Two-dimensional nature of the active Brownian motion of catalytic microswimmers at solid and liquid interfaces

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Keywords: colloids, active matter, liquid interfaces, catalytic microswimmers, self-propelled particles

Abstract
Colloidal particles equipped with platinum patches can establish chemical gradients in \( \text{H}_2\text{O}_2 \)-enriched solutions and undergo self-propulsion due to local diffusiophoretic migration. In bulk (3D), this class of active particles swim in the direction of the surface heterogeneities introduced by the patches and consequently reorient with the characteristic rotational diffusion time of the colloids. In this article, we present experimental and numerical evidence that planar 2D confinements defy this simple picture. Instead, the motion of active particles both on solid substrates and at flat liquid–liquid interfaces is captured by a 2D active Brownian motion model, in which rotational and translational motion are constrained in the \( xy \)-plane. This leads to an active motion that does not follow the direction of the surface heterogeneities and to timescales of reorientation that do not match the free rotational diffusion times. Furthermore, 2D-confinement at fluid–fluid interfaces gives rise to a unique distribution of swimming velocities: the patchy colloids uptake two main orientations leading to two particle populations with velocities that differ up to one order of magnitude. Our results shed new light on the behavior of active colloids in 2D, which is of interest for modeling and applications where confinements are present.

Main text
Self-propelling colloidal particles, originally inspired to mimic living microorganisms, offer exciting opportunities to engineer smart active materials [1]. Amongst them, catalytic microswimmers have for instance been realized using Janus particles [2–5]. These are colloidal particles (e.g., silica spheres) equipped with a surface patch (e.g., a platinum coating) that can catalyze the chemical reaction of a ‘fuel’ present in the medium (e.g., \( \text{H}_2\text{O}_2 \) decomposed into \( \text{H}_2\text{O} \) and \( \text{O}_2 \)), leading to an asymmetric chemical gradient around the particles and subsequent propulsion by phoretic forces [6].

The magnitude of the swimming velocity for a single particle, \( V \), is given by the local fuel concentration [2]. The direction of motion is along the asymmetry axis of the particle (i.e. the axis that links the poles of the two different surface portions of a spherical Janus particle) and reorients with a characteristic time \( \tau \) set by the particle size, the solvent viscosity and thermal energy [2, 7]. Importantly, in the absence of gravitational effects [8] or interactions with confinements [9–11], the unit vector representing the direction of motion is allowed to freely diffuse on the surface of a unit sphere, so that reorientation occurs in 3D. Therefore, the resulting self-propelled motion can be described by a 3D active Brownian motion model [12, 13].

\( V \) and \( \tau \) are responsible for complex phenomena including clustering [14, 15], active self-assembly [16, 17] and swarming [18], and can be altered using external fields (e.g. magnetic [19] and optical [20, 21]) or by modifying the swimmer’s geometry [22–25]. However, this simple picture is strictly valid only for free-swimming particles. The presence of physical confinement such as planar walls [9, 10, 26, 27], interfaces [28–31], microchannels [11] or fixed obstacles [32] can affect \( V \) and \( \tau \) and lead to active trajectories that are quantitatively

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and qualitatively different from those in bulk. These differences have important consequences when modeling the particle’s active motion or when exploiting it for applications.

Here, we experimentally and numerically study the active motion of spherical catalytic microswimmers in the presence of two different sources of planar confinement: a solid substrate and a liquid–liquid interface. In both cases, we demonstrate that the presence of the planar confinement not only constrains the translational motion of the particle to the xy-plane, but also constrains their orientation, so that the unit vector representing the direction of motion only diffuses on a circle. A 2D active Brownian motion model is therefore required to describe the resulting active trajectories successfully. Furthermore, we observe that planar confinement entails that the direction of propulsion does not correspond to the asymmetry axis of the active particles. At fluid–fluid (oil–water) interfaces, rotational diffusion is also slowed down due to local pinning of the three-phase contact line and the effective swimming velocity is determined by the particle orientation with respect to the interfacial plane. Interestingly, two populations are observed: we see slow and fast particles corresponding to Pt coatings immersed mostly in the water or in the oil phase, respectively. Our results ultimately show that two-dimensionally confined active particles show a radically different behavior compared to the simple expectations of a bulk model. Understanding and harnessing this behavior is both of high interest for the physics of active systems under confinement and to design and engineer active systems with novel physical properties, e.g. a persistency or speed tunable by contact line properties at fluid interfaces.

