Spontaneous spin-sliding of volatile drops on swelling sheets

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When a volatile solvent droplet is deposited on a freely floating swellable sheet, it can spontaneously become lobed, asymmetric, and either spin, slide or move via a combination of the two. This process of symmetry-breaking is a consequence of the solvent droplet swelling the membrane and its inhomogeneous evaporation from the membrane, coupled with the hydrodynamics within the droplet. By tuning the membrane thickness and the droplet size, we find a critical threshold that determines the transition from a quiescent spherical cap state to a self-piloted motile state. Simple scaling laws determine the angular and linear velocities of the droplets, and a 1D analog experiment confirms the relative roles of evaporation, swelling and viscoelastic dissipation.

Generating and controlling autonomous motion in physical systems has been a subject of long standing interest both in science and technology. Liquid drops are particularly suited for this, given both their ease of manipulability and a range of applications. Here we report observations of the spontaneous symmetry breaking driven autonomous motion of a volatile solvent droplet on a freely floating permeable sheet. The motion of the droplet is generated by a combination of inhomogeneous evaporation and swelling of the membrane that lead to the formation of asymmetric lobes that spin or translate spontaneously.

Our starting point is a volatile liquid droplet of acetone (volume ranging from 1–40 µl) placed on a thin permeable membrane (thickness \( H \sim 10–50 \mu m \)), of polydimethylsiloxane (PDMS, Sylgard 184, 10:1) floating on aqueous glycerol (Fig. 1(a)) at ambient conditions. The liquid initially forms a spherical cap on the film (Fig. 1(a)). Within fraction of seconds, the droplet spontaneously breaks symmetry, becomes lobed, the lobes subsequently chiralize, and the drop starts to spin (Fig. 1(b) and SI, Movie 1). The number of lobes is a function of the drop size for a given film thickness; bigger drops have more lobes (Fig. 1(c) and SI, Movie 1). While there is no preferred chirality, once chosen, the drop continues to spin in the same direction as it evaporates and eventually stops. Sufficiently large drops do not spin, and instead become polarized in the form of a keratocyte shape and oscillate back and forth in a manner reminiscent of cell crawling (Fig. 1(d) and SI, Movie 2) or show directional migration on films (SI, Movie 3).

If we replace acetone by other volatile liquids such as isopropanol and butanol, we see similar phenomena as for acetone for the film thicknesses explored here (\( H \sim 10–50 \mu m \)). However, methanol droplets deposited on the same membranes remain stationary while adopting a spherical cap shape, and hexane droplets cause the film to wrinkle but again with no accompanying motion (SI). This suggests that there is a sweet spot in volatility, swelling and film thickness that is conducive to spontaneous symmetry breaking and motion, leading to a phase diagram for their occurrence shown in Fig. 1(e) obtained by varying the film thickness and the evaporation rate based on solvent vapor pressure (scaled by a poroelastic relaxation rate). Based on prior studies to quantify affinity between solvents and PDMS, methanol is a non-solvent (degree of swelling, \( S \sim 6\% \)); acetone, isopropanol and butanol are classified as poor solvents (\( S \sim 20\%–30\% \)), and hexane is a good solvent (\( S \sim 80\% \)) for PDMS. When the solvent swells the film, it diffuses through the elastic network at a rate \( kE/\eta R^2 \), where \( k \) is the permeability of PDMS, \( E \) is its Young’s modulus, \( \eta \) is the dynamic viscosity of the solvent and \( R \) is the lateral length across which solvent migrates. The imbibed solvent leaves the film via an evaporation rate of \( J/H \), where \( J \) is the evaporative flux. The relative importance of the two rates can be quantified in terms of the Péclet number \( Pe \sim \eta JR^2/kEH \). Infrared imaging of the drops undergoing spinning gives a direct estimate of \( R \sim 2a \) (SI, Movie 4), where \( a \) is the contact radius of the droplet. By independently measuring the evaporative flux of acetone from fully soaked pieces of PDMS membranes (area \( \sim 1 \text{ cm}^2 \)), we estimate \( J \sim 5.4 \times 10^{-7} \text{ m/s} \). By substituting the parameters of \( \eta \sim 3 \times 10^{-4} \text{ Pa·s}, k \sim 3.3 \times 10^{-18} \text{ m}^2, E \sim 2 \text{ MPa} \), we find the Péclet number for acetone in the PDMS membranes to be \( O(10) \), for which we see the lobe formation. Similar estimates for other solvents (SI) show that butanol and isopropanol form lobes when \( Pe \sim O(10) \) whereas droplets of methanol (\( Pe < O(10) \)) and hexane (\( Pe > O(10) \)) do not show the instability. Additionally, in environments of saturated acetone vapors, we do not observe drop rotation. However, motion resumes when vapor pressure of acetone is decreased back to ambient conditions, suggesting that the phenomenon of spinning and lobe formation of the droplets on PDMS films is possible for \( Pe \sim O(10) \) when there is a balance between evaporation, swelling and hydrodynamics.

