along the axial length of the capillary diode decreases the imbibition time by more than 30% compared to a capillary diode with uniform wettability.

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I. INTRODUCTION

It is common knowledge that when capillary tubes are partially dipped in water, the liquid-gas interface inside the tube moves spontaneously along the length of the capillary. The physical phenomenon of spontaneous motion of the liquid-gas interface into the capillary is known as imbibition. The direction of spontaneous motion depends on the local curvature of the liquid-air interface inside the capillary tube. The formation of a curved interface causes a pressure drop across the interface, resulting in imbibition of the fluid into the capillary tube. For a concave interface (concave side toward air), liquid imbibes into the capillary, whereas in the case of a convex interface, air drives liquid out of the capillary.

The curvature of the liquid-air interface depends on the local wetting condition and geometry of the capillary tube. For capillary tubes of uniform cross section, the direction of spontaneous motion depends on the solid-liquid contact angle. For a contact angle $\theta < 90^\circ$ the liquid-gas interface

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advances in the direction of air, whereas for a contact angle $\theta > 90^\circ$ the liquid-gas interface moves toward the liquid. In other words, a small contact angle $\theta < 90^\circ$ promotes the advancement of liquid into the capillary toward the gas (vapor or air). On the other hand, a large contact angle $\theta > 90^\circ$ inhibits the advancement of liquid into the capillary and instead drives the liquid-gas interface toward the liquid. The imbibition of liquid into a straight capillary was described by Bell and Cameron [1], Lucas [2], and Washburn [3]. These studies have shown that the distance of imbibition of liquid into the capillary is directly proportional to the square root of the time. This square-root dependence of liquid imbibition length on time is known as the Bell-Cameron-Lucas-Washburn (BCLW) law. As the curvature and thus the imbibition depends on the cross-sectional geometry [4,5] of the capillary, many studies have been performed to examine the applicability of the Washburn's law to different geometries [6–10]. For example, Gorce *et al.* [6] and Reyssat *et al.* [7] demonstrated that imbibition of liquid into an axially converging capillary shows a square-root dependence only at short times. That is, liquid imbibition is diffusive in nature at the beginning of the capillary. At long times, that is, at large distances from the inlet, the liquid imbibition show nondiffusive dynamics that are dependent on the geometry of the capillary.

Unlike capillaries with a uniform cross section, the local curvature of the liquid-air interface in the case of capillaries with a variable cross section depends on the local angle of inclination. Therefore, even a capillary with a contact angle $\theta = 90^\circ$ can have a gas-liquid interface with nonzero curvature. We show that capillaries with an axial variation in the cross section, in principle, can be used to obtain passive unidirectional liquid transport. We show that capillaries with a converging profile allow imbibition of liquid into the capillary, whereas capillaries with a diverging profile inhibit liquid transport through capillary action. Thereafter, we show that varying the contact angle along the axial length of the converging capillary can enhance the rate of liquid imbibition into the capillary diode. Using a quasisteady, one-dimensional mathematical model, we show that axially increasing the contact angle reduces the imbibition time of liquid into the diode capillary. The wettability gradient can be generated on a variety of surfaces using various surface treatment methods such as photochemical degradation of an alkyl siloxane self-assembled monolayer on a glass substrate [11] and silane diffusion on a silicon surface [12]. The concept of the diode capillary that we introduce here can potentially be used to build diode microheat pipes [13] and stop valves for microfluidic applications such as medical diagnostics [14] and drug delivery [15].

II. THEORY

We first illustrate how a converging capillary can act as a liquid diode. To explain the mechanics behind the workings of a converging capillary as a liquid diode, we compare the interface curvatures of the liquid-gas interface of axis-symmetric straight ($\phi = 0$) and converging capillaries ($\phi \neq 0$) having a uniform contact angle $\theta = 90^\circ$. Here, ϕ denotes the wall inclination angle of the capillary. For a capillary with a uniform cross section, the local curvature depends only on local wettability. Therefore, for a capillary with a contact angle $\theta = 90^\circ$, the liquid-air interface has zero curvature, as shown in Fig. 1(a). As a result, the liquid does not imbibe into the capillary. However, for a capillary with a variable cross section, the local curvature of the liquid-gas interface depends on local wettability and inclination angle ϕ. Therefore, in the case of a converging capillary with a uniform contact angle, $\theta = 90^\circ$, liquid forms a curved interface with gas.