Results

Our model microswimmers consist of fluorescent, platinum-coated Janus polystyrene microspheres (radius $R = 1.4 \, \mu m$, thickness of the Pt-layer $= 2 \, nm$) which self-propel in $H_2O_2$-enriched aqueous solutions due to the catalytic reaction promoted by the Pt-patch [2]. Experiments are carried out in a custom cell as illustrated in figures A1(a) and (b). When dispersed in water/$H_2O_2$ solutions (figure A1(a)) the particles sediment onto the bottom glass slide. For experiments at fluid interfaces (figure A1(b)), we spread a diluted (0.35% w/v) suspension of Janus particles at a flat interface between $H_2O_2$-enriched water ([H$_2$O$_2$]$_{vol}$ up to 3%) and ultrapure hexadecane (Arcos Organics). After spreading, the particles remain irreversibly confined at the interface and their vertical position with respect to the oil–water interface is described by each contact angle $\theta$ [37]. The water reservoir ensures that the $H_2O_2$ concentration is kept constant throughout each entire experiment, lasting up to 20–30 min. The active motion is imaged using a fluorescence microscope and a CMOS camera at 5 fps and trajectories are later analyzed with custom Matlab codes. Details of the particle fabrication and the sample preparation are in the methods section.

Figures A1(c) and (d) show some active trajectories of 40 s duration at three different $H_2O_2$ concentrations on the glass substrate and at the water–oil interface. Here and in the following, we consistently use blue and red colors for data that correspond to particles on the substrate and at the fluid interface, respectively. The particles’ effective diffusivity (i.e., the ability of the swimmers to self-propel away from their initial position) and persistency (i.e., the propensity to swim in straight paths) both grow with $H_2O_2$ concentration [2, 29], on the substrate (figure A1(c)) as well as at the fluid–fluid interface (figure A1(d)). All the active trajectories at the substrate look alike for any given $H_2O_2$ concentration (figure A1(c), only one example per concentration shown), whereas confinement at the interface leads to qualitatively very distinct trajectories within a single experiment for all $H_2O_2$ concentrations (the red traces in figure A1(d) have the same time duration but very different persistence length and effective diffusion). The same qualitative behavior is displayed in the supplemental movies S1 (substrate) and S2 (interface).

Figures 1(a) and 2(a) show the mean swimming velocities $\nabla$ calculated using the time derivative of spatial displacements at consecutive frames, for different $H_2O_2$ concentrations, averaged on all particles (methods). Without $H_2O_2$, the particles exhibit Brownian diffusion with diffusion coefficients $D_{0.5}$ and $D_{0.1}$ which are extracted from the slope of the linear MSD, on the substrate and at the interface, respectively (methods). The increase of $\nabla$ with [H$_2$O$_2$] qualitatively agrees with previous works on catalytic active particles [2], even though the measured velocities are considerably larger in our experiments due to the use of non-stabilized H$_2$O$_2$ (methods). At the interface, $\nabla$ is reduced by a factor 2–3, which could be explained by the increase of the friction coefficient at the oil–water interface ($D_f$ for passive particles is also approximately 2–3 times smaller at the interface, as shown in methods). Nonetheless, the large standard deviations of the red data are a clue that catalytic particles at liquid–liquid interfaces feature a more complex behavior, which is investigated in the remainder of the manuscript.

