Topological liquid diode

Jiaqian Li,1* Xiaofeng Zhou,2* Jing Li,1 Lufeng Che,2 Jun Yao,3 Glen McHale,4 Manoj K. Chaudhury,5† Zuankai Wang1,6†

The last two decades have witnessed an explosion of interest in the field of droplet-based microfluidics for their multifarious applications. Despite rapid innovations in strategies to generate small-scale liquid transport on these devices, the speed of motion is usually slow, the transport distance is limited, and the flow direction is not well controlled because of unwanted pinning of contact lines by defects on the surface. We report a new method of microscopic liquid transport based on a unique topological structure. This method breaks the contact line pinning through efficient conversion of excess surface energy to kinetic energy at the advancing edge of the droplet while simultaneously arresting the reverse motion of the droplet via strong pinning. This results in a novel topological fluid diode that allows for a rapid, directional, and long-distance transport of virtually any kind of liquid without the need for an external energy input.

INTRODUCTION

Directed and spontaneous transport of a liquid on a solid surface is highly desired in various settings that range from microfluidics, printing, and oil-water separation to water harvesting technologies (1–8). Although this field of research has blossomed over the last two decades, the available technologies are far from what would be needed for controlling a desired fluidic process with a high degree of fidelity. The principal detriment to the generation of this type of fluidic motion arises from surface defects that pin the droplet edge, thus thwarting its motion. To combat the pinning forces, an external source of energy is generally needed that often mimics the rectification of the random motion of particles manifesting in various natural and man-made settings (9–15). Remarkably, many living organisms [such as the pitcher plant, cactus, and lizard (16–18)] perform the task of liquid transportation at a small scale with immaculate precision by taking advantage of surface topography alone. In recent years, extensive efforts have been directed toward mimicking these types of transport diversity that fundamentally resort to the breaking of wetting symmetry (7, 19–26). Despite commendable progress, it remains a daunting undertaking to mimic the structural and the functional sophistication inherent in living organisms in a facile and reproducible manner.

The inherent challenge in attaining a unidirectional and continuous liquid transport stems from the fact that one edge of the droplet needs to be activated, whereas its other edge needs to remain pinned. To meet this objective, we resort to the fundamental fact that pinning barriers can be mitigated by allowing droplets to coalesce with each other near a pinning boundary (5, 27, 28). By building upon this science and taking advantage of topographical complexities, we demonstrate here that a desired unidirectional motion of the liquid droplet can be achieved by leveraging the coalescence of a pinned droplet with a thin precursor film that spreads rapidly ahead of the edge. In turn, the same topographical complexity or structure leads to a simultaneous arrest of the reverse motion of the droplet via strong pinning. The design of this novel liquid diode shifts away from the conventional paradigm in which a continuous gradient of wettability is invariably used to generate droplet motion.

RESULTS

Figure 1A shows the scanning electron microscope (SEM) image of the as-designed liquid diode, consisting of U-shaped island arrays spatially confined in periodically patterned fences. The width of the U-shaped islands is designed to decrease gradually from the opening end to the other end; thus, two diverging side-channels are naturally formed within fences (Fig. 1B). Moreover, as shown in Fig. 1C, the inner side of the cavity in the U-shaped island is specially designed with a reentrant structure based on inspiration of previous studies (29–32) to direct the flow of the liquid. The width (d) and length (l) of the cavity, the total width and length of the island (D and L), and the spacing between individual islands can be varied. All surfaces are fabricated on a silicon wafer using standard microelectromechanical system (MEMS) processes (fig. S1 and table S1). A water droplet (~5 μl) deposited on the as-fabricated surface displays an asymmetric transport behavior. As shown in Fig. 1D and movie S1, there is a dominant propagation of the liquid in the lateral direction toward the opening of the U-shaped islands, denoted as the preferential direction. In the first few milliseconds, the droplet also spreads slightly in the direction opposite to the opening of cavities (denoted as the reverse direction), which, nevertheless, becomes rapidly pinned by the convexity of the U-shaped channel. Together, these two functions display the typical signature of a directed liquid transport, which is also manifested with any other liquid including ethanol, ethylene glycol, and alkanes (Fig. 1E) that meet the Concus-Finn corner flow conditions (33), in which the intrinsic contact angle (θ) and the half-angle (β) of the corner in the microchannel follow the inequality condition: θ < π/2 − β. After a sufficiently long time, the elongated droplet stops spreading. By denoting the spreading length of the droplet in the major spreading direction (Lp) relative to that in the pinning direction (Lp), a rectification coefficient (k) can be defined as Lp/Lp, that quantifies such diode-like behavior. For the as-fabricated liquid diode shown in Fig. 1, k is measured to be 5.76, which is larger than that of any surfaces reported previously (7, 16, 19–25).