The nature of the curved liquid-gas interface, that is, whether the interface is convex or concave, depends on the local slope (ϕ) of the capillary wall. The slope is said to be negative if the cross-sectional area of the capillary decreases along the axial length and positive if the cross-sectional area increases. A negative slope ($\phi < 0^\circ$) leads to the formation of a concave liquid-gas interface, as shown in Fig. 1(b) (see the left end of the capillary), whereas a positive slope results in a convex liquid-gas interface (see the right end of the capillary). In other words, if $\delta < 90^\circ$ (see Fig. 1), a concave interface is formed, and if $\delta > 90^\circ$, a convex interface is formed. The angle δ is defined as the angle between the liquid-gas interface and the line parallel to the capillary axis at the three-phase contact point. We call δ the effective imbibition angle and it is numerically equal to $\delta = \theta \pm \phi$.

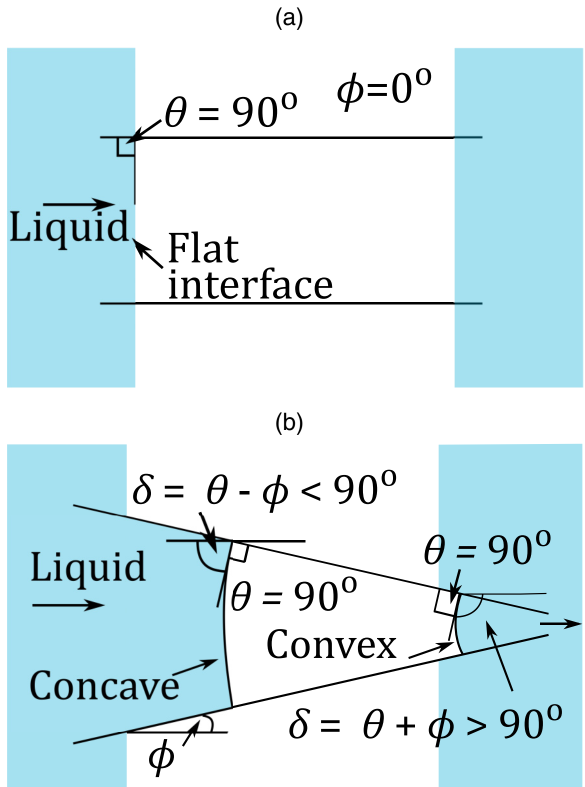

FIG. 1. Schematic illustrating the physical mechanism behind the workings of a converging capillary as a liquid diode. (a) A straight capillary with uniform contact angle of $\theta = 90^\circ$ forming a fluid-liquid interface of zero curvature. (b) A converging capillary with uniform contact angle of $\theta = 90^\circ$ and inclination angle $\phi > 0$. Due to the converging profile, the liquid imbibing from the left end of the capillary forms a concave interface with air, whereas the liquid imbibing from the right end of the capillary forms a convex interface with air.

A concave liquid-gas interface causes imbibition of liquid into the capillary whereas a convex interface leads to gas displacing liquid in the capillary. Therefore, for a converging capillary to work as a liquid diode, the imbibition angle δ should be less than 90° at one end and greater than or equal to 90° at the other. Note that we used a converging capillary with uniform wettability $\theta = 90^\circ$ only for illustrating the working mechanism of a liquid diode. In practice, the wettability of the liquid diode does not need to be uniform and can vary within the range $90^\circ - \phi < \theta < 90^\circ + \phi$. This is because, for the wettability range ($90^\circ - \phi < \theta < 90^\circ + \phi$), the imbibition angle of the fluid-liquid interface is less than 90° ($\delta < 90^\circ$ as $\delta = \theta - \phi$) for the liquid entering from the broad end of the capillary and $\delta > 90^\circ$ (as $\delta = \theta + \phi$) for the liquid entering from the narrow end of the capillary. Therefore, even in the presence of contact angle hysteresis a converging capillary can act as a liquid diode. Passive liquid diodes have been proposed previously in studies by Buchberger *et al.* [16] and Li *et al.* [17]. The liquid diodes proposed in these studies work on the principle of pinning of a three-phase contact line at the surface defects (Buchberger *et al.*) and the geometric edge of the capillary (Li *et al.*), whereas the liquid diode proposed in the current study, as described above, relies on the formation of a liquid-air interface of opposite curvatures due to converging geometry and wettability of the capillary. Besides the working mechanism, these liquid diodes use a complex geometric design compared to the simple geometry proposed in the current study.