In order to gain insight on the type of motion performed by the particles, we first compare the experimental velocity distributions $p(V)$ with the distributions obtained from Brownian dynamics simulations [13]. We have considered two different models for the active motion of our microswimmers based on the ABP model (methods): a first one where the ABP rotational diffusion occurs in three dimensions (ABP-3D, dark gray), and a
second one where it occurs in two dimensions (ABP-2D, light gray). In both models, we use the average experimental speeds as input parameters and compute the resulting velocity distributions. On the substrate (figure 1(b)), the experimental data agree with the ABP-2D model, i.e. the boundary wall hinders 3D rotational diffusion of catalytic swimmers and rotation only occurs within an \(xy\)-plane parallel to the glass substrate \([9–11, 20, 38]\). Figure 1(c) shows the velocity distributions of \(\sim 30\) active particles at the substrate (each curve corresponds to the \(p(V)\) of a single active particle). Increasing \([\text{H}_2\text{O}_2]\), the velocity distributions shift towards larger values but the underlying physics remains the same, i.e. there exists one population of swimmers undergoing 2D active Brownian motion with a given velocity. When we examine the motion of particles adsorbed at the liquid–liquid interface, we again measure velocity distributions that are consistent with the ABP-2D model (figure 2(b)). Here, 3D-rotation out of the interface plane is prevented by pinning of the three-phase contact line (water–oil–particle) when the colloids are irreversibly adsorbed at the interfacial plane \([37, 39]\), as it will be discussed later. However, as opposed to particles that swim on the substrate, in figure 2(c) two distinct populations of active colloids are clearly present for any \([\text{H}_2\text{O}_2]\). The two populations correspond to slow and fast self-propelling particles. The existence of these two populations is directly linked to the configuration of the particles at the liquid–liquid interface, i.e. to their orientation and contact angle. The configuration in turn determines how the swimmers exploit the \(\text{H}_2\text{O}_2\) ‘fuel’ dissolved in water, i.e. the shape and the strength of the chemical gradients.

To gain information about particle orientation and contact angle, we carried out complementary GTT \([34]\) and FreSCa \([35]\) cryo-SEM measurements. A detailed description of the procedures is given in the methods section. Briefly, the particles are immobilized at the interface, either by gelling the water phase or by shock-freezing, and are later imaged using a SEM (figures 3(a) and (b)) operated in back-scattering mode. This imaging mode is sensitive to material contrast and unveils the orientation of Pt cap with respect to the interfacial plane.
High-brightness regions correspond to the metal cap. SEM images of GTT (figure 3(a)) show a view of the interface from the water side, whereas in FreSCa (figure 3(b)) the observation takes place from the oil side. In figures 3(a) and (b) we distinguish two main particle configurations of distinctively different brightness, corresponding to particles with the platinum cap facing either the oil or the water phase, respectively. Very few
particles are slightly tilted and none has the asymmetric axis parallel to the xy-plane (i.e., plane corresponding to the interface). We combined these observations with independent measurements of the contact angle \( \theta \) of the particles (figure 3(c)), done by scanning the GTT samples with an AFM tip [36] (methods). Figure 3(c) shows \( \theta \) for identical uncoated (green) and Pt-coated (brown) PS particles. Both batches display a similar protrusion height (corresponding to \( \theta = 123^\circ \pm 8^\circ \) and \( \theta = 104^\circ \pm 10^\circ \) for bare and coated particles), suggesting that the two families observed in figures 3(a) and (b) correspond to the Pt or the PS surface crossing the interface. The small difference in contact angle implies that the two populations have rather similar immersion depths. The values of the single-particle contact angles agree very well with macroscopic contact angle measurements of water droplets on flat Pt-coated and uncoated PS substrates immersed in hexadecane (contact angles of \( \theta = 129.2^\circ \) and \( \theta = 102.0^\circ \) for bare and coated PS surfaces, respectively—see methods). These measurements reveal that the Pt-coated surface is slightly hydrophobic and that a low wettability contrast between the two hemispheres of the Janus swimmers exists, implying that both the bare PS surface and the Pt coating can be exposed to the oil.

