Stop-and-go droplet swimmers

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Abstract

To explore and react to their environment, living micro-swimmers have developed sophisticated strategies for locomotion — in particular, motility with multiple gaits. To understand the physical principles associated with such a behavioural variability, synthetic model systems capable of mimicking it are needed. Here, we demonstrate bimodal gait switching in autophoretic droplet swimmers. This minimal experimental system is isotropic at rest, a symmetry that can be spontaneously broken due to the nonlinear coupling between hydrodynamic and chemical fields, inducing a variety of flow patterns that lead to different propulsive modes. We report a dynamical transition from quasi-ballistic to bimodal chaotic motion, controlled by the viscosity of the swimming medium. By simultaneous visualisation of the chemical and hydrodynamic fields, supported quantitatively by an advection-diffusion model, we show that higher hydrodynamic modes become excitable with increasing viscosity, while the recurrent mode-switching is driven by the droplet’s interaction with self-generated chemical gradients. We further demonstrate that this gradient interaction results in anomalous diffusive swimming akin to self-avoiding spatial exploration strategies observed in nature.

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In response to physical constraints in nature, microorganisms have adapted and developed various locomotion strategies. Depending on cues from the environment, these strategies include helical swimming [1, 2], run-and-tumble and switch-and-flick motility [3], but also more sophisticated transient behaviours, e.g. peritrichous bacteria switching poles in response to a steric stress [4], octoflagellate microalga exhibiting run-stop-shock motility with enhanced mechanosensitivity [5], and starfish larvae maximising fluid mixing, and thereby nutrition uptake, through rapid changes of ciliary beating patterns [6]. Such intricate gait-switching dynamics [7, 8] can enable organisms to navigate in external flows [9, 10], follow gradients [11] or efficiently explore their environment [12, 13].

To understand the physical mechanisms behind the locomotion strategies of biological swimmers, one requires motile synthetic protocells which mimic these sophisticated behaviours. This is ideally done in a minimal model system based on fundamental principles of non-equilibrium physics, rather than building on intricate biochemical machinery. Examples include autophoretic microswimmers powered by chemical activity which leave long-living chemical traces in their wake [14].

We show that self-interaction with the swimmer’s own slowly diffusing chemical field can lead to nonlinear feedback triggering unsteady swimming and chaotic dynamics. Specifically, we report the emergence of such unsteady dynamics for a self-propelled isotropic droplet, in the absence of any bio-complexity. The droplet, driven by micellar solubilization [15], adapts to an increase in the viscosity of the swimming medium with increasingly unsteady motion — a counter-intuitive response given that increasing viscosity generally tends to stabilise non-inertial dynamics. Using time-resolved \textit{in situ} visualisation of the chemical and the hydrodynamic fields around the droplet interface, we have found that the emergent unsteady dynamics of the droplet correlate with the onset of higher hydrodynamic modes. The experiments agree quantitatively with theoretical predictions of dominant higher hydrodynamic modes for large Péclet numbers, which characterise the underlying advection-diffusion-driven transport of the chemical species necessary for droplet activity. Once these higher modes prevail, the droplet exhibits an unsteady bimodal exploration of space triggered by its interaction with self-generated chemical gradients, which is reminiscent of gait-switching dynamics in biological organisms. The visualisation technique and the findings presented here lay the groundwork for future investigations of emergent dynamics in active phoretic matter, from the individual to the collective scale.
Oil droplets that are slowly dissolving in supramicellar aqueous surfactant solutions can spontaneously develop self-sustaining gradients in interfacial surfactant coverage, resulting in Marangoni stresses which lead to self-propulsion [16]. This interfacial instability may be understood as follows (Fig. 1a,b): During the solubilisation of the droplet, oil molecules migrate into surfactant micelles in a boundary layer around the droplet interface, causing the micelles to swell and take up additional surfactant molecules from the aqueous phase. This depletes the interfacial surfactant concentration, unless there are empty micelles present to replenish it by disintegration. The interfacial tension therefore increases with the local ratio of filled to empty micelles. Following an advective perturbation in the vicinity of the droplet, the radial symmetry of the filled micelle distribution is spontaneously broken; the resulting fore-aft asymmetry generates a surface tension gradient which drives the droplet towards more empty micelles leading to sustained self-propulsion, while leaving behind a trail of swollen micelles. Such spontaneous self-propulsion stemming from the advection-diffusion driven interfacial instability arises only if the Pécel number, $Pe$, which characterises the ratio of advective to diffusive transport, exceeds a critical threshold [17–20]. For the active droplet system, $Pe$ can be shown to be a monotonically increasing function of the swimming medium (outer) viscosity $\mu^o$, here non-dimensionalised as $\mu = \mu^o/\mu^i$ using the constant inner viscosity $\mu^i$:

$$Pe = \frac{V_t R_d}{D} \approx \frac{18 \pi^2}{k_B T} q_s r_s^2 \zeta R_d^2 \mu^i \left[ \frac{2\mu + 3\zeta/R_d}{2\mu + 3} \right]$$

where $V_t$ is the theoretical terminal droplet velocity in an external surfactant gradient [19, 21], $R_d = 30 \mu m$ the droplet radius, $D = \frac{k_B T}{6\pi r_s \mu^o}$ the diffusion coefficient for the surfactant monomer (length scale $r_s \sim 10^{-10}$ m), $q_s$ the isotropic interfacial surfactant consumption rate per area, and $\zeta \sim 10$ nm the characteristic length scale over which the surfactants interact with the droplet [18, 21] (see Supplementary section S3B for details). In experiments, we controlled $\mu^o$ by using water/glycerol mixtures as the swimming medium (see Supplementary Fig. S1). Henceforth, we represent an increase in $\mu^o$ by the corresponding increase in $Pe$. 
SIMULTANEOUS VISUALISATION OF CHEMICAL AND HYDRODYNAMIC FIELDS

To visualise the chemical and hydrodynamic fields involved in the droplet activity, we directly imaged the chemical field of swollen micelles by adding the hydrophobic dye Nile Red to the oil phase (Fig. 1 c,d). The dye co-migrates with the oil molecules into the filled micelles, which fluoresce when illuminated. We seeded the surrounding medium, a supram-
FIG. 2. Destabilized droplet motion with increasing Péclet number $Pe$. a-d, Example trajectories of droplets for $Pe \in \{4, 16, 71, 667\}$, with zoomed-in insets colour-coded by propulsion speed $V$. All scale bars are 50 $\mu$m. e, Distribution of the velocity reorientation angle, $|\delta \theta|$ for increasing $Pe$, measured during a time step $\delta t = 0.1$ s set by the video recording rate of 10 Hz. Profiles of the velocity auto-correlation function, $C_{VV}$, in the inset, show the loss of directionality in swimming. f, Distribution of propulsion speeds $V$ for increasing $Pe$, with mean and standard deviation of speeds in the inset. See the corresponding videos S2-S5. The color bar relating $Pe$ to the viscosity ratio $\mu = \mu^o/\mu^i$ applies to all subsequent figures.