As the imbibition angle should be $\delta < 90^\circ$ at the entrance and $\delta > 90^\circ$ at the exit of the liquid diode, this allows us to vary the contact angle such that $\delta = 0^\circ$ at the entrance and $\delta \geqslant 90^\circ$ at the exit. Varying the contact angle along the axial length of a converging capillary can enhance the imbibition rate of a liquid in the liquid diode. This is because a small contact angle increases the imbibition rate.

III. MATHEMATICAL MODEL

Next, we mathematically show that using a wettability gradient along the axial length of a liquid diode enhances the rate of imbibition compared to a liquid diode with uniform wettability. Imbibition of liquid into the capillary occurs due to a Laplace pressure drop across the curved liquid-air interface. Figure 2 shows the schematic of a converging capillary along with various dimensional coordinates. The Laplace pressure drop across the liquid-air interface with a radius of curvature R is given by the Young-Laplace equation, which is expressed as

$$P_a - P = \frac{2\sigma}{R}, \tag{1}$$

where P_a is the fluid pressure on the concave side of the liquid-air interface which in the present case is air and P the pressure on the convex side of the interface. The radius of curvature of the liquid-air interface R depends on the local radius of the capillary $h(l)$, inclination angle ϕ, and local contact angle $\theta(l)$. Mathematically, the relationship between R, h, ϕ, and θ is expressed as

$$R = \frac{h(l)}{\cos[\theta(l) - \phi]}, \tag{2}$$

where l is the length along the axial direction of the capillary. Here, we assume the capillary to be perfectly smooth and therefore has no contact angle hysteresis. For surfaces with contact angle hysteresis, the equilibrium contact angle should be replaced with an advancing contact angle [7]. The pressure drop across the curved interface creates a pressure gradient between the bulk liquid and the liquid present in the region just below the liquid-air interface. This pressure difference causes the liquid to flow in the capillary, leading to the motion of the liquid-air interface along the length of the capillary.

The capillaries have a long and slender geometry, and therefore the liquid flow can be treated as quasi-one-dimensional in the axial direction. We assume the liquid flow to be quasisteady and use the lubrication approximation of the Navier-Stokes equation to describe the liquid flow inside the capillary [6,7]. The lubrication approximation of the Navier-Stokes equation in a cylindrical

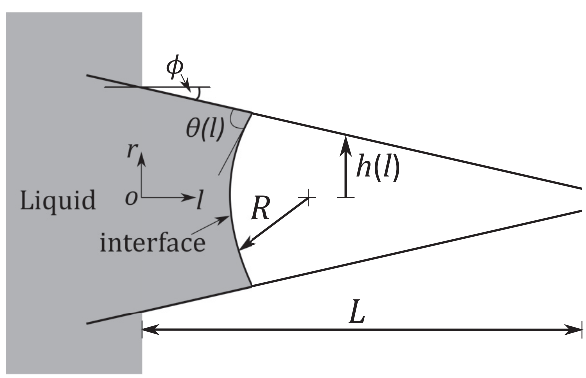

FIG. 2. Schematic showing a imbibition into a converging capillary with a wall inclination angle ϕ and whose local solid-liquid contact angle $\theta(l)$ and radius of the capillary $h(l)$ is a function of the axial distance l from the inlet.