After revealing the particle configurations at the interface, we use fluorescence microscopy to determine the link between particle orientation and swimming speed. In figure 4(a), the sample is observed from below through the water phase and the brightness of each particle is measured while tracking its active motion. In particular, the measured fluorescence brightness \( I \) of each swimmer, normalized by the maximum brightness \( I_{\text{max}} \) (defined as the total intensity of a fully saturated circular region around the particle center), is directly connected to the orientation of the Pt cap (see also figure S1(a)). In fact, when the Pt cap is oriented downwards into the water phase (figure 4(c)), it largely screens the emitted fluorescence and the particle appears darker, while, when the cap points up (figure 4(b)), the fluorescent light is not screened and the particle appears brighter. All particles show self-propulsion, indicating that parts of both the Pt and PS surfaces are always exposed to the water phase for both cap orientations (see sketches in figures 4(b) and (c)). A wetting configuration corresponding to the equilibrium contact angle of the PS surface \( \theta \sim 120^\circ – 130^\circ \), would see no exposure of the Pt to the fuel, and thus no propulsion (see figure 4(d)). Analogously, the configuration corresponding to the equilibrium contact angle of the Pt cap (\( \theta \sim 100^\circ – 105^\circ \)) depicted in figure 4(e), would also not trigger any self-propulsion since no ‘fuel’ gradient is established in the water, despite Pt being exposed to \( \text{H}_2\text{O}_2 \). The origin of self-propulsion is therefore connected to contact line undulations (see inset of figure 3(a)), which lead to the exposure of both Ps and Pt surface portions upon adsorption. Comparing configurations 4(b) and (c) with the data in figure 4(a), we conclude that low brightness values, i.e., particles with maximum immersion of Pt in the water phase, correspond to the slow-swimming population (\( \sim 20\% \) of the total number of particles), whereas colloids with the Pt in oil (\( \sim 80\% \) of the total number of particles) propel up to ten times faster. This observation defies the misleading intuition that Janus swimmers always navigate along the asymmetry axis and that more catalytic material exposed to the water/\( \text{H}_2\text{O}_2 \) solution leads to faster propulsion. Phoretic microswimmers are exclusively driven by local concentration gradients (i.e., reactants and products of the catalytic decomposition of \( \text{H}_2\text{O}_2 \)) between the Pt-coated and the bare PS portions of the particle surface: the steeper the gradients, the faster

![Figure 4](image.png)
the propulsion. Due to the presence of the interface, the reactant is only found on one side of the particle and the diffusion of the reaction products is hindered by the presence of the oil phase; as a consequence, concentration gradients form preferentially in the direction parallel to the interface. A smaller Pt patch exposed to water (figure 4(b)) allows creating more pronounced gradients compared to the case when most of the coating is immersed in water (figure 4(c)).

The persistence length $L$ and the effective diffusion coefficient $D_{\text{eff}}$ of the trajectories shown in figures A1(c) and (d) are determined not only by the swimming speed $V$ but also by the characteristic (2D) reorientation time $\tau_r$, i.e. $L = V\tau_r$ and $D_{\text{eff}} = D_0 + 1/2V^2\tau_r$, where $D_0$ is the Brownian diffusion coefficient [1]. For each active particle trajectory, we extract $\tau_r$ from the fitting of the 2D MSD [1, 33], with $D_0$ and $V$ as fixed parameters (methods).