In what follows, we demonstrate that the overall spreading dynamics of various liquids on such a surface results from discrete events. Discrete
flow in wetting has been previously reported. For example, Chaudhury and Chaudhury (34) reported an experiment about a decade ago, in which a drop of oil spreads fast through a linear array of small water droplets placed on a hydrophobic surface via repeated events of accumulation of oil under each drop, followed by its spreading to the next droplet. Although similar discrete wetting has also been observed with other systems (7, 20, 22), the crucial physics of how the spreading liquid overcomes the pinning barrier has not been discussed in the previous studies. On the basis of the observations reported below, we find that the unidirectional spreading results from the combination of events in which a precursor film spreading ahead of the bulk of the drop plays an important role. The bulk drop undergoes a hydraulic jump (35, 36) because its flow is arrested at the pinning edge, which subsequently coalesces with the precursor film, thus reinitiating its spreading until the next pinning edge is reached.

In Fig. 1E, we plot the time-dependent spreading length normalized by a characteristic geometric length \((\Omega/b)^{0.5}\) of the spreading droplet, where \(\Omega\) is the volume of the droplet and \(b\) is its lateral width. With a modest dynamic range of data spanning over three decades, two different spreading regimes can be clearly identified. Initially, the spreading length increases almost linearly with time, suggesting that the velocity of the droplet remains more or less constant, signifying a unique characteristic of the designed liquid diode. In the linear growth regime, the higher viscosity droplet spreads more slowly than a relatively inviscid droplet. Nondimensionalization of the experimental spreading time with an intrinsic visco-capillary time scale \(\tau = \mu b/\gamma\) brings the scattered data for various liquids quite close to each other (Fig. 1F), which encourages us to state that the scaling \(L_s/(\Omega/b)^{0.5} \sim t/\tau\) captures the essential physics of the unidirectional spreading behavior of the droplet during the initial stage. At the later stage, the spreading exhibits a logarithmically slowing-down kinetics as evidenced in the semi-log plot of \(1 - L_s/L_{\text{sm}}\) versus \(t/\tau\) (inset of Fig. 1F), where \(L_{\text{sm}}\) is the maximum spreading length. Such a weak temporal evolution of its spreading length departs from the classical slowing-down behavior (34), which is reminiscent of various processes in nature (37), such as the time evolution of frictional strength, compactification of grains, magnetization relaxation in spin glasses, conductance relaxations, and diffusion under a random force.

From various observations, including that of a slowly spreading silicone fluid on such a substrate structure, it is clear that a visually perceptible thin liquid film continues to spread ahead of the primary droplet (fig. S2). Figure 2A presents time-resolved wetting dynamics of the advancing precursor liquid in two periodic units of the structure that displays the diode-like effect (movie S2). Initially, the precursor liquid preferentially wets the straight sidewall of side-channels (0 to 400 ms). Upon contact with the sidewall of U-shaped islands (428 ms), it progresses spontaneously in the side-channels, with a spreading velocity 2.8-fold larger than that of the primary droplet (fig. S3). Subsequently, the reentrant cavities and asperities between two neighboring U-shaped islands become wetted, triggering a global propagation of liquid and characteristic of a domino effect.