icellar aqueous surfactant solution, with green fluorescent tracer colloids (Fig. 1 c,d; see also Supplementary Section S1 E and Video S1), and measured the flow field using particle image velocimetry (PIV). The emission spectra of dye and colloids are sufficiently non-overlapping to be separately detected in dual channel fluorescence microscopy. Consequently, both fields can be simultaneously observed and analysed; we provide an example micrograph with an overlay of the extracted droplet trajectory in Fig. 1 d. Due to the large size ($O(10 \text{ nm})$) of the filled micelles, the time scale of their diffusive relaxation exceeds that of the droplet motion; thus, there is a persistent fluorescent trail in the wake of the droplet.
DESTABILISED MOTION WITH INCREASING PÉCLET NUMBER

We begin, however, with an overview of the droplet dynamics using trajectory plots and statistical analyses of speed and orientational persistence taken from bright-field microscopy (Fig. 2). With increasing $Pe$, the droplet propulsion changes from uniform speeds and persistent motion to unsteady motion with abrupt reorientations (Fig. 2 a-d). We define $P(|\delta \theta(t)|)$ as the distribution of the reorientation angle $\delta \theta$ of the 2D droplet velocity $V(t)$ during a fixed time step $\delta t$ [22],

$$
\delta \theta(t) = \arctan \left( \frac{V(t) \times V(t + \delta t)}{V(t) \cdot V(t + \delta t)} \right).
$$

(2)

$P(|\delta \theta(t)|)$ broadens significantly, corresponding to more frequent and sharper reorientation events (Fig. 2 e). The faster decay of the angular velocity autocorrelation function,

$$
C_{VV}(t) = \left\langle \frac{V(t_0 + t) \cdot V(t_0)}{||V(t_0 + t)|| ||V(t_0)||} \right\rangle_{t_0},
$$

(3)

illustrates the loss of directionality with increasing $Pe$ (Fig. 2 e, inset). Fig. 2 f shows that at sufficiently large $Pe$, the speed distribution $P(V)$ includes values as small as zero (stopping events) and, surprisingly, as large as $70 \mu m/s$, much greater than the uniform speed of $30 \mu m/s$ observed for low $Pe \approx 4$. While the mean speed barely changes with $Pe$, the standard deviation of $V$ grows by over one order of magnitude (Fig. 2 f, inset). Hence, both the rotational and the translational motion of the swimmer are destabilised with increasing $Pe$, similar to recent numerical studies of solid phoretic particles [23]. Note that the thermal fluctuations ($O(k_bT/2R_d) \sim 10^{-16} N$) are negligible compared to the hydrodynamic drag force ($O(6\pi \mu^o R_d V) \gtrsim 10^{-10} N$), such that thermal noise is an unlikely cause for the unsteady swimming.

SIGNATURES OF UNSTEADY DYNAMICS IN THE TIME EVOLUTION OF CHEMICAL AND HYDRODYNAMIC FIELDS

To investigate the origin of this unsteady behaviour, we studied the evolution of chemical and hydrodynamic fields around the droplet. We extracted the tangential flow velocity $u_\theta(\theta)$ and the red fluorescence intensity $I(\theta)$ of the chemical field close to the interface (Fig. 3 d, Supplementary section S2), and mapped them in kymographs $I(\theta,t)$ and $u_\theta(\theta,t)$. 
FIG. 3. **Signatures of unsteady dynamics in the time evolution of chemical and hydrodynamic fields.** Rows a, b and c correspond to \( Pe = 4 \), \( Pe = 28 \) and \( Pe = 190 \), respectively; Left column, trajectories colour coded by time; middle column, kymographs of \( I \) and \( u_\theta \) during 45 seconds of propulsion; right column, selected red channel images, overlaid by the flow streamlines. Each frame corresponds to the point in time indicated on the kymographs by I, II or III. Panel d defines the mapping of the profiles of red light intensity \( I \) (filled micelle concentration) and tangential velocity, \( u_\theta \), around the droplet circumference onto the \( y \) axis of the kymographs in the middle column. All \( u_\theta \) profiles are in droplet reference frame. In c, the third kymograph corresponds to the radial velocity \( u_r \) in the laboratory reference frame to better depict the quadrupolar symmetry of the flow field. The second hydrodynamic mode starts to appear at intermediate \( Pe \) and dominates the dynamics for high \( Pe \). See also Fig. S4. All scale bars are 50 \( \mu m \).

For low \( Pe \approx 4 \), at persistent propulsion, \( I(\theta, t) \) shows a single fixed-orientation band marking the origin of the filled micelle trail at the rear stagnation point of the droplet (Fig. 3a and video S6). The two bands in \( u_\theta(\theta, t) \) correspond to a steady flow field with dipolar symmetry that is consistent with the \( I(\theta, t) \) profile. On the right side of Fig. 3a we have superimposed the streamlines of this dipolar flow field on the corresponding chemical micrograph at the time marked by I in the \( I(\theta, t) \) kymograph.

For intermediate \( Pe \approx 28 \) (Fig. 3b, Video S7), \( I(\theta, t) \) shows secondary branches forming at the anterior stagnation point of the droplet and subsequently merging with the main filled
micelle trail. This coincides with a transient second hydrodynamic mode with quadrupolar symmetry (Fig. 3 b,II), causing the accumulation of an additional aggregate of filled micelles at the droplet anterior (see also Supplementary Fig. S4).

The ratio of the diffusive \( \frac{R_d^2}{D_{fm}} \) to advective \( \frac{R_d}{V} \) time scales for the migration of filled micelles is \( VR_d^2 D_{fm} \gg 1 \) for all experiments, assuming a diffusion coefficient \( D_{fm} = \frac{k_B T}{6\pi \mu r_{fm}} \), with a micellar radius of \( O(r_{fm}) \sim 10 \text{ nm} \). Therefore, the aggregate is unlikely to dissipate by diffusion, and will continue to grow as long as the quadrupolar mode exists. However, this mode is not stable. Eventually, the dipolar mode dominates and advects the secondary aggregate towards the main trail (Fig. 3 b,III; also see Fig. S4). The transport of the aggregate along one side of the droplet locally disturbs the interfacial flow, leading to an abrupt reorientation of the swimming direction (Fig. 3 b,I-III). As shown in the trajectories in Fig. 2 b and c, these reorientation events become more frequent with increasing \( Pe \); accordingly, \( u_\theta \) in Fig. 3 b exhibits quasi-periodic reorientation patterns.