coordinate system is expressed as

$$\frac{dP}{dl} = \frac{\mu}{r}\frac{\partial}{\partial r}\left(r\frac{\partial V}{\partial r}\right), \tag{3}$$

where V is the liquid velocity in the axial direction, μ is the liquid viscosity, and l and r are coordinates in the axial and radial direction of the capillary, respectively. Equation (3) is solved using the no-slip boundary condition $V = 0$ at $r = h$ (h is the local radius of the capillary and is a function l) and $dV/dr = 0$ at $r = 0$, which gives

$$V = \frac{r^2 - h(l)^2}{4\mu}\frac{dP}{dl}. \tag{4}$$

The mass flow rate of liquid at a given time can be expressed as

$$Q(t) = \int_0^h 2\pi r V dr = -\frac{\pi[h(l)]^4}{8\mu}\frac{dP_l}{dz}. \tag{5}$$

We assume the reference pressure at the capillary inlet and that of air is $P_a = P(l = 0) = 0$. As we have assumed the liquid flow to be quasisteady, the pressure at any point in the liquid can be expressed as

$$P(l) = -\frac{8\mu Q}{\pi}\int_0^l [h(l)]^{-4} dl. \tag{6}$$

Using $P(a) = 0$ in Eq. (1) gives

$$P(l) = -\frac{2\sigma\cos[\theta(l) - \phi]}{h(l)}. \tag{7}$$

Using Eq. (7) in Eq. (6) gives

$$\frac{2\sigma\cos[\theta(l) - \phi]}{h(l)} = \frac{8\mu Q}{\pi}\int_0^l [h(l)]^{-4} dl. \tag{8}$$

The mass flow rate of liquid at a given instant of time can be expressed as $Q(t) = \pi[h(l)]^2(dl/dt)$, where l is the imbibition length at time t. Using the above expression of mass flow rate in Eq. (8) gives the rate of imbibition as

$$\frac{dl}{dt} = \frac{\sigma\cos[\theta(l) - \phi]}{4\mu}\frac{[h(l)]^{-3}}{\int_0^l [h(l)]^{-4} dl}. \tag{9}$$

The above equation shows that imbibition rate depends on the variation in geometry $h(l)$ and wettability $\theta(l)$ of the inner wall of the capillary tube. We assume a geometric variation of the form [6]

$$h(l) = h_o\left(\frac{L - l}{L}\right) \tag{10}$$

for the converging geometry. In Eq. (10), h_o is the capillary radius at the beginning of the capillary and L is the axial length of the capillary. Using Eq. (10) in Eq. (9) gives the imbibition rate as

$$\frac{dl}{dt} = \frac{3\gamma\cos[\theta(l) - \phi]}{4\mu h_o}\frac{L(L - l)^{-3}}{(L - l)^{-3} - L^{-3}}. \tag{11}$$

For a diode with an axial wettability gradient, we assume a contact angle variation of the form

$$\cos[\theta(l) - \phi] = \left(\frac{L - l}{L}\right). \tag{12}$$

Using Eq. (12) in Eq. (11) and integrating (subject to $l = 0$ at $t = 0$) gives the imbibition time as

$$t = \frac{4\mu L^2}{3h_o\gamma}\left[\ln\left(\frac{L}{L-l}\right) + \frac{1}{3}\left(\frac{L-l}{L}\right)^3 - \frac{1}{3}\right]. \tag{13}$$

For a capillary diode with uniform wettability, integration of Eq. (11) gives the imbibition time as

$$t = \frac{4\mu L}{3h_o\gamma\cos(\theta-\phi)}\left(l + \frac{(L-l)^4 - L^4}{4L^3}\right). \tag{14}$$

IV. RESULTS AND DISCUSSION

To show how the axial variation of wettability affects liquid transport in a liquid diode, we analyze the imbibition of liquid into the capillary as a function of time. The effect of variable geometry on the liquid imbibition into a capillary has been discussed elsewhere [6,7], therefore here we limit our discussion to the effect of wettability on liquid imbibition. Before showing the effect of the wettability gradient on liquid imbibition into the capillary diode, we first explain the effect of the contact angle on the curvature of the liquid-air interface. Figure 3 shows the schematic illustrating the effect of the contact angle on the curvature of the air-liquid interface. A smaller contact angle decreases the radius of curvature of the liquid-fluid interface, as shown in Fig. 3. Reduction in the radius of curvature, in turn, increases capillary suction and thus increases the imbibition rate. Keeping the above-described effect of wettability in mind, we next present the effect of the wettability gradient on the liquid imbibition into a capillary diode and compare it with liquid imbibition into a capillary diode with uniform wettability.

