ABSTRACT: Droplet motion arises in many natural phenomena, ranging from the familiar gravity-driven slip and arrest of raindrops on windows to the directed transport of droplets for water harvesting by plants and animals under dry conditions. Deliberate transportation and manipulation of droplets are also important in many technological applications, including droplet-based microfluidic chemical reactors and for thermal management. Droplet motion usually requires gradients of surface energy or temperature or external vibration to overcome contact angle hysteresis. Here, we report a new phenomenon in which a drying droplet placed on a periodically compliant surface undergoes spontaneous, erratic motion in the absence of surface energy gradients and external stimuli such as vibration. By modeling the droplet as a mass-spring system on a substrate with periodically varying compliance, we show that the stability of equilibrium depends on the size of the droplet. Specifically, if the center of mass of the drop lies at a stable equilibrium point of the system, it will stay there until evaporation reduces its size and this fixed point becomes unstable; with any small perturbation, the droplet then moves to one of its neighboring fixed points.

INTRODUCTION

Spontaneous droplet motion is of great importance in a variety of industrial applications such as the design and fabrication of microfluidic devices and superhydrophobic coatings. Typically, droplet motion is induced using a surface with gradients in curvature, in droplet apparent contact angle, or by external stimuli. By external stimuli, we mean a gradient provided by the substrate or an external source of vibration. Spatial gradients in apparent contact angle can be induced by variation in thermal, chemical, electrical, and elastic properties of the surface. Continuous transportation of a droplet requires a continuous input of free energy, such as by vibration; it can also be provided by evaporation of the droplet itself. For example, by controlling the direction of vapor flow, a droplet placed on a hot ratchet can propel itself in a specified direction. Evaporation can also cause pinning and unpinning of a contact line on a structured surface and thus generate droplet motion. More recently, Cira et al. have demonstrated that two-component droplets of well-chosen miscible liquids on a clean glass slide can move and interact with each other by emitting vapor.

Here, we report a new phenomenon in which a water droplet moves spontaneously on a surface with periodic variation in compliance. The motion is spontaneous in the sense that it requires no surface energy gradient or external stimuli. Specifically, we fabricated an elastomeric substrate with periodic variation of surface compliance. We found that a small droplet placed on such a substrate undergoes random motion over significantly larger than the drop size and the spatial period over which compliance varies. This phenomenon is surprising because it is unclear what drives it; there is no long-range gradient in surface energy or in surface compliance. In particular, this phenomenon is quite different from that reported by Style et al., where droplet motion is driven by a long-range gradient in substrate stiffness. If the motion
observed in our system were driven by a stiffness gradient, the droplet would be trapped at a position of minimum substrate stiffness and would not be able to move a distance of more than one period of compliance variation. This indicates an agent other than substrate stiffness alone drives droplet motion. What makes the phenomenon even more counterintuitive is that increasing surface compliance and surface undulations both usually lead to an increase in contact angle hysteresis compared to that of a flat unstructured control surface. Therefore, compared to a flat unstructured control on which drops show no long-range motion, a structured surface with a periodic variation in compliance should make droplet motion less likely, not more. However, we observe the reverse.

**EXPERIMENTAL PROCEDURE**

Panels a–d in Figure 1 show a series of still images from a top-view video of the phenomenon: a droplet of deionized water moves spontaneously on a compliant surface whose stiffness varies periodically in both directions. Before analyzing the details and cause of the motion, let us clarify the experimental setup. A typical micrograph of the type of structure used in our studies, and a schematic of the cross-section with a droplet on top, are shown in Figure 1e and f, respectively. The structure comprises a thin poly(dimethylsiloxane) (PDMS) film (thickness $t \approx 10$ μm) bonded to a periodic square array of fibrils with center-to-center spacing $a$. The fibrils are circular pillars 10 μm in diameter. The architecture of this surface was inspired by the surface of contact surfaces in many insects and small animals that have arrays of fibrils to make contact for enhanced and modulated adhesion and friction.[6,7] Naturally, the specimen surface is stiffer if probed directly above a fibril and relatively compliant if probed between fibrils. Therefore, the surface compliance of this structure varies periodically with a period equal to interbrillar spacing.