For high \( Pe \approx 190 \) (Fig. 3 c, Video S8), the quadrupolar mode eventually prevails, resulting in a predominantly symmetric extensile flow around the droplet (Fig. 3 c,I), as shown by a pronounced fourfold pattern in the additional kymograph \( u_r(\theta, t) \) of the radial velocity. In the absence of the dipolar mode, the droplet is trapped in place. The gradual accumulation of filled micelles at the two stagnation points with radially outward flow manifests in two stable branches in the chemical kymograph (marked by I in Fig. 3 c). The growth of the two micellar aggregates locally generates a lateral chemical gradient, which eventually pushes the droplet out of its self-made trap. Concomitantly, the two points of filled micelle emission move along the droplet interface and merge on the new rear side of the droplet into a single filled micelle trail (Fig. 3 c,II and III). The chemorepulsion from the local field micelle gradient induces an apparent dipolar mode which gradually decays as the droplet leaves the self-made trap. Now, the dominant quadrupolar mode re-saturates, with an aggregate growing at the droplet anterior, until the droplet is trapped again and a new bimodal ‘stop-and-go’ cycle begins. Since the escape direction is always lateral, consecutive runs are approximately perpendicular, resulting in the sharp reorientation events apparent in the trajectories in Fig. 3 c and Fig. 2 d, as well as the broadening \( |\delta \theta| \) distribution in Fig. 2 e.
**FIG. 4. Dependence of hydrodynamic modes on the Péclet number.** a, Critical Péclet $Pe_{cr}$ values (black lines), necessary for the onset of different hydrodynamic modes ($n$), with varying $\mu$; The markers (□) show the Péclet number $Pe$ (Eq. 1) which increases with $\mu$. The colour code is taken from Fig. 2. b, (top) Steady self-propulsion of the active droplet; theoretical solution for $n = 1$ mode (left) and experimental streak image for low $Pe$ (right); (bottom) the extensile flow corresponding to $n = 2$ mode (left) and the experimental image for higher $Pe$ (right). The theoretical and the experimental flow fields are in the swimmer reference frame. c, Instability growth rates corresponding to the first two hydrodynamic modes as a function of $Pe$. Beyond the dashed vertical line (grey region) $\lambda_{n=2} > \lambda_{n=1}$ and thus the $n = 2$ mode is dominant.

**DEPENDENCE OF HYDRODYNAMIC MODES ON THE PÉCLET NUMBER**

In order to understand the dependence of the dominance of the hydrodynamic modes on $Pe$, we analysed the underlying advection-diffusion problem for the active droplet within the framework of an axisymmetric Stokes flow (see Fig. 4, Supplementary section S3 and [19, 20, 24]). At the smallest value of $\mu$, $Pe$ is approximately equal to the critical value of 4 necessary for the onset of the first hydrodynamic mode ($n = 1$), i.e. the mode with dipolar flow symmetry [17, 19, 20]. With increasing $\mu$, $Pe$ (markers in Fig. 4a) eventually exceeds the critical values necessary for the onset of the higher hydrodynamic modes (lines in Fig. 4a), specifically the second hydrodynamic mode ($n = 2$), i.e. the mode with quadrupolar symmetry. A linear stability analysis around a motionless base state (see Supplementary section S3C and [17, 20]) shows that for small to moderate $Pe$, the non-dimensionalised instability growth rate $\lambda$ for $n = 1$ exceeds that for $n = 2$ (Fig. 4c). Accordingly, for lower $Pe$, $n = 1$ dominates, representing steady self-propulsion stemming from the fore-
aft asymmetry of the surfactant distribution (Fig. 4 b, I). Consequently, the active droplet exhibits persistent steady translation (trajectories in Fig. 2 a-b) with a dominant dipolar flow field (Fig. 4 b,II and Fig. 3 a). However, for $Pe \gtrsim 92$, $n = 2$ (Fig. 4 b,III) has a faster instability growth rate, thereby becoming the dominant mode (Fig. 4 c). Consequently, for experiments with $Pe > 92$, the active droplet experiences periods of dynamical arrest during which it remains stationary with a surrounding extensile flow (Fig. 4 b,IV and Fig. 3 c). As discussed above, the subsequent genesis of the bimodal ‘stop-and-go’ motion of the droplet for moderate to higher $Pe$ (trajectories in Fig. 2 c-d) is due to the synergy between the $n = 2$ mode and the transiently-growing filled micelle field. Note that we restrict our analysis to the first two hydrodynamic modes since these two are solely responsible for the droplet propulsion and the associated far-field hydrodynamic disturbance.

**INTERACTIONS WITH SELF-GENERATED CHEMICAL GRADIENTS CAUSE SPEED BURSTS**

It remains to explain the broadening of $P(V)$ with increasing $Pe$ (Fig. 2 e), particularly the remarkable bursts in speed for high $Pe$. While the dipolar mode is propulsive, the quadrupolar mode is not. Hence, the growth and decay of the respective modes will affect the droplet speed. As shown in Fig. 3, recurrent transitions between the two hydrodynamic modes lead to abrupt reorientation events; we therefore investigated the correlation between changes in speed and reorientation angle $|\delta \theta|$.

In a typical trajectory for intermediate $Pe = 28$, each sharp turn is preceded by a deceleration and followed by an acceleration, as shown in the plot of the positional data colour-coded by speed in Fig. 5 c. Signatures of these correlations in the droplet dynamics appear in the conditional averages of $|\delta \theta|$, $V$ and tangential acceleration $a_t$ for all sharp reorientation events in the trajectory, centered at $t = 0$ of maximum $|\delta \theta|$ (Fig. 5 a); the events were identified by choosing a threshold value of $|\delta \theta| > 0.2$ (see Fig. S5). We can now directly compare these dynamics to the higher resolution fluorescence data taken at $Pe = 28$ presented in the kymographs in Fig. 3 b. Fig. 5 b shows a series of micrographs of the chemical field, with arrows marking the droplet velocity vector (black) and the position of the secondary filled micelle aggregate (white). The aggregate accumulates, is then entrained and finally merges with the posterior trail, corresponding to the creation and merging of a
FIG. 5. Interactions with self-generated chemical gradients cause speed bursts at re-orientation events. a, Conditional averaging of tangential acceleration, $a_t$, speed, $V$, and re-orientation angle, $|\delta \theta|$, for abrupt reorientation events at $Pe = 28$ (see Fig. S5, for identification criteria). The dotted line marks the maximum speed at $t = \tau_1$ after reorientation. b, Video stills of the chemical field for one such event with $t = 0$ s set to the point of minimum speed; white arrows track the accumulation of the secondary filled micelle aggregate at the anterior stagnation point and its advection along the interface, black arrows correspond to the droplet velocity vector. The droplet speed is maximal when the secondary aggregate and the trail merge at $t = 0.93$s. See video S9 and S10. c, An example trajectory for $Pe = 28$. Any reorientation event (curved arrows) is preceded by a deceleration and followed by an acceleration. The lowest speed occurs at the point with the highest curvature. d, Correlation function between reorientation angle and speed, $C_{|\delta \theta|, V}(\Delta t)$ for increasing $Pe$. Times $\tau_1$ and $\tau_2$ (next reorientation event) are identified by the respective peak and dip in $C_{|\delta \theta|, V}$. e, Time scale for the growth of the $n = 2$ mode vs. corresponding $Pe$: experimentally obtained, $\tau_2 - \tau_1$ (○), compared to values from stability analysis, $\lambda_{n=2}^{-1} R_d/V_t$ (□).

For $t < 0$ the droplet decelerates while the secondary aggregate is accumulating. $t = 0$ marks the point in time where $V$ is minimal and the aggregate is on the cusp of leaving the anterior stagnation point. For $t > 0$, the aggregate is advected to the droplet posterior and the droplet accelerates due to the re-saturation of the dipolar mode. $V$ peaks once the
aggregate has merged with the main trail — creating an amplified fore-aft gradient — at \( t \approx 1 \) s, which is comparable to the advective timescale \( R_d/V \approx 1 \) s. In the wide-field data analysis in Fig. 5a, this is the time \( \tau_1 \) it takes the droplet to reach maximum speed after a reorientation.