What appears to be a precursor film is, in fact, a consequence of a Concus-Finn type corner flow (33) that is generic to two wettable surfaces producing a corner. In our diode structure, such a flow manifests in the
form of thin liquid threads with a smoothly varying curvature spreading along the side fences and then distributing to other available corners. The role of corner flow in dragging a liquid in a diverging channel can be easily demonstrated by placing a small droplet of water near the narrow gap of two slightly nonparallel glass slides, as shown in Fig. 2B (movie S3). Upon invading the diverging channel through the narrow gap, the water fills it up rather fast. However, as the liquid continues to spread along all the four corners of this structure, it is eventually depleted (see movie S3), illustrating that the pressure gradient in the liquid along the corners is stronger than the Laplace pressure gradient that is produced across the concave meniscus of the liquid joining the two walls of a diverging channel.

To elucidate how the corner flow in the precursor regulates the unusual unidirectional spreading behavior, we further analyze the local contact line dynamics of the primary droplet. We find that the advancing edge of the primary droplet does not move continuously. Instead, it stops for a brief period during which the precursor film continues to flow. When the bulk flow of the liquid drop is suddenly arrested, Bernoulli’s equation suggests that the conserved energy of the liquid has to be converted to another form of energy. This happens in our case with the liquid bulging up near the arrested edge (the semicircular edge, Fig. 2C and movie S4), thus creating more surface area and, consequently, more surface free energy. This bulging up leads to a hydraulic jump (35, 36) that results in an increase of the local contact angle. The pinned edge moves forward when the local contact angle increases above a certain critical value dictated by the intrinsic contact angle and the slope of pinning edge. As different segments of the pinned edge are successively depinned, a nearly straight frontal edge is formed, following which the entire liquid front jumps forward like an avalanche (Fig. 2D). Because the advancing edge relaxes from a semicircle of diameter ~b, the characteristic time scale of this process can be written as $\tau = \mu b^4/g$. For a droplet with a constant volume ($\Omega$) and a lateral spreading width b, the intrinsic length of spreading is $b/\Omega b^{0.5}$. Thus, the scaling for the spreading distance in the fast spreading regime becomes $L_c/\Omega b^{0.5} \sim t/\tau$, which is consistent with the results summarized in Fig. 1F. In closing, we believe that the hydraulic jump rendered by the corner flow provides a unique mechanism for the droplet to overcome the contact line pinning in the preferential flow direction.

Despite the corner flow and hydraulic jump, the backflow of the liquid droplet is strongly thwarted around the reentrant edge (29, 30), as evidenced by the SEM image of the contact line in Fig. 3A (figs. S4 and S5). As shown in Fig. 3B, the presence of unique reentrant structure gives rise to an upward capillary force to resist the liquid penetration into the cavity. Such a pinning is also assisted kinetically by the continual removal of liquid through the corner flow in the diverging channel, as the curvature of the liquid meniscus becomes progressively concave starting from the mouth of the diverging channel toward its tail. Collectively, these two effects nullify the possibility of the droplet relaxing from the pinned edge. However, for the surface without the presence of reentrant structure (inset of Fig. 3C), the advancing liquid in the pinning direction easily penetrates the cavity, and the pinning effect is broken down, as depicted by the continuous advancing edge shown in Fig. 3C (fig. S6). In summary, the spreading droplet can only flow in one, but not its reverse, direction.
The decoupling of the side-channels responsible for the corner flow from the reentrant cavities responsible for the pinning of backflow creates distinct hydrodynamic flow resistances (38) in the spreading and pinning directions (Fig. 3D and fig. S7). In the spreading direction, the fluid propagates along both side-channels and cavities. By contrast, in the reverse direction, the pathway is confined to side-channels alone owing to the reasons discussed above. When the droplet spreading comes to a complete halt, an interesting relation emerges, which connects the asymmetric spreading lengths to the hydraulic flow resistances in two directions. Such a unique relation arises from the fact that the rate of the decay of the droplet volume is exactly the same as that carried in two opposite directions. The flow in the precursor film is mainly driven by the negative pressure (outward by the precursor films in two opposite directions. The flow in the reverse direction relative to the asymmetric spreading lengths to the hydraulic flow resistances comes to a complete halt, an interesting relation emerges, which connects the asymmetric spreading lengths to the hydraulic flow resistances in two directions. Here, the $R'$ can be tailored by varying sizes in the cavity length or width. The red triangles indicate a series of surfaces with increasing cavity length ($l\parallel = \frac{1}{20}, \frac{1}{10}, \frac{1}{5}, \frac{1}{3}, \frac{1}{2}$ and $\frac{1}{3}$), as shown in table S2 and fig. S8A. The blue squares indicate a series of surfaces with increasing cavity width ($l\perp = \frac{1}{20}, \frac{1}{10}, \frac{1}{5}, \frac{1}{3}, \frac{1}{2}$ and $\frac{1}{3}$), but with constant length ($l\parallel = \frac{1}{3}$), as shown in table S3 and fig. S8B. (F) Comparison of the transport performances between different surfaces. The blue and green symbols indicate the spreading lengths normalized by the droplet radius at the spreading direction and pinning direction, respectively. The red symbol denotes the rectification coefficient ($k$) on different designs. The inset images present the optical image of spreading drops on the respective surfaces.