To explain our observations, we first describe how an initially axisymmetric solvent drop breaks symmetry to form lobes. Solvent imbibition in the vicinity of the drop causes the thin film (\( H \sim \text{tens of microns} \)) to swell and sag down in the form of a ‘crater’ that houses the drop, as depicted by shadows due to gradients in the slope of the film. When the drops are larger on the PDMS films, the excess area of the swollen film undulates due to buckling,
spontaneously, but evaporation condensation processes tend to stabilize the droplet boundary [16]. Moreover, since the droplets are composed of one solvent only, we do not expect any compositional Marangoni forces to arise. Differential evaporation rates can also lead to temperature driven surface tension gradient that in turn could give rise to liquid transport within the drop. However, the infrared movies (SI, Movies 4,5) show that the temperature differences across a single lobe of the droplet are a few degrees C, which implies a surface tension difference of less than 1 mN/m [17]. Estimating the velocity of the regions of putative higher surface tension due to temperature driven Marangoni effects [18] [19], would imply the lobe tips to keep growing at around 0.1 m/s, which we never see, showing that the lobed shape of the drop is stable against Marangoni effects.

For a given liquid, e.g. acetone, the phase space of possible lobe numbers, i.e. the shape of the contact line of the droplet, is thus determined by its volume and the PDMS film thickness. On film thicknesses $H < 20 \mu m$, acetone droplets ($V \sim 3-40 \mu L$) form $n$-lobed chiral shapes that spin spontaneously (Fig. 2a). On thicker films ($H > 40 \mu m$), small and large drops form spherical caps that stay pinned. The shape of the lobed drops can be quantified using a simple polar representation [20] with coordinates $(r(s), \theta(s))$ in the domain $s \in [-\pi, \pi]$, where $r(s) = a(1 + b \cos(ns))$ and $\theta(s) = s + \frac{a}{n} \cos(ns + \tau) + \phi$. Here, $a$ represents the overall radius of the drop, $b$ represents the non-dimensional amplitude of the lobes, $c$ defines the asymmetry of the lobes, $\tau$ accounts for the local phase shift at the lobes and $\phi$ accounts for the global phase shift (Fig. 2b inset; SI). The shape of the droplets in either regime of lobe formation are similar to those of cell fragments and primitive cells [11] [21] [22] - this is not an accident, since the first few unstable modes of active drops always take the same forms.

The symmetry-breaking of the droplet-film system can be parameterized in terms of the elastocapillary number $a/\ell$, a dimensionless parameter given by the ratio of drop size $a$ to the elastocapillary length $\ell = \sqrt{EH^3/T}$, where $T$ is the tension in the film ($T \sim EH\ell$). The vertical component of surface tension of the droplet ($\gamma_{tv} \sin \theta_v$) can deform the thin film at the contact line due to a strain $\epsilon \sim \gamma_{tv} \sin \theta_v / EH$, where $\gamma_{tv}$ is the surface tension of the drop and $\theta_v$ is its contact angle with the film. Substituting for the tension gives us the scaling for the elastocapillary length, $\ell \sim \sqrt{EH^3 / \gamma_{tv}}$. Plotting the number of lobes ($n$) of the experimentally observed shapes as a function of the elastocapillary number reveals that when $a/\ell \geq 3$, i.e. when the drop is “soft” enough, its contact line becomes asymmetric and forms lobes (Fig. 2b). Any small deviations from a symmetric lobe lead it to becoming chiral with one edge being convex and the other edge being concave (Fig. 2a), inducing chirality of the subsequent lobes.