We now use the correlation function between \( V \) and \( |\delta \theta| \), \( C_{|\delta \theta|,V}(\Delta t) = \langle |\delta \theta(t)| \cdot V(t + \Delta t) \rangle_t \), plotted in Fig. 5d, to estimate the growth times of the second mode from our data for \( Pe > 10 \). Since \( V \) is minimal at maximum \( |\delta \theta(t)| \) (Fig. 5a), \( C_{|\delta \theta|,V}(\Delta t) \) dips at \( \Delta t = 0 \). It subsequently peaks at the point of maximum \( V \) with a time delay \( \Delta t = \tau_1 \), when the contribution of the propulsive dipolar flow is maximal. The next dip at a time \( \tau_2 > \tau_1 \) marks the next reorientation event; based on the discussion pertaining to Fig. 3 and Fig. 4c, for moderate to high \( Pe \), \( \tau_2 - \tau_1 \) should correspond to the time scale for the growth and re-saturation of the \( n = 2 \) mode. To test this, we compare the experimentally obtained \( \tau_2 - \tau_1 \) with the theoretical growth times for the \( n = 2 \) mode, \( \lambda_{n=2}^{-1} R_d/V_t \) (Fig. 4c), for different values of \( Pe \). Fig. 5e shows that indeed these two are of the same order of magnitude and decrease with increasing \( Pe \). We note that the growth time of the dipolar flow above \( Pe \approx 100 \) cannot be used for comparison to \( \lambda_{n=1}^{-1} \), since this flow is imposed by the lateral chemical gradient. However, we can assume that this gradient increases with \( Pe \), resulting in faster acceleration, markedly higher swimming speeds, and hence, reduced \( \tau_1 \), as observed experimentally (Fig. 5d).

**CONSEQUENCES FOR SPATIAL EXPLORATION**

Reminiscent of gait switching dynamics in biological locomotion, we have demonstrated the emergence of complex swimming behaviour in a minimal active droplet system by tuning the Péclet number. We found a transition from persistent swimming at low \( Pe \) to chaotic bimodal swimming at high \( Pe \) — the latter results from the excitation of higher hydrodynamic modes beyond critical \( Pe \) values, while the continuous switching between them is caused by the self-generated chemical gradient in the environment.

This gradient sensitivity causes trail avoidance [25], which in turn affects the way these droplet swimmers explore their environment. With increasing reorientation frequency, we find a transition from quasi-ballistic propulsion to a 2D self-avoiding walk (2D SAW). This effect is illustrated by the trajectories in Fig. 2a-d, and also by the fact that \( C_{VV} \) in Fig.
Anomalous diffusive swimming. a, Mean squared displacement profiles of experimental trajectories for different $Pe$. Dashed lines mark the predicted scaling for ballistic motion, $\propto t^2$, 2D self-avoiding walk (SAW), $\propto t^{3/2}$, and random walk (RW), $\propto t$. For higher $Pe$, there is a transition from ballistic to 2D SAW. b, A segment of the trajectory associated with the SAW and schematics of the droplet exhibiting bimodal swimming which is responsible for the SAW. Also see Fig. S6.

2e does not decay to zero. For a statistical analysis we have plotted mean squared displacements for selected $Pe$ values in Fig. 6a, which reproduce the expected scaling with $t^2$ (ballistic) for $Pe = 4$ and a transition to $t^{3/2}$ (2D SAW, [26]) for $Pe \geq 28$, with the crossover time decreasing with increasing $Pe$. While transitions to random walks governed by run-and-tumble gait switching are common in bioswimmers [27], self-avoidance requires chemical self-interaction [28]. Examples of anomalous diffusion driven by repulsive biochemical signalling have been found in the spreading of slime molds [29, 30] — active droplets can show analogous behaviour based on purely physicochemical mechanisms.

OUTLOOK

As demonstrated above, the manner in which hydrodynamic and self-generated chemical fields are coupled significantly determines the dynamics of autophoretic micro-swimmers. The fluorescence-based analysis technique used to simultaneously probe these can provide insight into many recent autophoretic models [15, 17, 18, 31–34]. We propose this minimal
droplet paradigm as a testing bed to investigate a number of current problems in biomimetic swimmers and active matter, where research is primarily theoretical, or experiments have not yielded a clear picture yet.

For example, the capability to approach each other or form bound states is vital to nutrient entrainment, food uptake and mating in bioswimmers. Extensive theoretical studies [35–38] have shown the importance of quantifying far-field and near-field contributions, coupling to chemical fields and the effects of confinement in these interactions.

Beyond binary interactions, chemo-hydrodynamic interactions mediate collective behaviours, leading to a variety of clustering and swarming states that can diverge widely even in closely related systems [39–42].

Unlike many micro-swimmer models which incorporate unsteady dynamics via stochastic fluctuations, the interplay of nonlinear dynamics and interaction with the history of motion allows for the emergence of memory-driven chaotic behaviour. A particularly interesting example are droplet walkers on a vibrated bath [43], which show a transition from persistent to a bimodal, stop-and-go motion based on an effective ‘system memory’ parameter [44, 45]. The corresponding theoretical framework [44] is general enough to also apply to bimodal chaotic motion in droplet swimmers.

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S1. MATERIALS AND METHODS

A. Materials and characterisation

Our samples consisted of droplets of (S)-4-Cyano-4’-(2-methylbutyl)biphenyl (CB15) doped with the fluorescent dye Nile Red in an aqueous solution of the anionic surfactant tetradecyltrimethylammonium bromide (TTAB) corresponding to 5 wt.% in pure water, with a critical micelle concentration of $CMC = 0.13$ wt.% (50 mg in 1 ml of solution). We purchased CB15, TTAB, and Nile Red from commercial suppliers (Synthon Chemicals and Sigma-Aldrich) and used them as is. We controlled the viscosity of the swimming medium, $\mu^0$, by adding glycerol to the aqueous TTAB solution. We used an Anton Paar MCR 502 rotational rheometer to characterise the shear viscosity of water-glycerol-surfactant solutions (Fig. S1). Experiments were carried out using a cone-plate geometry, to find shear-rate versus shear-stress curves at a fixed temperature, and viscosity versus temperature a fixed shear rate. To limit effects of solution evaporation, the cone-plate geometry was surrounded by a water bath and covered by a Peltier hood. The shear-rate region of interest chosen was guided by experimental observations of the droplet swimming speed divided by the size of the droplets, which is of order $1 \text{s}^{-1}$. Over the shear rate range $0.01 < \dot{\gamma} < 100$, viscosity was found to be constant, such that our solutions are well-described as Newtonian for the parameters relevant to this work.

B. PDMS soft lithography for droplet generation

For the production of monodisperse oil droplets, we fabricated microfluidic channels in-house, using standard soft lithography techniques. First, 2D photomasks were designed in AutoCad, and then printed onto an emulsion film in high-resolution (128,000 dpi) by a commercial supplier (JD Photo-Tools). Next, the photoresist SU-8 3025 (MicroChem) was spin-coated onto a 4 inch diameter silicon wafer (Si-Mat), where spin-speed and duration were adjusted to give a controllable uniform thickness. A negative mold was cured in the
SU-8 through the photomask by UV light exposure. After further chemical treatment with photoresist developer, uncured SU-8 was removed, leaving behind cured SU-8 microstructures on the silicon wafer.