Figure 4 shows liquid imbibition as a function of time for a capillary diode with uniform wettability and a diode with a wettability gradient. These calculations have been performed for a converging capillary with an axial length $L = 10$ mm, $h_o = 1$ mm, and $\phi = 5^\circ$. The diode capillary with uniform wettability has a contact angle $\theta = 90^\circ$ which gives $\delta = 85^\circ$ for liquid entering from the broad end, whereas $\delta = 95^\circ$ for liquid entering from the narrow end of the diode capillary. In the inset of Fig. 4, we compare the predictions of our mathematical model with the experimental results of Gorce *et al.* [6] for a converging capillary with uniform wettability. In their experiments Gorce *et al.* used a converging capillary with a base radius $h_o = 330$ μm, $L = 6$ mm, $\theta = 75^\circ$, and glycerol as the working fluid. Predictions of our mathematical model agree well with the experimental results of Gorce *et al.* Consistent with our discussion in Sec. II, the results presented in Fig. 4 show that a diode capillary with a wettability gradient indeed has a lower time of liquid imbibition compared to a diode capillary with uniform wettability. Predictions of our mathematical model show that creating a wettability gradient along the axial length of the diode capillary decreases the imbibition time by more than 30%. This reduction in imbibition time can be attributed to the higher capillary suction due to the smaller contact angle at the beginning of the diode capillary with a wettability gradient compared to a diode capillary with uniform wettability. The effect of the contact angle is

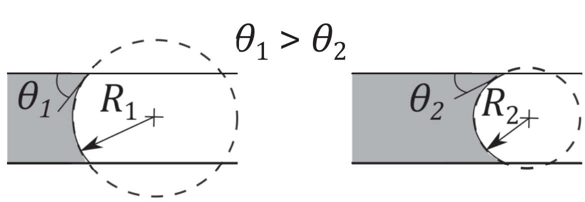

FIG. 3. Schematic illustrating the effect of wettability on the radius of curvature of a gas-liquid interface. For a capillary with a uniform cross section, the radius of curvature of the gas-liquid interface is smaller for a lower value of the contact angle, that is, $R_2 < R_1$ for $\theta_2 < \theta_1$. The small radius of curvature, in turn, leads to higher capillary suction.