Figure 5(a) shows the probability distributions of the reorientation times $\tau_r$, $p(\tau)$, for $\sim 1000$ active particles. The width of $p(\tau)$ is narrower for particles that self-propel on the solid substrate compared to colloids that swim at the fluid–fluid interface. The mean value of the reorientation times averaged over all particles for a given $\text{H}_2\text{O}_2$ concentration $\tau_r$ does not depend on the amount of fuel (figure 5(b)) and, on average, is ten times larger at the interface. In table 1, we report the mean values of the reorientation times calculated over all particles, at the substrate $\tau_s$, and at the interface $\tau_I$ (corresponding to the solid lines in the graph). We also compare them with the free rotational diffusion time $\tau_R = 8\pi\eta R^2/k_BT$ of a sphere of radius $R$, where $\eta$ is the fluid viscosity and $k_BT$ is the thermal energy. Since at the interface the particles experience drag both from the water and the oil phase, we calculate the bounds of $\tau_R$ using either the water ($\tau_{R,W}$) or the oil ($\tau_{R,O}$) viscosity only. Experimental values of the Brownian diffusion times $R^2/D_{0,5}$ (substrate) and $R^2/D_{0,1}$ (interface) are also reported. In water and next to the solid substrate, $\tau_s < \tau_{R,W}$ indicating that the active particles feature a tendency to rotate faster than what would be expected from standard diffusion. Together with the observations showing the 2D nature of their active motion (figure 1(b)), this finding suggests that the asymmetry axes of the particles is not parallel to the substrate and that the effective rotation happens along a circle with radius smaller than $R$. In particular, by estimating the $\tau_s/\tau_{R,W}$ ratio, we find that the particles are oriented with a mean angle $\sim 40^\circ$ between the asymmetry axis and the

Figure 5. Reorientation times. (a) Cumulative probability distribution of the reorientation times $\tau$ for approximately 1000 particles at 8 different $\text{H}_2\text{O}_2$ concentrations. Particles confined at the liquid–liquid interface (red data) feature a higher mean and a much broader distribution than particles swimming on the substrate (blue data). (b) Average $\tau_s$ as a function of the $\text{H}_2\text{O}_2$ concentration. Each data point is an average of 40–80 particles. $\tau_s$ is constant within error bars for all $\text{H}_2\text{O}_2$. The horizontal solid lines indicate the mean values averaged over all $\text{H}_2\text{O}_2$ concentrations at the interface (red) and at the substrate (blue). The error bars correspond to the standard deviations (in log-scale).

Table 1. Experimental and theoretical diffusion times at the substrate and at the oil–water interface. We report the experimental reorientation times ($\tau_s$ and $\tau_I$) and the theoretical values of the free rotational diffusion time in oil ($\tau_{R,O}$) and water ($\tau_{R,W}$). For comparison, we also provide the experimental characteristic diffusion time $R^2/D_{\text{eff}}$.

| $\tau_s$ (s) | $\tau_I$ (s) | $\tau_{R,W}$ (s) | $\tau_{R,O}$ (s) | $R^2/D_{0,5}$ (s) | $R^2/D_{0,1}$ (s) |
|--------------|--------------|------------------|------------------|-------------------|------------------|
| 7.37         | 81.91        | 16.75            | 57.79            | 15.43             | 36.30            |
| $\tau_s/\tau_I$ | $\tau_{R,W}/\tau_{R,O}$ | $(R^2/D_{0,5})/(R^2/D_{0,1})$ |
| 11.11        | 3.45         | 2.35             |
substrate plane. Another possible reason calls for hydrodynamic interactions between the colloids and the planar wall [9]. Conversely, $\tau$ is larger than the upper bound $\tau_{R,O}$ at the liquid–liquid interface. Here, not only out-of-plane rotation is prevented by contact line pinning caused by surface asperities in the Pt coating, but the latter also causes a slowing down of the in-plane 2D rotational motion within the interface [29, 39].

Discussion and conclusions

Understanding the behavior of microswimmers confined in a 2D space, including near solid walls and at flat liquid–liquid interfaces, is of great importance both for fundamental and applied studies: 2D active colloidal systems are the standard due to the experimental difficulties in imaging 3D active suspensions. Artificial microswimmers have also been envisioned for medical and environmental applications (e.g., drug delivery in blood vessels [40–42] or water remediation [43]) where liquid interfaces and solid walls are naturally present. Our results shed light on the 2D nature of the active motion of self-propelling particles confined above solid walls and at flat fluid interfaces, and thus have important implications both for numerical models that aim to mimic experimental data and for the development of new applications.