We then poured a poly(dimethyl siloxane) (PDMS, Sylgard 184, Dow Corning) mixture of 10:1 volumetric ratio of base to cross-linker over the wafer, and baked for 2 hours at 80 °C, producing a solid PDMS layer with microstructured indentations. We then peeled the indented PDMS from the wafer, and punched holes through it to create liquid inlets/outlets at opposing ends of the channels. The structured PDMS surface, as well as a glass coverslip, were cleaned and treated with partial pressure air-plasma (Pico P100-8; Diener Electronic GmbH + Co. KG) for 30 seconds, and then pressed together, bonding the two surfaces. Fig. S2 shows a micrograph of such a PDMS chip during droplet production.

The walls of these microfluidic chips were selectively treated to hydrophilise the channels where surfactant solution will flow. This prevents oil from wetting the walls during droplet production. We followed the technique of Petit et al.[46]: First, the channel walls were
FIG. S2. The microfluidic chip used to produce mono-dispersed oil droplets in a surfactant solution.

oxidised by a 1:1 mixture of hydrogen peroxide solution (H2O2 at 30 wt.% , Sigma-Aldrich) and hydrochloric acid (HCl at 37 wt.% , Sigma-Aldrich). This mixture was flushed through the channels for approximately 2 minutes by using a vacuum pump system. After the oxidation, the channel was rinsed by flushing double distilled water for 30 seconds. Next, a 5 wt.% solution of the positive polyelectrolyte poly(diallyldimethylammonium chloride) (PDADMAC, Sigma-Aldrich) was flushed for 2 minutes through the oxidised channel of the device. The PDADMAC binds to the activated channel walls by ionic interactions. Finally, a 2 wt.% solution of the negative polyelectrolyte poly(sodium 4- styrenesulfonate) (PSS, Sigma-Aldrich) was flushed for 2 minutes.

C. Droplet generation

Once the chips had been treated, we mounted syringes of oil and 0.1 wt.% aqueous TTAB solution to a microprecision syringe pump (NEM-B101-02B; Cetoni GmbH), and connected these to the two inlets of the microfluidic chip via Teflon tubing (39241; Novodirect GmbH), and tuned the flow speed through the chip until the desired droplet size was reached. Once droplet production was monodisperse (after approximately 5 minutes) and at a steady state, these droplets were collected in a bath of 0.1 wt.% TTAB solution. This solution is of a high enough concentration to stabilize the droplets against coalescence, but not high enough to induce solubilization.

D. Fabrication of the observation Hele-Shaw cell

The swimming behaviour of the droplets was observed in a Hele-Shaw reservoir, which we fabricated directly from SU-8 photoresist without PDMS casting. To fabricate the reservoirs
we therefore used a photo-mask with inverted polarity. We spin-coated the photoresist directly onto a glass slide (50×75 mm²) and followed the same procedure for photo-lithography as explained in the previous section. This resulted in a layer of crosslinked SU-8 (thickness ≈ 60 µm) with reservoirs of the dimensions 8 × 13 mm. These reservoirs were filled with the samples, sealed with a glass cover slip and put under a microscope.

E. Double-channel fluorescent microscopy technique

We used double-channel fluorescent microscopy for simultaneous imaging of the chemical and hydrodynamic fields. A schematic of the setup is shown in figure Fig. S3. Two laser units excite the test section. The Nile Red dye (Thermo Fisher Scientific), which visualises the oil phase, is excited with a 561 nm laser and emits light at a maximum of ∼ 630 nm. The green fluorescent particles (FluoSpheres™, yellow-green fluorescent, 500 nm in diameter), which visualise the fluid flow around the droplet, are excited with a 488 nm laser and emit light at a maximum of ∼ 510 nm. The emitted light was separated using a beam splitter and appropriate filters for each emission maximum. We also used a spatial pinhole (confocal microscopy) to enhance image quality. Examples of snapshots recorded on each channel are shown in figure Fig. S3b,c.

S2. IMAGE PROCESSING AND DATA ANALYSIS

To observe the long time statistical behaviour of the active droplets, as in Fig. 2, we observed their motion in a glass-bounded Hele-Shaw cell (quasi-two dimensional reservoir, 13 × 8 mm and height h ≈ 60 µm) under a bright field microscope (Leica DM4000 B) at low magnification (5×) compared to the double-channel fluorescence microscopy setup. Videos were recorded at a frame rate of 10 fps using a Canon (EOS 600d) digital camera (1920 × 1080 px). The droplet coordinates in each frame were extracted from video frames via standard Python libraries for numpy, PIL and openCV (scripts available on request). Steps include background correction, binarisation, blob detection by contour analysis and minimum enclosing circle fits. Swimming trajectories were obtained using a frame-by-frame nearest-neighbour analysis.

To acquire the kymographs of the chemical field and tangential and radial velocities
around the droplet interface, we observed the droplet behaviour by double-channel fluorescent microscopy as described in section S1 E. We used a 512 × 512 pixels camera at a frame rate of 14 fps connected to a 20× objective. First we split the red (NileRed, filled micelles) and green (tracer particles) channels. Then, the red frames were used to extract the droplet coordinates via the blob detection algorithm described above. We developed a MATLAB script that centred the droplet and recorded the red light intensity value along the interface at a distance 15.6 µm for Pe = 4 and 28 and 20.4 µm for Pe = 190. We note that it was not possible to record the intensity closer to the interface because the strong fluorescence from the large amounts of dye inside the droplet created a very bright region extending several micrometres beyond the actual interface. We plotted the extracted profiles versus time to generate spatiotemporal kymographs.

For a quantitative analysis of the flow field around the droplet we performed particle image velocimetry (PIV) on the tracer particles images (green channel) using the MATLAB-based PIVlab interface [47]. The objective was focused on the mid-plane of the Hele-Shaw cell.
We defined a moving mask for the area covered by the droplet. We performed the analysis in 16 × 16 pixel interrogation windows with 75% overlap. After obtaining the velocity vector field, we centred the the droplet and read the velocity vectors at a certain distance from the droplet interface (3.6 $\mu$m for $Pe = 4$ and 28 and 8.4 $\mu$m for $Pe = 190$). The tangential ($u_\theta$, in the droplet reference frame) and radial ($u_r$, only for $Pe = 190$, in the lab reference frame) velocity components were then calculated and plotted in kymographs. Due to the no-flux boundary condition at the interface the radial component of the velocity is supposed to be zero. However, since we read the values at a certain distance we were able to observe the radial inward and outward flows. In particular, this was done for $Pe = 190$ to show the quadrupolar symmetry of the flow field at the stopping moment.

In Fig. 1a and supplementary video S1, we tracked the droplet and centred it in the image. To obtain the pathlines of the tracer particles in the video we used FlowTrace [48] to convolve a superposition of 10 frames for each image. For Fig. 1a we superimposed 30 frames. To visualise the motion of the tracer particles in Fig. 4b,IV and the supplementary videos S6-S9, we processed the green channel of the input video (8 bit RGB) as follows: for each pixel coordinate, the intensity was replaced by its standard deviation within a 20 frame window around the current frame. Each frame was subsequently contrast maximised within a [0, 255] intensity range. The red and blue channels were not modified. This procedure was inspired by ImageJ’s Z projection algorithm; the respective Python code is available on request.