Right after the lobes acquire chirality, drops with less number of lobes ($n < 6$), synchronize quicker and rotate. However, for drops with $n > 7$, the lobes fail to synchro-

FIG. 1. (a) The experimental setup comprises of a thin elastic film ($H \sim$ tens of microns) made of PDMS afloat aqueous glycerol. Acetone droplets undergo spontaneous rotation as demonstrated via a single cycle of: (b) the bean mode with $n = 1$ undergoing clockwise rotation (3 $\mu L$ drop on 9 $\mu m$ PDMS film) and (c) a star shaped mode with $n = 5$ undergoing anti-clockwise rotation (20 $\mu L$ drop on 19.5 $\mu m$ PDMS film), and (d) a 30 $\mu L$ drop of acetone undergoing oscillatory and fro motion on a 28.5 $\mu m$ PDMS film. The scale bars in (b)–(d) denote 2 mm. (e) When a drop ($V = 20 \mu L$ each) of methanol is placed on different PDMS films, it assumes a spherical cap state. For intermediate film thicknesses ($\sim 20 \mu m$) isopropanol, butanol and acetone spontaneously undulate into a chiral shape with $n$ lobes. A hexane droplet wrinkles the films dramatically. The phase space of the shapes assumed by various solvents on PDMS films helps in identifying a regime where spontaneous lobe formation of the droplet occurs. Inset in each image is its Péclet number, $Pe$. Similar to a swollen polymer disk [15], which move with an accompanying membrane deformation mode. As the drop sits in the topographically undulated region with $n$ buckles, it takes the shape of the film forming $n$ lobes along its contact line within fractions of seconds (SI, Movie 1). If the swelling degree is either too small (methanol) or too large (hexane), we see that there is no lobe formation in the former case, whereas, many wrinkles form in the latter case. As the droplets evaporate, a natural guess for the instability causing mechanism in its boundary would be that of inhomogeneous evaporation at the contact line. For pure component droplets, mild fluctuations of the contact line may give rise to variations in the partial pressures


![Diagram](a)

![Diagram](b)

**FIG. 2.** (a) Phase space of instantaneous snapshots of droplets of acetone (volume $V$) when they are deposited on PDMS films (thickness $H$). Smaller droplets on thicker films are “pinned” in spherical cap state whereas larger droplets on thinner films spontaneously form lobes $n (= 1$ to 6) that undergo rotation. (b) Bifurcation diagram of the shapes comprising spherical pinned state (*) with $n = 0$ and chiral spinning state depicting number of lobes $n$ as a function of the dimensionless elastocapillary number $(a/\ell)$, where $\ell = \sqrt{\gamma H^2/\eta v}$. The color of each filled symbol depicts the amplitude of the lobes normalized by the radius of the drops $(|b|)$. There is a critical threshold around $a/\ell \simeq 3$ where the shapes bifurcate from spherical cap to lobed state. (Inset) An example of a fitted shape ($n = 3$) with contact radius $a$ and amplitude $|b|$ labelled.

Although, and show quivering traveling waves (SI, Movie 6). Introducing neutrally buoyant hollow glass spheres in the droplet show that for $n \sim 3 - 6$, the particles only move in the neighborhood of the contact line, and the drop rotation corresponds to coordinated traveling waves carrying the liquid along the edges (SI, Movie 8), whereas for drops with $n \sim 1$, particles translocate with the liquid showing global rotation of the drop. In all the experiments, the chirality determines the direction of motion of each lobe such that it moves from the convex side of the lobe towards its concave side (SI, Movie 1). To understand why this is so, we turn to the Kelvin equation [24] that suggests it is easier to evaporate from convex surfaces than from concave surfaces as the vapor pressure due to positive curvature is higher than that due to negative curvature. For the chiral lobes observed in our system, this would imply asymmetric evaporation from the convex and concave sides of the lobe, leading to motion from the high evaporation (convex) to the low evaporation (concave), provided their contact line is mobile [25]. The contact line of the droplet in our system sits on a saturated film, therefore being minimally pinned, as also confirmed by the observation that particles are not deposited along the contact line unlike in the well-studied coffee-ring effect [20]. Together, the asymmetric evaporation and the synchronized motion of lobes from convex to concave sides of the lobes give rise to an overall rotation of the drops on the PDMS film.

In previous studies, experiments have mainly identified how droplets translate on rigid surfaces and theoretical models have looked at the possibility of rotational versus oscillatory motion arising due to spontaneous symmetry breaking [23, 27, 28]. To the best of our knowledge, the only study that has observed drop rotation without imposing an *a priori* gradient was that of dichloromethane drops albeit on surfactant solutions [5]. A reason for why the drops spin instead of translating can be understood by comparing the viscous drag in the solvent phase, which is proportional to $|b|a^2\xi$ for the lobed drop undergoing rotation, and proportional to $a^2\xi$ for translational motion, where $\xi$ is the average thickness of the drop. Since the amplitude of the lobes $|b| \sim 10\%$, it implies rotation is preferred over translation.