To ascertain how the preferential motion of droplet is mediated by structural topography, we also designed and fabricated control surfaces without the presence of a side-channel, cavity, or reentrant structure (Fig. 3F and table S1). The results show that the manifestation of a superior diode-like behavior demands the delicate control over the diverging channel, cavity, and reentrant structure. Briefly, with the obstruction of the side-channel or the cavity, both the spreading length of droplet and rectification coefficient are markedly reduced (Fig. 3F). For the control surface without the presence of side-channels (fig. S10A and table S1), the droplet displays an almost symmetric spreading with a
short spreading distance in all directions (fig. S11A). This result suggests that corner flow serves as an energetically favorable pathway to guide the lateral liquid flow. For the control surface in which the cavity is obstructed (fig. S10B and table S1), the droplet spreading is spatially confined in the lateral direction (fig. S11B). However, in this case, the rectification coefficient is the smallest (fig. 3F), suggesting that the cavity structure is essential to the rectification of directional flow. Moreover, without the presence of reentrant structure in the cavity (fig. S10C), the rectification coefficient is reduced by about 40% (fig. 3F and fig. S11C). Together, these results convincingly reveal that the exquisite integration of diverging side-channels (corner flow) and re-entrant in one structure (hydraulic jump and reentrant pinning) is indispensable for the directional and fast liquid transport.

**DISCUSSION**

To illustrate the advantages of our liquid diode, in Fig. 4A, we benchmark the unidirectional spreading velocity and the range of transport with reported surfaces (fig. S12). Surfaces with an imposed wetting gradient (19, 25, 39–44) are associated with a large motion velocity (green area in Fig. 4A) and a short spreading distance owing to the inherent tradeoff in satisfying these two exclusive parameters. On the other hand, asymmetrically structured surfaces (7, 16, 20–22, 45, 46) enable a long range of liquid self-transport, but with a small velocity (blue area in Fig. 4A). We also demonstrate that the intriguing liquid transport on the as-designed liquid diode is general. First, as shown in Fig. 4B, the liquid can be transported along various pathways (such as rings and circles) and can climb uphill without the use of gravity or other gradient (movies S5 and S6). Second, as shown in Fig. 4C, the unidirectional liquid transport is further enhanced when there is a gradual temperature gradient (fig. S13) along the spreading direction. When the temperature gradient is applied against the spreading direction, there is only a slight decrease in the rectification coefficient, suggesting the stability of the directional transport even when subject to an externally applied temperature field. Such a capability holds many potential applications, such as in heat pipes (47). Finally, the directional droplet transport applies to any liquid including low-surface tension liquid, such as hexane (~18.4 mN/m), and high-viscosity liquid, such as ethylene glycol (~16.06 mPa s) (Fig. 4D and table S4). However, the high-viscosity liquid (ethylene glycol) displays a counterintuitive behavior in which its rectification coefficient is higher than that of water.

The criterion of rectification as discussed above is based on uniform reduction in the thickness of the bulk of the liquid when spreading comes to a complete halt. With more viscous liquid, the rate of thinning of the liquid film in the bulk of the droplet should be spatially uneven, because another resistance corresponding to the horizontal internal flow of the liquid drop needs to be considered. Although a rigorous solution of this problem requires a full consideration of the so-called “thin-film” equation (36), we expect the bulk flow of the liquid to occur (internally) from the pinned direction to the spreading direction of the drop, such that $\frac{dh}{dt} > \frac{dR}{dt}$. Because the rectification coefficient would be of the form $k = \frac{R_p}{R_s} \frac{dR}{dh}$, we expect $k$ to increase for a viscous liquid in comparison to that of a more inviscid liquid (Fig. 4D).