S3. VISCOSITY DEPENDENCE OF HYDRODYNAMIC MODES

A. Governing equations and boundary conditions for the active droplet system

Considering an axisymmetric Stokes flow (Reynolds no. for the swimming of the active droplet $Re \sim 10^{-4}$), and the impermeability of the droplet interface, the flow field around and inside the spherical active droplet (capillary number $Ca << 1$) can be expressed in terms of the non-dimensional stream function $\psi$, in $(r, \theta)$ co-ordinate system, as [19, 20, 24]:

25
$$\psi^o = a_1 \left( \frac{1}{r} - r^2 \right) (1 - \eta^2)P'_1(\eta)$$

$$+ \sum_{n=2}^{\infty} a_n \left( \frac{1 - r^2}{r^n} \right) (1 - \eta^2)P'_n(\eta)$$

$$\psi^i = \sum_{n=1}^{\infty} b_n (r^{n+1} - r^{n+3})(1 - \eta^2)P'_n(\eta)$$

(S1)

(S2)

Here, and in the subsequent discussions, superscripts ‘o’ and ‘i’ refer to quantities outside and inside the active droplet respectively, \(r\) is the radial coordinate non-dimensionalised by droplet radius \(R_d\), \(\eta = \cos \theta\), and \(P_n(\eta)\) is the Legendre polynomial of degree \(n\) with the prime denoting its derivative; \(n\) here physically represents the \(n^{th}\) hydrodynamic mode.

The non-dimensional radial and tangential flow velocity components around and inside the droplet are related to \(\psi\) as

\[ u_r = -\frac{1}{r^2} \frac{\partial \psi}{\partial \eta} \quad \text{and} \quad u_\theta = -\frac{1}{r (1 - \eta^2)^{1/2}} \frac{\partial \psi}{\partial r} \]

The coefficients \(a_n\) and \(b_n\) in Eqs. S1 and S2 are constrained by the following boundary conditions [19, 24]:

(i) tangential velocity \((u_\theta)\) condition at the droplet interface \((r = 1)\):

\[ u_\theta^o - u_\theta^i = m \left( \frac{2\mu + 3}{1 + 3m} \right) (1 - \eta^2)^{1/2} \left( \frac{\partial c}{\partial \eta} \right)_{r=1} \]

(S3)

(ii) tangential stress \((\tau_{r\theta})\) condition at the droplet interface \((r = 1)\) (Marangoni effect):

\[ \tau_{r\theta}^o - \tau_{r\theta}^i = -\frac{1}{\mu} \left( \frac{2\mu + 3}{1 + 3m} \right) (1 - \eta^2)^{1/2} \left( \frac{\partial c}{\partial \eta} \right)_{r=1} \]

(S4)

The coefficients on the right hand side of Eqs. S3 and S4 essentially stem from the non-dimensionalization of the classical boundary conditions. Note that the flow velocity is non-dimensionalized using \(V_t = \frac{q_t(\gamma c R_d + 3\mu^o M)}{D(2\mu^o + 3\mu^o)}\), which is a theoretical estimate for the terminal velocity of the active droplet considering the contributions of both the Marangoni and the diffusiophoretic effects [19, 21]. Furthermore, \(\mu\) is the ratio of the swimming medium viscosity \(\mu^o\) to the droplet viscosity \(\mu^i\), and the non-dimensional parameter \(m\) represents the relative strengths of diffusiophoretic to Marangoni effects [19]. Essentially, \(m\) can be considered as a ratio of the diffusiophoretic velocity scale to the viscocapillarity velocity scale representing the Marangoni effect. Accordingly, \(m = \frac{\mu^i M}{\gamma c R_d} \approx \frac{\zeta}{2R_d \mu}\), where \(M \approx \frac{k_B T \zeta^2}{2\mu^o}\) is the diffusiophoretic mobility [18, 21], \(\gamma c \approx k_B T \zeta\) is the leading order change in the interfacial surface tension \(\gamma\) with surfactant concentration \(c\) (alternatively, \(\gamma c = \frac{d\gamma}{dc}\) can be considered to be a measure of the change in \(\gamma\) with \(c\) assuming a linear variation) [18, 19], and \(\zeta \sim 10\).
nm is the characteristic length scale over which the surfactants interact with the droplet in the interfacial region. For the active droplet system, $O(m) \sim 10^{-3} - 10^{-2}$ for the entire range of experiments; hence, for the present physical problem the diffusiophoretic effect is much weaker as compared to the Marangoni effect. However, the former is considered in the analysis here for the sake of generality. In the definition of $V_t$, $q_s$ is an isotropic and constant interfacial surfactant consumption rate per unit area necessary for the droplet activity, and $D = \frac{k_B T}{6\pi r_s \mu_o}$ is the diffusion coefficient for the surfactant monomer (length scale for surfactant monomer $r_s \sim 10^{-10}$ m).

Eqs. S3 and S4 delineate the dependence of the swimming hydrodynamics on the distribution of the non-dimensional surfactant concentration $c$ in the vicinity of the droplet. Naturally, $c$ is governed by an advection-diffusion relation [19, 20, 24]:

$$\text{Pe} \left[ u_r^0 \frac{\partial c}{\partial r} - u_\theta^0 \frac{1}{r} (1 - \eta^2)^{1/2} \frac{\partial c}{\partial \eta} \right] = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) + \frac{1}{r^2} \frac{\partial}{\partial \eta} \left( (1 - \eta^2) \frac{\partial c}{\partial \eta} \right) \quad (S5)$$

The distribution of $c$ is subject to the following boundary conditions:

(i) **isotropic and constant surfactant consumption at the droplet interface** ($r=1$)

$$\left( \frac{\partial c}{\partial r} \right)_{r=1} = 1 \quad (S6)$$

(ii) **the bulk condition**

$$c(r \to \infty) \to c_\infty \quad (S7)$$

Note that Eq. S6 addresses the depletion of the interfacial surfactant monomers due to the creation of the filled micelles by considering the isotropic and constant interfacial surfactant adsorption rate per unit area of $q_s$, corresponding to a flux with unit of number per area per time (in dimensional form: $D \nabla c^* \cdot \hat{n} = q_s$; this gives a scale for the surfactant concentration as $\sim \frac{q_s R_d}{D}$) [19, 20]. $Pe$ in Eq. S5 is the system Péclet number— the details of which are discussed in the following sub-section. The above system of equations (Eqs. S1–S7) can be solved for $\psi$ (therefore $u_r$, $u_\theta$), and $c$ using the singular perturbation technique for certain limiting cases [19, 20]. The solvability condition clearly shows that the actuations of different hydrodynamic modes depend on certain threshold values of $Pe$ (Fig. 4a in the main
text) [19]. Furthermore, the asymptotic analysis also provides a physical understanding of the hydrodynamic and surfactant concentration fields corresponding to the different modes, specifically $n = 1$ and $n = 2$ (Fig. 4b in the main text).