The sample preparation method is similar to the process described in Glassmaker et al.[6] Briefly, using standard photolithography and deep reactive ion etch techniques, arrays of circular holes of diameter 10 μm are formed on silicon wafers. Next, the etched master silicon wafers are coated by a hydrophobic self-assembled monolayer so that liquid PDMS (Sylgard 184; Dow Corning; 10:1 mass ratio of elastomer base to curing agent) is cast into the master silicon wafer. A clean glass slide is used to confine the material and is separated from the master by 0.635 mm using a clean spacer to form the backing layer. The liquid PDMS is cured at 80 °C for 1 h and manually removed from the master. The resulting PDMS array with backing layer is then placed on a thin liquid PDMS film spin-coated on a glass slide. The entire structure is cured at 80 °C for 1 h and then peeled off from the glass slide. In our experiment, the height $h$ of the fibrils is set to be 10, 20, 30, or 40 μm, and the center-to-center spacing $a$ between the fibrils is 20, 35, 50, 65, 80, 95, or 110 μm. Figure 1f shows a schematic of this structure.

A single deionized water droplet of volume 0.1 μL was placed on the film. The volume of the droplet was controlled by an air displacement pipet. The sample together with the droplet was then placed under a white light interferometer (Zegage; Zygo Corporation) for observation.

**RESULTS AND DISCUSSION**

Initially, the droplet has the shape of a spherical cap, and the contact line between the droplet and the film is roughly circular (Figure 1g) with small undulations near the fibrils. Typical snapshots of the deformed and moving droplet are shown in Figure 1a–d. The droplet gradually becomes smaller as it evaporates, and the contact line becomes irregular. As evaporation continues, the droplet starts to move spontaneously, as shown in Movie SM1. The motion of the droplet is relatively slow at first, but then picks up speed as it becomes smaller with further evaporation; it eventually slows down and stops, usually when the size of the droplet becomes smaller than the spacing between fibrils. The surface tension and Laplace pressure of the droplet can induce significant deformation of the substrate (see Figure 1g). As expected, deformation is smaller at or near the fibrils, where the compliance is lowest. This variation of spatial deformation leads to local variation of the apparent contact angle along the contact line.[9]

As the Movie SM1 indicates, droplet motion has the appearance of a random walk. To test if the motion is truly

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**Figure 1.** Droplet on a film-terminated fibrillar surface. (a–d) Beginning at $t = t_p$ micrographs of a droplet of deionized water placed atop a film-terminated fibrillar surface show (i) significant distortion of interferometric contours, indicating out-of-plane deformation driven by liquid surface tension, and (ii) spontaneous movement of the droplet. In this series of optical micrographs, the droplet moves over a distance much larger than its own size and the interbrillar distance. (e) Scanning electron micrograph image of the film-terminated fibrillar surface. The fibril height is 40 μm; the interbrillar spacing is 115 μm, and the diameter of the fibrils is 10 μm. (f) Schematic showing a droplet on the structured surface and the deformation caused by droplet surface tension. The experiments are repeated on samples with height $h$ varied from 10–40 μm and interbrillar spacing $a$ varied from 20 to 110 μm. (g) Contours and 3D representation of the vertical displacement of the substrate caused by surface tension of the drop.
random, or if there is some unknown gradient on the surface driving the motion, we repeated the experiment several times using a new droplet deposited on the same sample and recorded the motion of the droplet. (A Matlab program was used to detect the droplet contact line and to compute the centroid of its contact area for every frame of the video.) Trajectories of the centroid for different drops placed on the same substrate are shown in Figure 2a. In Figure 2a, the different colors correspond to different trials. The size of the markers (circles centered at the droplet’s centroid) are proportional to the contact area between the drop and the substrate. The time between two consecutive markers is 3 s. For a specific region of the sample, the experiments could only be repeated approximately 3–7 times, after which new droplets lost their ability to move. This is likely because of the deposition of some impurities during droplet drying, which increases the contact angle hysteresis.

From both Figure 2a and Movie SM1, we see that the motion of the drop is quite substantial and that the distance it travels is typically much larger than the interfibrillar spacing $a$. From the recorded trajectories, the drop motion appears random and very sensitive to the initial conditions. For example, the black and red paths in Figure 2a start at almost the same location, but the trajectories are completely different. In several instances, for example the case illustrated by the purple and cyan paths, the droplets follow similar paths at the beginning but later on deviate from each other. These observations rule out a hidden gradient driving the process and suggest that the dynamics of droplet motion may be sensitive to the initial conditions and small perturbations along the way. Large droplets move slowly or not at all; their sluggishness is probably because of inertia or contact angle hysteresis. As a drop evaporates and becomes smaller, the speed of its motion increases. When the size of a droplet becomes smaller than the interfibrillar spacing $a$, drop motion slows and eventually stops and dries.