In this work, we have studied the paradigmatic case of PS colloidal particles that are propelled by the catalytic decomposition of $\text{H}_2\text{O}_2$, on a hemispherical patch deposited on their surface and which are left to sediment onto a glass substrate, or spread at water–oil interfaces. We described the active trajectories on the substrate (see figure A1(c) and movie S1) and at the interface (see figure A1(d) and movie S2) in terms of swimming velocities and characteristic reorientation times. We demonstrated that in both environmental conditions catalytic microswimmers behave as 2D ABPs, i.e. as particles that move and reorient within the $\tau_{R,O}$ plane rotation is prevented by contact line pinning caused by surface asperities in the Pt coating, but the latter also causes a slowing down of the in-plane 2D rotational motion within the interface [29, 39].

In contrast, particles that are trapped at the fluid–fluid interface swim with high or low velocities depending on the Pt cap orientation at the interface and their reorientation time is enhanced due to contact-line pinning. The combination of these two properties gives rise to active trajectories with two distinct effective diffusivities (see figure A1(d) and movie S2) and with large persistency, i.e. particles moving along straight paths for distances easily two orders of magnitude greater than their diameter. The adsorption and orientation of Janus passive colloids at fluid interfaces has been extensively studied in the past and, among others, two main conclusions can be made. First, the wettability contrast and the relative size of the patches define the equilibrium orientation and protrusion of the particle at the interface [44–47]. The situation of 50:50 wetting, where the Janus boundary is located at the interface is only realized for hydrophilic/hydrophobic patches of comparable size. Second, the presence of surface heterogeneity due to the preparation of the Janus particles can lead to contact-line pinning and the presence of metastable orientations departing from the equilibrium one [48]. In the case of our particles, both lobes are hydrophobic, with a small wettability contrast ($\text{Pt} \approx 105^\circ$ versus PS $\approx 120^\circ–130^\circ$). As a consequence, the minimum energy configuration is that represented in figure 4(e), while the configuration of figure 4(d) is a metastable one that never relaxes within the experimental timescale, as shown by the constant brightness of individual particles in figure S1(b). Both cases are in mechanical equilibrium and switching between the two is prevented by pinning of the three-phase contact line. The fact that the active configurations of figures 4(b) and (c) are seen is a direct consequence of the fact that the asymmetry axis of the particles is fixed in a specific direction relative to the interfacial plane. The large gap between the swimming velocities of these two configurations (up to one order of magnitude) cannot be explained by different Stokes drag coefficients alone. Using a first-order approximation of the complex 3D hydrodynamic drag experienced by a sphere at a fluid–fluid interface [49], the particles in figures 4(d) and (e) only experience a 20% difference of viscosity due to a variation of their protrusion height into the oil phase, corresponding to $\sim30^\circ$ difference in their contact angle. For catalytic swimmers at a liquid–liquid interface, the classical picture of diffusiophoretic propulsion has to be revisited, as illustrated in figures 4(b)–(e).

The behavior of self-propelling silica/Pt particles at air–water interfaces has been recently investigated by Wang et al [28, 29], showing both analogies and striking differences when compared with our observations. These authors similarly reported larger values of some rotational diffusion times and a consequent enhancement of the persistence length of the corresponding active trajectories. However, their catalytic swimmers were faster at the water–air interface than on the substrate and their orientation, i.e. the angle between the asymmetry axis and the interfacial plane, was randomly distributed. The reason for this discrepancy lies in small, yet critical, experimental details that affect the particle configurations: the particles used in [24] are mostly hydrophilic and have a 30 nm thick metallic coating, as opposed to the 2 nm Pt-layer used in this work. As a consequence of the enhanced surface roughness of their coating, stronger pinning of the contact line can trap any orientation and does not lead to the selection of particle populations with distinct swimming speeds. In this context, but beyond the scope of the present work, a systematic study of the thickness/roughness of the coating together with a
systematic investigation of the chemical functionality of the surfaces of the two lobes would prove a very interesting screening exercise to establish design rules for interfacial microswimmers.