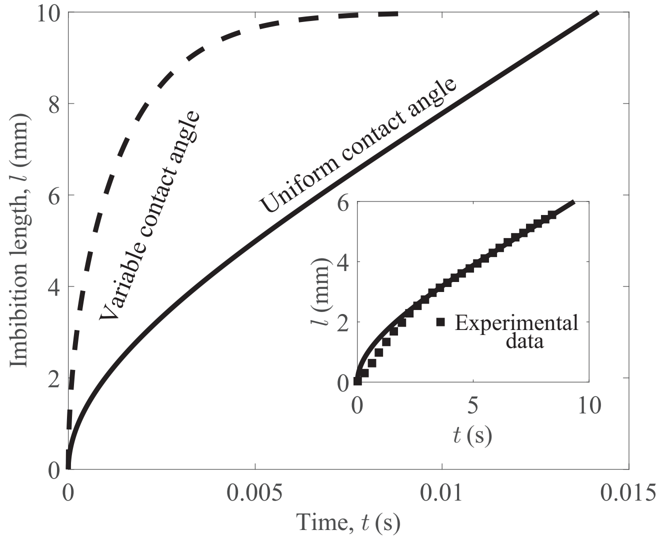

FIG. 4. Liquid imbibition into a diode capillary (converging capillary) with uniform wettability and a diode capillary with an axial contact angle variation. The contact angle of the inner surface of the diode capillary varies such that the cosine of the sum of the contact angle θ and inclination angle ϕ vary linearly along the axial length of the capillary. These calculations have been performed for $\phi = 5^{\circ}$, $h_o = 1$ mm, and water as the working fluid. For a diode capillary with uniform wettability, $\theta = 90^{\circ}$. The inset shows a comparison of predictions of our mathematical model with the experimental results of Gorce *et al.* [6], wherein the radius $h_o = 330\ \mu$m, $L = 6$ mm, $\theta = 75^{\circ}$, and glycerol is used as the working fluid. Using an axial wettability gradient in a capillary diode reduces the time of liquid imbibition by more than 30% compared to a capillary diode with uniform wettability.

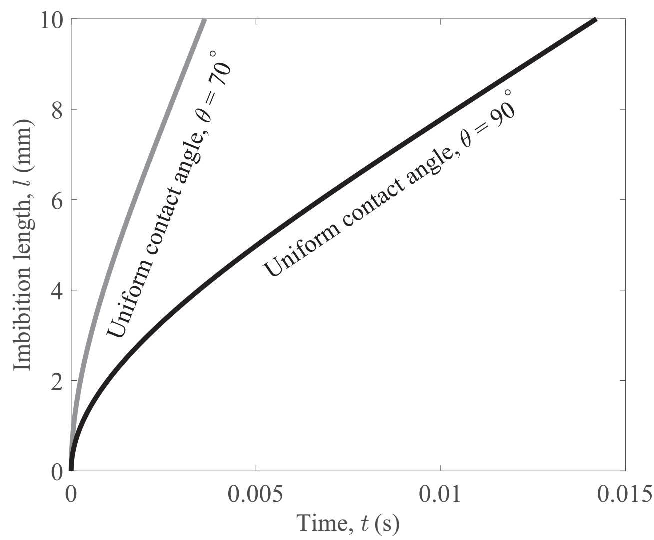

FIG. 5. Effect of the contact angle on liquid imbibition into converging capillaries with uniform wettability. These calculations have been performed for converging capillaries with $\phi = 5^{\circ}$ and water as the imbibing liquid. A converging capillary with $\theta = 90^{\circ}$ is a diode, as $\delta > 90^{\circ}$ for liquid entering from the narrow end. However, a converging capillary with $\theta = 70^{\circ}$ is not a diode, as $\delta < 90^{\circ}$ for liquid entering from the narrow end.

evident from the rapid rise (nonlinear) in the imbibition length in Fig. 4 at early times ($t < 0.0025$ s) when the contact angle is small ($\theta < 70$). Near the narrow end of the diode capillary, the change in imbibition length with time slows down due to the higher value of the contact angle. Consistent with previous studies [6], the imbibition length changes linearly with time for the majority of the length of the diode capillary with uniform wettability. Figure 5 shows a comparison of imbibition time for two converging capillaries with uniform wettabilities having contact angles $\theta = 90^{\circ}$ and $\theta = 70^{\circ}$. In Fig. 5, we note that out of the two converging capillaries, the capillary with $\theta = 90^{\circ}$ can act as a diode. This is because $\delta > 90^{\circ}$ only for liquid entering from the narrow end of the capillary with $\theta = 90^{\circ}$. The slope of the linear relationship between length and time depends on the solid-liquid contact angle; the larger the contact angle, the smaller is the slope, as shown in Fig. 5. Due to the high value of the contact angle ($\theta = 90^{\circ}$) in the case of a diode capillary with uniform wettability, its imbibition time is greater than a diode capillary with a wettability gradient. In other words, a converging capillary with a small value of the uniform contact angle has a lower imbibition time than the converging capillary with a wettability gradient. However, such a converging capillary would lose its functionality as a liquid diode as the effective imbibition angle δ for the liquid entering from the narrow side would be less than 90°.