Movie SM1 and the velocity data in Figure 2b show that the motion of droplets can be jerky. Figure 2b indicates that most of the time the drop moves slowly and continuously but suddenly speeds up and darts across the surface at certain locations, as indicated by the spikes in Figure 2b. Similar trends are observed for samples with different fibril spacings and heights, as shown in the Supporting Information.

To support the notion that evaporation is needed for droplet motion, we repeated our experiment (a) with water in a vapor-saturated environment where droplet shrinkage is prevented and (b) using a liquid (DMSO, dimethyl sulfoxide) that does not dry over the time-scale of the experiment. (Details are provided in the Supporting Information.). No drying was observed nor was there any drop motion.

**Model for Droplet Motion.** The erratic motion observed in our experiments rules out the possibility that an overall gradient drives the droplet motion. Furthermore, compared with a flat surface, the structured surface should make contact angle hysteresis larger. Thus, what provides the force to overcome the hysteresis and induce the motion? A clue comes from Figure 1g, in which the film deformation caused by surface tension can be as large as 4 μm (consistent with a simple calculation given in the Supporting Information). Such large deformation can reduce the apparent contact angle $\theta$ from its equilibrium value on a rigid substrate, $\theta_c$ (a material constant). This is illustrated in Figure 3 for a particular position of the droplet. When the contact line sits right on top of a fibril ($A, x = x_c$), the local substrate stiffness is much higher and the apparent contact angle is approximately equal to $\theta_c$. On the other hand,
at B, the contact line lies on the compliant film and the apparent contact angle is smaller than \( \theta_c \). As reported by Chaudhury et al., the difference between contact angles on two sides of a drop, say \( \theta < \theta_c \) on one side and \( \theta = \theta_c \) on the other as in the example drawn in Figure 3, will give an unbalanced force, which drives the motion of the drop. In our system, this force is periodic and depends on the shape of the contact line as well as the position of the drop on the periodic structure.

In our experiments, the contact line of the droplet is irregular; parts of it lie on fibris and the rest are on the compliant film. The elastic deformation of the film is coupled to the dynamics of motion. Furthermore, the amount of hysteresis depends on the position of the contact line, which can be very sensitive to surface impurities. Because of all these complications, it is extremely difficult to develop a comprehensive quantitative model to compare directly against the experiment. Instead, in the following, we present a simple one-dimensional model that captures some of the key features of this system, namely, the periodic driving force and shrinking volume of the droplet. We use it to show that the combination of shrinking size due to drying and periodic variation in surface compliance sets up spontaneous motion of the drop with dynamics of droplet motion that can be extremely sensitive to its shape, size, and position.

Consider a 2D droplet (a droplet that is infinitely long in the out-of-plane direction) on a one-dimensional periodic structure consisting of a thin film on top of identical parallel ridges with center-to-center spacing \( a \). The geometry of the cross-section of the sample is the same as drawn schematically in Figure 3. The droplet is constrained to move along the \( x \)-axis, which is perpendicular to the ridges. Because there is only a weak dependence of PDMS’s moduli on temperature, we neglect the variation of stiffness due to temperature change caused by evaporation. We choose the origin \( x = 0 \) to be midway between two ridges, where the film is most compliant. At time \( t \), the coordinates of the contact lines are \( x_L(t) \) and \( x_R(t) \), respectively. The size of the droplet is \( l(t) \equiv x_R(t) - x_L(t) \), which decreases linearly according to (see Supporting Information)

\[
l(t) = l_0(1 - \beta t)
\]