Acknowledgments

KD, MZ, IB and LI acknowledge financial support from the Swiss National Science Foundation grant PP00P2_144646/1 and the ETH Zurich research grants ETH-16 15-1 and FEL-02 14-1. André Studart and Nicholas D Spencer are acknowledged for instrumentation access and the microscopy center of ETH Zurich. ScopeM is acknowledged for technical support.

Appendix

Methods

Fabrication of active colloids. We assemble monolayers of the sulfate PS spherical microparticles (radius $R = 1.4$ μm, $SO_4^-$ functional groups, Microparticles GmbH) by drying a $200$ μl droplet of a diluted suspension (0.35% w/v) on a pre-cleaned microscope slide (Thermo Scientific). We then sputter 2 nm of Platinum onto the monolayer with 90° glancing angle in order to coat one hemisphere of the colloids. The process pressure is set to 0.5 Pa in order to obtain a smooth deposition. The particles are released from the substrate into 50 ml milliQ water via ultra-sonication for approximately 2 min.

Sample preparation. Non-stabilized hydrogen peroxide ($H_2O_2$, 30% v/v, Merck Millipore) is first added to milliQ water to prepare fuel-rich aqueous solutions at the prescribed concentration. The oil phase consists of hexadecane (Arcos Organics) that is preventively purified through a column containing alumina powder (EcoChromTM, MP Alumina B Act.1) and silica gel 60 (Merck) in order to remove surface-active contaminants. The measuring cell (figure A1(b)) is made of two rings of different heights: an inner stainless steel ring (5 mm inner diameter) and an outer Teflon ring (2 cm inner diameter). The inner ring is filled with the water/$H_2O_2$ solution until the surface is pinned to the edge. Hexadecane is then poured in the rest of the cell in order to create a flat oil/water interface, as shown in figure A1(b). The Pt-coated colloids are dispersed in a 50/50 water/isopropyl alcohol spreading solution and sonicated for approximately 10 min. Finally, 1 μl of the spreading solution is placed at the liquid–liquid interface using a thin pre-cleaned syringe (Exmiré Microsysringe cleaned with ethanol and deionized water). Janus particles are also dispersed in the water phase and let sediment onto the bottom microscope slide (figure A1(a)). We remark that the use of non-stabilized $H_2O_2$ leads to swimming velocities that are larger than values reported in the literature [2, 3] (values compared at the substrate). This is because standard commercial stabilized $H_2O_2$ (which lasts in stock for a longer time) contains sulphur and phosphor, which poison the Pt catalyst thus reducing the propulsion efficiency. The duration of the experiments (20–30 min) ensures that the concentration of $H_2O_2$ in the sample cell remains constant.

Data acquisition and analysis. The particles are imaged using an inverted optical microscope in fluorescence mode (Zeiss, Axio Observer). Videos are recorded at a high resolution (2560 × 2160 pixels, 12 bits) and at 5 fps (dt = 0.2 s) for up to 600 s and analyzed with custom Matlab codes. The acquisition rate is sufficiently fast to measure the active trajectories accurately, since the particles swim straight for long enough distances (i.e., $L > Vdt$). The swimming velocity $V$ is calculated from the time derivative of spatial displacements of the individual particles in consecutive frames ($V = |dr/dt|$). Quantitative information about the particles motion is also obtained by measuring the mean square displacement (MSD) of the trajectories, i.e.