V. CONCLUSION

In this Rapid Communication, we have theoretically shown that a capillary with an axially converging profile, in principle, can act as a liquid diode (capillary diode). We described the conditions under which an axially converging capillary works as a liquid diode. A capillary with a converging profile works as a liquid diode only when the imbibition angle of the fluid-liquid meniscus is less than 90° for the liquid entering from the broad end and higher than 90° for the liquid entering from the narrow end of the converging capillary. The imbibition angle is defined as the sum of the local contact angle and angle of slope of the capillary wall in the direction of liquid flow. Furthermore, we described a methodology to enhance the rate of liquid imbibition in the proposed capillary diode. Using a quasisteady one-dimensional mathematical model, we showed that creating an axial wettability gradient reduces the liquid imbibition time into a capillary diode compared to a capillary diode with uniform wettability. Our model predictions showed that axially increasing the contact angle from the broad end toward the narrow end of the diode capillary decreases the time of liquid imbibition by more than 30% compared to a capillary diode with uniform wettability. Here, we note that the linear wettability gradient scheme used in the present work is only for illustrating the effect of the wettability gradient on the enhancement of the liquid imbibition rate in the proposed liquid diode. To find the optimal geometry and wettability gradient that will give the smallest imbibition time into the liquid diode, we would need a formal optimization, which will be presented in future work.

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[1] J. M. Bell and F. Cameron, The flow of liquids through capillary spaces, J. Phys. Chem. **10**, 658 (1906).

[2] R. Lucas, Rate of capillary ascension of liquids, Kolloid Z **23**, 15 (1918).

[3] E. W. Washburn, The dynamics of capillary flow, Phys. Rev. **17**, 273 (1921).

[4] V. Krotov and A. I. Rusanov, *Physicochemical Hydrodynamics of Capillary Systems* (World Scientific, Singapore, 1999).

[5] K. Polzin and E. Y. Choueiri, A similarity parameter for capillary flows, J. Phys. D **36**, 3156 (2003).

[6] J.-B. Gorce, I. J. Hewitt, and D. Vella, Capillary imbibition into converging tubes: Beating Washburn's law and the optimal imbibition of liquids, Langmuir **32**, 1560 (2016).
[7] M. Reyssat, L. Courbin, E. Reyssat, and H. A. Stone, Imbibition in geometries with axial variations, J. Fluid Mech. **615**, 335 (2008).
[8] D. Erickson, D. Li, and C. Park, Numerical simulations of capillary-driven flows in nonuniform cross-sectional capillaries, J. Colloid Interface Sci. **250**, 422 (2002).
[9] S. Ashraf, G. Visavale, S. Bahga, and J. Phirani, Spontaneous imbibition in parallel layers of packed beads, Eur. Phys. J. E **40**, 39 (2017).
[10] W.-B. Young, Analysis of capillary flows in non-uniform cross-sectional capillaries, Colloids Surf., A **234**, 123 (2004).
[11] A. D. Price and D. K. Schwartz, Anchoring of a nematic liquid crystal on a wettability gradient, Langmuir **22**, 9753 (2006).
[12] S. Daniel, M. K. Chaudhury, and J. C. Chen, Fast drop movements resulting from the phase change on a gradient surface, Science **291**, 633 (2001).
[13] M. Singh, Capillarity enhancement of micro heat pipes using grooves with variable apex angle, Int. J. Therm. Sci. **150**, 106239 (2020).
[14] A. Olanrewaju, M. Beaugrand, M. Yafia, and D. Juncker, Capillary microfluidics in microchannels: From microfluidic networks to capillaric circuits, Lab Chip **18**, 2323 (2018).
[15] N.-T. Nguyen, S. A. M. Shaegh, N. Kashaninejad, and D.-T. Phan, Design, fabrication and characterization of drug delivery systems based on lab-on-a-chip technology, Adv. Drug Delivery Rev. **65**, 1403 (2013).
[16] G. Buchberger, A. Kogler, A. Weth, R. Baumgartner, P. Comanns, S. Bauer, and W. Baumgartner, "Fluidic diode" for passive unidirectional liquid transport bioinspired by the spermathecae of fleas, J. Bionic Eng. **15**, 42 (2018).
[17] J. Li, X. Zhou, J. Li, L. Che, J. Yao, G. McHale, M. K. Chaudhury, and Z. Wang, Topological liquid diode, Sci. Adv. **3**, eaao3530 (2017).