Together, the ease of fabrication, generality, and intriguing transport performances of our liquid diode will open up new avenues to tailor advanced microstructures for self-propelled liquid manipulation in a variety of applications, including water harvesting, heat management, ink-jet printing, and emulsion separation.
MATERIALS AND METHODS

Sample fabrication

We used standard MEMS processes to fabricate the liquid diode based on silicon wafer [(100) type, 420 ± 5 μm thick]. To form side-channels, we first used the photolithography process to deposit a layer of photoresist as a protective mask, followed by anisotropic etching (~5 μm deep) using deep reactive ion etching (DRIE). Subsequently, plasma strip and wet cleaning were performed to remove the photoresist. To fabricate the cavities with reentrant structure, we used thermal oxidation to deposit a layer of SiO2 with a thickness of 1 μm on the silicon wafer, followed by photolithographic patterning and selective removal of the SiO2 layer using reactive ion etching. The silicon exposed at the cavity structure was isotropically etched (~5 μm deep) by DRIE or XeF2. After final wet cleaning treatment, the liquid diode with reentrant structure was formed.

To investigate the effect of surface topography on the liquid diode behavior, we also fabricated a series of surfaces with varying sizes of cavity structure and side-channels, as well as control surfaces without the design of cavity, reentrant, or side-channel. The control surface without the cavity structure was fabricated with the first three steps of the process described above. The procedure to fabricate the control surface without the reentrant structure is basically similar to that developed for the fabrication of the liquid diode with a reentrant feature, except that the Si was anisotropically etched to form the cavity with a straight sidewall. The control surface without side-channels was fabricated using the same procedure as developed for the liquid diode surface, except that the masks for photolithography in the first step were different. Compared to the liquid diode surface, the side-channel was blocked on the control surface without the design of side-channel. We also designed liquid diodes with spiral or circular pathways to demonstrate the generality of the directional transport. To fabricate the curved pathways, we divided the surfaces into a variety of parts, and each part was fabricated by the procedures developed for the liquid diode surface with the reentrant structure. Note that owing to the existence of defects between neighboring parts, the flow widened slightly during the directional liquid transport on the surface with spiral or circular pathways.

Surface treatment and contact angle measurement

We treated the as-fabricated surfaces and the flat silicon substrate with Plasma Cleaner PDC-32G (Harrick Plasma) at high radio frequency levels for ~90 s to obtain hydrophilic surfaces. To quantify how the intrinsic wettability affects the droplet spreading behavior, we measured the intrinsic contact angle on the flat surface using a contact angle goniometer (ramé-hart M200 Standard Contact Angle Goniometer). At room temperature with 50% relative humidity, a deionized water droplet of ~3 μl was deposited on the tested substrates at a volume rate of 1 μl/s. We also performed contact angle measurements every 10 min for a total of 1 hour to evaluate the variation of contact angle. The apparent contact angle on the flat wafer surface within an hour remained 14.7° ± 3.3°. These values are the average of five measurements.

Characterization of macroscopic transport behavior of liquid diode

We performed the unidirectional spreading experiment on the as-fabricated liquid diode and control surfaces at room temperature. The liquid droplet was generated with a stainless steel needle having an outer diameter of 0.5 mm, which was connected to a syringe pump. The spreading dynamics was recorded from the plan view by a high-speed camera (FASTCAM SA4, Photron). Next, to demonstrate the generality of the directional transport, we performed liquid transport experiments on the liquid diode surfaces with circular and spiral pathways in which the water was continuously infused on these surfaces. Finally, four other liquids were also used to demonstrate the generality of the directional liquid transport.

Characterization of microscopic transport behavior of liquid diode

To improve the visual clarity and the spatial resolution of water spreading on the liquid diode, we stained the deionized water (about 1 μl) with a blue dye. The spreading dynamics on the liquid diode was observed with an Olympus BX60 microscope connected to a high-speed camera. To examine the pinning dynamics on the liquid diode and the control surface without reentrant structure, we used a long working distance microscope equipped with a high-speed camera.