A simple one-dimensional experiment crystallizes the mechanisms at work. We start with a thin strip of sagging PDMS film clamped at opposite ends and deposit a drop of acetone that spans its width, and observe that the drop moves to and fro in an oscillatory fashion (Fig. 3a) and SI, Movie 9). These oscillations arise as the PDMS film underneath the drop swells due to solvent imbibition, so that its thickness increases rapidly locally to $H_{\text{max}} \sim (1 + \epsilon_f)H$ ($\epsilon_f$ being the swollen fraction, or the swelling degree S for a solvent/PDMS pair [14]) over the imbibition time scale $\eta H^2/kE$. This also implies that the increase in the lateral size of the film under drop is of the same order, $R_{\text{max}} \sim (1 + \epsilon_f)R$. Thus, the swelling of the film leads to a local bulge of amplitude $\sim \lambda$, which in turn gives rise to a global tilt $\sin \Theta \sim \lambda/R$ ($\sim \sqrt{1-1/(1+\epsilon_f)^2}$), causing the acetone droplet to slide away from the swollen region as there is no contact line pinning. This exposes the swollen region to the ambient atmosphere causing the solvent to evaporate, thus regenerating the film. The global sag in the film prevents the drop from running away, and the cycle of swelling, bulging, motion and regeneration leads to an oscillating state. Since the capillary forces due to the drop deforms the soft film underneath, the mechanical deformations propagate when the droplet moves on the film thereby inducing dissipation due to viscoelastic braking [29, 30]. Therefore, balancing the driving gravitational power of the drop with the viscoelastic dissipation in the film yields...
The chirality in the lobe leads to asymmetric evaporation where its motion is caused due to unbalanced surface tension forces at the drop contact line. Our films start out being uniformly thick, and can swell in the presence of the solvent drop, therefore, being different in the initial conditions from Liu’s system [9] system.

A generalization of this mechanism for the lobed drop on a large sheet is depicted in Fig. 3(b). A local concentration gradient induced by the sessile solvent droplet causes fluid to diffuse into the permeable film which swells inducing film buckling. For large drops on soft thin substrates, the contact line undulates forming a lobed structure which becomes chiral due to spontaneous symmetry breaking. The chirality in the lobe leads to asymmetric evaporation between the convex and concave sides of the lobes leading to their motion towards their concave side. If the time scale of the evaporation and that for swelling become comparable, i.e. $Pe \sim \mathcal{O}(10)$, the droplet starts to spin with a frequency $(f)$ determined by the poroelastic timescale, i.e. $\tau_p = \eta a H / kE$ that depends on both the film thickness ($H$) as well as the lateral length of the film ($R$) across which the solvent migrates. Our experiments are consistent with this simple scaling law, as shown in Fig. 3(c) where the data from droplets with varying lobe numbers collapse for the relationship $f \sim 1 / n \tau_p$, which is consistent with Eq. 1 where the slope is of $\mathcal{O}(1)$. Note that the form of $\tau_p$ differs from the expression for the imbibition time scale that has the classical form of $\tau \sim \eta H^2 / kE$ [31] due to poroelasticity, each one being determined by the length scales relevant in estimating the timescale.

Our observations sit at the junction of three non-equilibrium processes: evaporation, solvent flow and solvent-driven swelling of a thin elastic film giving rise to buckling. Together these processes conspire to drive oscillatory and rotatory motion in drops over a robust range of parameters corresponding to a poroelastic Péclet number of order ten. In this regime, drops that are sufficiently large relative to a natural elastocapillary length spontaneously break symmetry and spin with a frequency that is controlled by the balance between fluid flow and film swelling dynamics. A detailed theoretical analysis and additional measurements to quantify evaporative fluxes from the destabilized drop will be carried out next. How this instability might be controlled in artificial settings is an obvious next question [34].

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**FIG. 3.** (a) 1D experiment of drop oscillation of volume $V = 25 \, \mu l$ on PDMS strip (4 mm wide, 36 $\mu m$ thick), which is clamped at the two ends and has a global sag to prevent the drop from running away. (b) Schematic of the phenomenon showing that the solvent droplet ($n = 5$) swells the PDMS film leading to undulations, which are enhanced here for visualization. The vapor pressure in convex part of the lobe ($P_I$) is higher than the vapor pressure in concave part of the lobe ($P_{II}$) leading to asymmetric evaporation rates from the drop ($j_I > j_{II}$). Exposed part of the PDMS film surrounding the drop advects out imbibed solvent due to evaporative flux ($J$). Overall, the lobes move from higher evaporation side (convex) to lower evaporation side (convex) giving rise to coordinated spinning of the drop with frequency $f$. (c) Frequency $(f)$ of the spinning drops scales as $1/n \tau_p$, where $\tau_p = \eta a H / kE$ is the poroelastic time scale.
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