where \( l_0 \) is the initial size and \( \beta \) is an evaporation rate. As argued above, the net driving force for droplet motion is given by the difference in the horizontal component of liquid vapor surface tension \( \gamma_{LV} \) at the two ends of the droplet. We take the configuration \( \theta = \theta_c \) as a reference and define a local force \( F \) on each of the two contact lines such that the difference between the forces, thus defined, is the net driving force. Periodicity of the structure implies that the variation of \( F \) has the same period, \( a \). Specifically, when the contact line is on top of a ridge, that is, when \( x = (2n + 1)a/2 \), where \( n \) is an integer, \( \theta = \theta_c \) and \( F \) is at its minimum. When the contact line lies between two ridges, \( x \approx na \), \( \theta \) is at its minimum \( \theta_{min} \) and \( F \) reaches its maximum. Because \( \theta_{min} \) is, by definition, the apparent contact angle at a specific location, it is a constant for a given structure. However, it is important to note that \( \theta_{min} \) depends on the elasticity of the substrate and the thickness of the film. As an estimate of the value of \( \theta_c \) we measured the receding contact angle on an unstructured PDMS substrate to be approximately 94°. On the basis of experimental measurements of film deformation (Figure 1), the value of \( \theta_{min} \) is estimated to be approximately 5–10° lower than \( \theta_c \). As the contact line moves, the contact angle varies between these bounds. In our 2D model, we assume \( F \) varies sinusoidally between these two limits, that is

\[
F(x) = \frac{1}{2} \gamma_{LV} \left( \cos \theta_{min} - \cos \theta \right) (1 + \cos(2\pi x/a)) + \gamma_{LV} \cos \theta
\]

(2)

where \( \gamma_{LV} \) is the surface energy of the liquid/air interface. Because the net horizontal force acting on the droplet is \( F(x_L) - F(x_R) \), the center of mass \( x_{cm} = (x_L + x_R)/2 \) moves according to

\[
\frac{dx_{cm}}{dt} = F(x_L) - F(x_R) = \Delta F
\]

(3)

The left-hand side in eq 3 models damping, including contributions from fluid viscosity and substrate viscoelasticity. We also assume that the droplet is relatively stiff so it is effectively shrinking rigidly in size. With these approximations, eqs 1–3 can be combined into one equation (we also assume that drop motion is slow enough that one may ignore inertia, see Supporting Information for details)

\[
\dot{\epsilon} \frac{dX_{cm}}{dL} = \sin(L/2) \sin X_{cm}
\]

(4)

where \( \epsilon = \frac{\rho k}{\gamma_{LV}(\cos \theta_{min} - \cos \theta)} \) is a dimensionless parameter and \( X_{cm} = \pi(x_L + x_R)/a \) and \( L = 2\pi/a \) are the normalized center-of-mass coordinate and length of the droplet, respectively. The dimensionless parameter \( \epsilon \) represents a ratio of characteristic relaxation \( \frac{\mu L}{\gamma_{LV}(\cos \theta_{min} - \cos \theta)} \) and drying \((1/\beta) \) times. For small
values of this parameter, drying is slower than relaxation, and the droplet center of mass is predicted to move jerkily. For large values of this parameter, drying is faster, motion is less jerky, and eventually the drop dries too fast for it to move much. Furthermore, because L is monotonically related to t via eq 1, it can play the role of a new time variable, as it does in eq 4, though it is important to keep in mind that L shrinks as t grows; hence, L plays the role of a backward time variable. Note that for \( X_{\text{in}} = n\pi, \frac{dX_{\text{in}}}{dt} = 0 \), and these are therefore fixed or equilibrium points. Furthermore, notice that as \( L \) decreases monotonically in time, the time-dependent coefficient \( \sin(L/2) \) in eq 4 oscillates periodically from positive to negative values. This has the effect of alternately stabilizing or destabilizing any given fixed point. For example, the fixed point at \( X_{\text{in}} = 0 \) (mod \( 2\pi \)) is stable when the coefficient \( \sin(L/2) > 0 \) and unstable when \( \sin(L/2) < 0 \).

Defining \( \Omega = \{0, 2\pi\} \cup \{4\pi, 6\pi\} \cup \{8\pi, 10\pi\} \cup \cdots \), \( \Omega^c = \{(2\pi, 4\pi) \cup \{(6\pi, 8\pi) \cup \{(10\pi, 12\pi) \cup \cdots \), the stability of a general fixed point as \( X_p = N\pi, n \in \mathbb{Z} \) can be summarized as

\[
X_p = 2k\pi \left\{ \begin{array}{ll}
\text{stable if } L \in \Omega & (5a) \\
\text{unstable if } L \in \Omega^c & 
\end{array} \right.
\]

\[
X_p = 2k\pi + \pi \left\{ \begin{array}{ll}
\text{stable if } L \in \Omega^c & (5b) \\
\text{unstable if } L \in \Omega & 
\end{array} \right.
\]

where \( k \) is any integer. If the center of mass of the drop lies at a stable fixed point, it will stay there until evaporation reduces its size by \( a \) so this fixed point becomes unstable, and any perturbation will cause the droplet to move to one of its neighboring fixed points. At which of the neighboring fixed points the droplet eventually ends up is sensitive to the slightest perturbation of the environment. Figure 4a plots the slope field of eq 4 for \( \varepsilon = 0.1 \), which indicates the direction of motion once the droplet is perturbed from the fixed points. Typical droplet motion predicted using this model with \( \varepsilon = 0.1 \) is recorded as a video in Movie SM2.