Technically, it is extremely challenging to capture the pinning profiles induced by the reentrant structure because the deionized water easily evaporates in the vacuum chamber of a SEM. To overcome this issue, we used uncured polydimethylsiloxane (PDMS) to replace water. We first deposited PDMS liquid on the liquid diode surface and then immediately heated it at 100°C for ~40 min. After a layer of silver was plated on the tested surfaces by a sputtering machine, we characterized the pinning morphology under a SEM. Likewise, we used this method to characterize the collapse of pinning effect on the control surface without the presence of reentrant structure.

Effect of temperature gradient on the directional transport

To examine the stability of directional, spontaneous transport manifested by the liquid diode, we imposed an additional temperature gradient. Briefly, one end of the liquid diode surface was fixed onto a heater, and the other end was exposed to air. The distribution of temperature was measured using an infrared camera with a 13-mm lens. Simultaneously, the spreading dynamics of the liquid was recorded with a high-speed camera.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/10/eaa03530/DC1

section S1. Characterization of microscopic spreading behavior of the precursor on liquid diodes
section S2. Comparison of liquid pinning behavior on liquid diode and control surfaces
section S3. Flow hydraulic resistance analysis
section S4. Characterization of macroscopic spreading dynamics on control surfaces
section S5. Comparison of liquid self-transportation on various surfaces
section S6. Temperature gradient effect on the liquid diode
fig. S1. Sample fabrication.
fig. S2. Characterization of precursor film and water droplet spreading velocity.
fig. S3. Selected snapshots showing the microscopic wetting dynamics on the liquid diode.
fig. S4. Representative SEM images showing the liquid pinning rendered by the reentrant structure.
fig. S5. Selected snapshots showing the pinning dynamics of water on the liquid diode.
fig. S6. Selected snapshots showing the breakdown of pinning on the control surface without the presence of a reentrant feature.
fig. S7. Schematic diagrams showing the flow pathways on the control surface without the presence of a cavity.
fig. S8. Effects of structural topography on the flow resistance parameter R’.
fig. S9. Effects of structural topography on the rectification coefficient k.
fig. S10. SEM characterization of control surfaces.
fig. S11. Spreading dynamics on the control surfaces.
fig. S12. Comparison of transport performances among different surfaces.

table S1. Structural parameters of the liquid diode and control surfaces.
REFERENCES AND NOTES


Acknowledgments
Funding: Z.W. is grateful for financial support from the National Natural Science Foundation of China (grant no. 51475401), Research Grants Council of Hong Kong (grant nos. 11275215 and 11231915), and City University of Hong Kong (grant nos. 9360410 and 9967139). X.Z. is grateful for financial support from the National Natural Science Foundation of China (grant no.41034014). M.K.C. thanks M. M. Weisgel for a pedagogical discussion on corner flow.

Author contributions: Z.W. supervised the research. Jiaqian Li, X.Z., and Jing Li designed the experiment. X.Z. and L.C. fabricated the device. M.K.C., G.M., and J.Y. analyzed the data.

Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 11 July 2017
Accepted 28 September 2017

Published 27 October 2017

10.1126/sciadv.aao3530

Topological liquid diode
Jiaqian Li, Xiaofeng Zhou, Jing Li, Lufeng Che, Jun Yao, Glen McHale, Manoj K. Chaudhury and Zuankai Wang

Sci Adv 3 (10), eaao3530.
DOI: 10.1126/sciadv.aao3530

ARTICLE TOOLS  http://advances.sciencemag.org/content/3/10/eaao3530

SUPPLEMENTARY MATERIALS  http://advances.sciencemag.org/content/suppl/2017/10/23/3.10.eaao3530.DC1

REFERENCES  This article cites 47 articles, 9 of which you can access for free  http://advances.sciencemag.org/content/3/10/eaao3530#BIBL

PERMISSIONS  http://www.sciencemag.org/help/reprints-and-permissions

Use of this article is subject to the Terms of Service