B. The system Pclet number

The important thing to understand now is the dependence of $Pe$ on $\mu$. Classically, $Pe$ can be written as $Pe = \frac{V_t R_d}{D}$, where $V_t = \frac{q_s (\gamma_c R_d + 3 \mu i M)}{D (2 \mu^o + 3 \mu i)}$ is the theoretical estimate for the terminal velocity of the active droplet considering the contributions of both the Marangoni and diffusiophoretic effects, as mentioned in the preceding sub-section [19, 21]. Utilizing the aforementioned definition of $V_t$, and following some simple algebraic manipulations, $Pe$ can be expressed in terms of system constants and the parameter $\mu$ as:

$$Pe = \frac{V_t R_d}{D} = \frac{q_s (\gamma_c R_d + 3 \mu i M) R_d}{D (2 \mu^o + 3 \mu i) D}$$

$$\Rightarrow Pe = \frac{q_s M (1 + 3m) R_d}{D m (2 \mu + 3)}$$

$$\Rightarrow Pe \approx \frac{18 \pi^2}{k_B T} q_s r_s^2 \zeta R_d^2 \mu \left[ \mu \left( \frac{2 \mu + 3 \zeta / R_d}{2 \mu + 3} \right) \right]$$

In the last step of Eq. S8, the approximate expressions for $M$ and $m$ (see sub-section 2.1), and the definition of $D$ (see sub-section 2.1) are utilized to derive the final expression for $Pe$. Eq. S8 expresses $Pe$ as a monotonically increasing function of the viscosity ratio $\mu$ (markers in Fig. 4a in the main text). It must be noted that $q_s$ is approximately estimated by relating the dissolution rate of the active droplet to the isotropic and constant surfactant consumption at the droplet interface [18]. We further note that the second term in the numerator within parenthesis $O \left( \frac{\zeta}{R_d} \right) \sim 10^{-4}$; this further substantiates the fact that the diffusiophoretic effect is much weaker compared to the Marangoni effect for the present system.

C. Linear stability analysis about a motionless (isotropic) base state

For the linear stability analysis (also see [17, 20]), the time-dependent form of the advection-diffusion equation (Eq. S5) is used:
\[ Pe \left[ \frac{\partial c}{\partial t} - \frac{1}{r^2} \frac{\partial \psi \partial c}{\partial \eta \partial r} + \frac{1}{r^2} \frac{\partial \psi}{\partial \eta} \frac{\partial c}{\partial r} \right] = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) + \frac{1}{r^2} \frac{\partial}{\partial \eta} \left( (1 - \eta^2) \frac{\partial c}{\partial \eta} \right) \]  

(S9)

Next, the desired quantities are expressed in terms of the unsteady (instability) modes—\( \psi = e^{\lambda t} \sum_n \tilde{\psi}_n(r) P_n(\eta) \) and \( c = -\frac{1}{r} + e^{\lambda t} \sum_n \tilde{c}_n(r) P_n(\eta) \), where \( \lambda > 0 \) is the non-dimensional growth rate for the instability modes. Using the aforementioned expressions for \( \psi \) and \( c \), and linearizing Eq. S9, the governing equations for the first two modes can be obtained as:

\[
\frac{d}{dr} \left( r^2 \frac{d\tilde{c}_1}{dr} \right) - (2 + \lambda_s^2 r^2) \tilde{c}_1 = 2 Pe a_1 \frac{1 - r^3}{r^3} \]  

(S10)

\[
\frac{d}{dr} \left( r^2 \frac{d\tilde{c}_2}{dr} \right) - (6 + \lambda_s^2 r^2) \tilde{c}_2 = 6 Pe a_2 \frac{1 - r^2}{r^4} \]  

(S11)

where \( \lambda_s = \sqrt{\lambda Pe} \), and \( a_1 \) and \( a_2 \) are the coefficients of the first and second modes respectively of the outer stream function (as in Eq. S1). Eqs. S10 and S11 are solved to evaluate \( \tilde{c}_1 \) and \( \tilde{c}_2 \), respectively:

\[
\tilde{c}_1 = Pe a_1 \left( \frac{2}{x^2} + \frac{\lambda_s^3}{2x^3} \right) + \alpha_1 \left( \frac{1 + x}{2x^2} \right) e^{-x} - Pe a_1 \lambda_s^3 \frac{4}{4x^2} \left[ \left( \frac{1 + x}{2} \right) (Chi(x) + Shi(x)) e^{-x} - \left( \frac{1 - x}{2} \right) (Chi(x) - Shi(x)) e^x \right] \]  

(S12)

\[
\tilde{c}_2 = Pe a_2 \frac{1}{8} \left( \frac{8\lambda_s^4}{x^4} + \frac{\lambda_s^4}{2x^3} - \frac{6\lambda_s^2}{2x^2} \right) + \alpha_2 \left( \frac{x^2 + 3x + 3}{2x^3} \right) e^{-x} + Pe a_2 \lambda_s^2 \frac{6 - \lambda_s^2}{16x^3} \left[ \left( x^2 + 3x + 3 \right) (Chi(x) + Shi(x)) e^{-x} - \left( x^2 - 3x + 3 \right) (Chi(x) - Shi(x)) e^x \right] \]  

(S13)

Here, \( x = r\lambda_s \) is a rescaled spatial variable, \( Chi(x) \) and \( Shi(x) \) are the hyperbolic cosine integral and hyperbolic sine integral functions, and \( \alpha_1 \) and \( \alpha_2 \) are the constants of integration. Note that Eqs. S12 and S13 are evaluated in a manner which satisfies the bulk condition for the surfactant distribution (Eq. S7) i.e. as \( r \to \infty, \ c - c_\infty \to 0 \). Furthermore, considering the expression for \( c \), the interfacial surfactant consumption condition (Eq. S6) reduces to the form:
\[
\left( \frac{\partial c}{\partial r} \right)_{r=1} = 1 \Rightarrow \left( \frac{d\tilde{c}_1}{dx} \right)_{x=\lambda_s} = 0; \quad \left( \frac{d\tilde{c}_2}{dx} \right)_{x=\lambda_s} = 0
\] (S14)

Using Eqs. S12 and S14, \( \alpha_1 \) can be evaluated as:

\[
\alpha_1 = -Pe \frac{e^{\lambda_s}}{4(\lambda_s^2 + 2\lambda_s + 2)} \left[ 2(\lambda_s^4 + 6\lambda_s^2 + 16) + \lambda_s^3 (\lambda_s^2 - 2\lambda_s + 2) (Chi(\lambda_s) - Shi(\lambda_s)) e^{\lambda_s} \right.
\]
\[
- \lambda_s^3 (\lambda_s^2 + 2\lambda_s + 2) (Chi(\lambda_s) + Shi(\lambda_s)) e^{-\lambda_s} \right]
\] (S15)

Similarly, using Eqs. S13 and S14, \( \alpha_2 \) can be evaluated as:

\[
\alpha_2 = Pe \frac{\lambda_s^2 e^{\lambda_s}}{8(\lambda_s^2 + 4\lambda_s^2 + 9\lambda_s + 9)} \left[ -2\lambda_s (5\lambda_s^2 + 2) + (\lambda_s^2 - 6) (\lambda_s^3 - 4\lambda_s^2 + 9\lambda_s - 9) \right.
\]
\[
\times (Chi(\lambda_s) - Shi(\lambda_s)) e^{\lambda_s} + (\lambda_s^2 - 6) (\lambda_s^3 + 4\lambda_s^2 + 9\lambda_s + 9) (Chi(\lambda_s) + Shi(\lambda_s)) e^{-\lambda_s} \right]
\] (S16)

Eqs. S12 and S13, along with Eqs. S15 and S16, give closed form expressions for \( \tilde{c}_1 \) and \( \tilde{c}_2 \).