Another way to visualize the dynamics is to note that the right-hand side of eq 4 can be interpreted as the force due to the potential, \( \sin(L/2)\cos X_{\text{in}} \), which depends on both the normalized droplet size and its position. Figure 4b shows the periodic energy landscape. Regions of high or low potential energies are labeled red or blue, respectively. As a drop shrinks, it will move toward regions of lower potential. In our one-dimensional system, this means that it can move to the right or left. Note that this simple one-dimensional model would predict a “stick and go” motion, whereas in the experiment the droplet motion is usually smoother even though some sudden fast motion can be observed (see Figure 2b). This can be partly attributed to the three-dimensional nature of the droplet where it can be stuck in one direction but ready to go in another direction.

### SUMMARY AND CONCLUSIONS

We report spontaneous random motion of water droplets on a periodic film-terminated fibrillar structure by a novel mechanism that operates with no external stimulus or long-range gradient. A droplet placed on such a substrate gradually becomes smaller due to evaporation. When the size of the droplet becomes small enough, it overcomes inertia and moves spontaneously and erratically. A droplet can move a considerable distance before it finally halts and vanishes by evaporation. This motion is counterintuitive for a number of reasons. First, it occurs in the absence of any overall gradients or external excitation, which often drive droplet motion. Second, surface undulation and compliance usually increase contact angle hysteresis and hence might be expected to work against drop motion. However, these are the very features that are necessary here for drop motion.

In our model, the position of the contact line depends on the size of droplet as well as the position of its center of mass. Droplet motion is caused by an imbalance of forces acting on the contact lines on either side of the droplet. These forces are determined by the liquid surface tension, surface properties of the substrate (such as surface energies and stresses), and local elastic deformation. The imbalance arises because of the periodic variation in substrate compliance, which manifests as a periodic variation of apparent contact angle. The direct role of evaporation is to reduce the droplet size, driving the system toward an instability that results in droplet motion. The role of evaporation is to provide a means to change the size of the droplet.

Many of the key features in our experiments, such as spontaneous motion and sensitivity to initial conditions, can be explained using a simple one-dimensional lattice model in which a 2D evaporating droplet is subjected to an unbalanced (sinusoidal) force with period equal to the spacing between fibrils. The source of this force is the difference in apparent contact angles on the two sides of the drop due to differences in deformability. The motion is damped by a viscous force that is much greater than the inertial force. This simple model explains the observed spontaneous and erratic motion.

There are obvious limitations in our 2D model. For example, the contact line can only occupy two points and hence the drop can only move left or right, whereas in reality, the contact line is irregular, and both it and the droplet itself can move in different directions. For the irregularity of the contact line to be captured, a 3-D model has to be established, which will be pursued in the future. Our model also does not account for the effect of fluid dynamics, which can alter contact angles and instantaneous driving forces. We believe that these two forgoing effects can account for the fact that, in experiments, the drop tends not to completely reverse direction. Furthermore, our analysis neglects contact line hysteresis, which is an important damping mechanism. It also imposes the constraint that maximum apparent contact angle change due to substrate deformation must exceed the contact angle hysteresis for motion to occur. However, we believe that our model answers the basic question of why motion occurs in the first place in terms of the stability of fixed points, but because of these simplifications, it cannot be used to quantify observations.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b01414.

Droplet spontaneously and erratically moving on our periodic structure (AVI)

Droplet behaviors predicted by our 1-D model (AVI)

Detailed model setup and simplification process for our 1-D droplet motion model and supplementary experiments performed to support our model (PDF)
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The contributions of T.L., N.N., Z.H., C.-Y.H., and A.J. were supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under award DEFG02-07ER46463. The research of S.H.S. was supported in part by NSF grants DMS-1513179 and CCF-1522054.

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