Considering the hydrodynamic boundary conditions (Eqs. S3 and S4), and using the orthogonality condition for Legendre polynomials, a set of two simple algebraic equations for the co-efficients \( a_n \), and \( b_n \) for each of the first two modes can be written as:

(i) first mode \((n = 1)\)

\[
3a_1 - 2b_1 = m \left( \frac{2\mu + 3}{1 + 3m} \right) \tilde{c}_1
\] (S17)

\[
\mu a_1 + b_1 = \frac{1}{6} \left( \frac{2\mu + 3}{1 + 3m} \right) \tilde{c}_1
\] (S18)

(ii) second mode \((n = 2)\)

\[
a_2 - b_2 = \frac{m}{2} \left( \frac{2\mu + 3}{1 + 3m} \right) \tilde{c}_2
\] (S19)

\[
\mu a_2 + b_2 = \frac{1}{10} \left( \frac{2\mu + 3}{1 + 3m} \right) \tilde{c}_2
\] (S20)

Note that \( \tilde{c}_n \) in the above equations is explicitly dependent on \( a_n \) (see Eqs. S12, S15 and S13, S16). Considering the closed form expression for \( \tilde{c}_1 \) (Eq. S12 and S15), the solvability condition for Eq. S17 and S18 gives:
\[- \frac{(Chi(\lambda_s) - Shi(\lambda_s)) e^{\lambda_s} \lambda_s^4 - \lambda_s^3 + \lambda_s^2 - 2\lambda_s + 6}{12 (\lambda_s^2 + 2\lambda_s + 2)} = \frac{1}{Pe} \]  

(S21)

Similarly, considering the closed form expression for \( \hat{c}_2 \) (Eq. S13 and S16), the solvability condition for Eq. S19 and S20 gives:

\[- \frac{(6 - \lambda_s^2) (Chi(\lambda_s) - Shi(\lambda_s)) e^{\lambda_s} \lambda_s^4 + (\lambda_s^2 + 2\lambda_s + 2) (\lambda_s^3 - 3\lambda_s^2 + 6)}{8 (\lambda_s^3 + 4\lambda_s^2 + 9\lambda_s + 9)} = \frac{10 (1 + \mu)(1 + 3m)}{Pe (2\mu + 3)(1 + 5m)} \]  

(S22)

Eqs. S21 and S22 are solved numerically to evaluate the variations of the non-dimensional growth rates \( \left( \lambda = \frac{\lambda_s}{Pe} \right) \) with \( Pe \) for the first and second instability modes respectively (Fig. 4c in the main text). Note that Eq. S21 is identical to that derived for the spontaneous motion of an autophoretic isotropic particle [17]. Furthermore, it is important to note here that the inverse of the time scale used for non-dimensionalizing the growth rate is \( \frac{V_t R_d}{\eta} \), which is consistent with the entire analysis.

S4. SUPPLEMENTARY FIGURES

Complementary to Fig. 3, Fig. S4 provides the chemical field kymographs plotted for 60 seconds. They include more frames of the transient behaviour of the swimmers. Videos S6-8 respectively correspond to the kymographs in Fig. S4 (a-c).

In Fig. S5, we have plotted the long-time tangential acceleration, speed and the reorientation angle for \( Pe = 28 \). This data set was used to identify the abrupt reorientation events. We identified these events based on the cutoff criterion \( |\delta \theta| = 0.2 \) rad (Fig. S5 c & d), then, aligned and overlaid the profiles of all events with the turning point (\( |\delta \theta_{max}| \) set as \( t = 0 \), and finally, calculated the average over time (\( \langle \rangle \) represents ensemble averaging over all events).

Signatures of bimodal space exploration can be seen in the long time acceleration signal for \( Pe = 190 \) plotted in Fig. S6. Such events can be identified as intermittent strong fluctuations in the acceleration profile. The zoomed in further demonstrates the difference between stopping \( (n = 2) \) and swimming modes \( (n = 1) \). A swimming strategy that results in anomalous diffusive behaviour is shown in Fig. 6.
FIG. S4. Kymographs of the chemical field with selected instantaneous frames. Rows a, b and c respectively correspond to $Pe = 4$, $Pe = 28$ and $Pe = 190$. In (b) the red arrow shows the location of the growing filled micelle blob. For the velocity kymographs refer to Fig. 3.
FIG. S5. Conditional averaging over reorientation events. a, b, and c are tangential acceleration, speed and the reorientation angle magnitude, respectively. In (c), the identified sharp reorientation events are shown by grey (◦) symbols. The zoomed in view is one example event that shows the general trend. The delay, \( \tau_1 \), between \( |\delta \theta| \) and \( |V| \) can be seen. (d) The distribution of \( |\delta \theta| \) and the cutoff value. The sharp turning events are shown with red colour.
FIG. S6. Signatures of bimodal space exploration in the long-time tangential acceleration signal.

The corresponding $Pe$ is 190.
S5. SUPPLEMENTARY MOVIES

Fig. S7-Fig. S11 provide thumbnail previews and explanatory captions for the supplementary movies. All movies are available for viewing under http://asm.ds.mpg.de/index.php/media/#stopandgo2020
FIG. S7. Supplementary Video S1. Simultaneous visualisation of hydrodynamic and chemical field. The videos from splitting colour channels (red and green) and the composite image obtained through double-channel fluorescent microscopy. The droplet is tracked and centred. The particle pathlines are obtained by superposition of 10 frames for each image. The video is played 1.5× faster than the real time.

FIG. S8. Supplementary Video S2-S5. The trajectories colour-coded with speed value. From left to right S2, S3, S4 and S5 correspond to $Pe = 4\ (\mu^o = 1.2\ \text{mPa.s})$, $Pe = 16\ (\mu^o = 2.6\ \text{mPa.s})$, $Pe = 71\ (\mu^o = 5.5\ \text{mPa.s})$ and $Pe = 667\ (\mu^o = 17.4\ \text{mPa.s})$. The increase in the swimming medium viscosity destabilises the propulsion dynamics. The videos are played 5× faster than the real time.

FIG. S9. Supplementary Video S6-S8. The kymographs of chemical fields ($I(\theta)$), tangential velocity component ($u_\theta$) and radial velocity component ($u_r$, only for $Pe = 190$). From left to right S6, S7 and S8 correspond to $Pe = 4$, $Pe = 28$ and $Pe = 190$. The particle pathlines are obtained by superposition of 20 frames for each image. Interactions with solubilisation history results in the emergence of unsteady spatiotemporal dynamics. The videos are played 3× faster than the real time.
FIG. S10. **Supplementary Video S9.** Growth and accumulation of filled micelle blob in the leading front of the droplet resulting in sharp reorientation. The corresponding $Pe$ is 28. First, the red channel is shown and later the green channel with the tracer particles pathlines are superimposed. The short-lived appearance of the quadrupolar flow field is followed by transitioning to the dipolar flow field.

FIG. S11. **Supplementary Video S10.** Temporal variation of propulsion speed during a sharp reorientation event, due to interaction with the secondary filled micelles aggregate. The trajectory of the droplet is colour-coded with instantaneous speed. The corresponding $Pe$ is 28.