$$\text{MSD}(\Delta t) = \langle (r(t + \Delta t) - r(t))^2 \rangle, \quad \text{(A.1)}$$

where $r(t)$ and $r(t + \Delta t)$ are the particle’s positions at times $t$ and $t + \Delta t$, respectively. The reorientation time $\tau$ is calculated from the fitting of the MSDs (up to the first inflection point) according to [1, 33]

$$\text{MSD}(\Delta t) = [4D_0 + 2V^2\tau] \Delta t + 2V^2\tau^2 e^{-\Delta t/\tau} - 1 \quad \text{(A.2)}$$

using the values of $V$ and $D_0$ as fixed parameters. The diffusion coefficient $D_0$ is extracted by fitting the MSD of ~10 particles without any propulsion (no $H_2O_2$ in water, data recorded at 20 fps). Small spurious drifts, e.g., due to directional convective flows at the interface, are taken into account using $\text{MSD}(\Delta t) = 4D_0\Delta t + V^2_{\text{drift}} \Delta t^2$.

We find $D_{0,8} = 0.127 \pm 0.001$ μm² s⁻¹ and $D_{0,9} = 0.054 \pm 0.009$ μm² s⁻¹, at the substrate and at the interface, respectively, emphasizing the greater viscous drag experienced at the interface.

The values of $\tau$ obtained using (A2) do not agree with theoretical free rotational diffusion (see main text). In order to check the reliability of our fitting procedure and make sure that such deviations are not introduced by
We characterize the wetting properties of Pt-coated particles using the following experimental techniques.

Measurements of single-particle wetting

We characterize the wetting properties of Pt-coated particles using the following experimental techniques.

1. Gel-trapping technique [34] (GTT). Petri dishes are rinsed by ultra-sonication in acetone, ethanol and deionized water for 5 min and treated with UV light for 15 min. The water–oil (water + Gellan-hexadecane) interface is generated with a hot (80 °C) 2 wt% Gellan Gum (AppliChem, A5354) water mixture and purified hexadecane. Particles are spread at high temperature and trapped as the system cools down. After cooling, the oil phase is removed and the particles are transferred into a UV glue (NOA 81, Norland Optical Adhesives, USA) replica of the interface, which was rinsed with warm water prior to further use. The GTT replicas of the particles are finally imaged (figure 3(a)) using a scanning electron microscope (SEM) operated in backscattering mode. The images give a view of the interface from the water side and the Pt-coated surface of the colloids appears bright.

2. Freeze-fracture shadow-casting [35] (FreSCA). 0.5 μl of milliQ water are pipetted in a custom-made, clean hydrophilised copper holder. The particles are spread at the water interface with a water-isopropanol (50:50) mixture. After evaporation of the alcohol, the aqueous phase is covered by 3.5 μl of n-decane (>99%, Sigma-Aldrich, Germany) and by a flat copper plate. The samples are then jet-frozen by liquid propane (Bal-Tec/Leica JFD 030, Balzers/Vienna). Due to the extreme cooling rates employed, the samples vitrify, ensuring solidification at constant volume. The samples are fractured in high-vacuum conditions (10−6 mbar) and cryogenic temperatures (−120 °C) in a freeze-etching device (Bal-Tec/Leica BAF060 device). After a freeze-drying step of 1 min at −100 °C, the samples are coated with 3 nm tungsten at a deposition angle of 30° followed by additional 3 nm at continuously varying angles between 30° and 90°. Freeze-fractured metal-coated samples are then transferred in a cryo-SEM (−120 °C) (Zeiss Gemini 1530, Oberkochen) for imaging in backscattering mode. The images give a view of the interface from the oil side and the Pt-coated surface of the colloids appears bright.

3. AFM contact angle measurements [36]. The GTT samples are scanned in tapping mode using an AFM (JPK Nanowizard3, JPK, Germany) equipped with a silicon nitride cantilever (spring constant 26 N m−1, scanning frequency 300 kHz). The measurements are done in air and under ambient conditions. The contact angles of the individual colloids are calculated from the protrusion heights, which are extracted using custom-written algorithms. Any tilt is removed by subtracting a plane fitted to three points of the local background.

4. Static contact angle measurements of water droplets on flat PS substrates, both bare and Pt-coated, are performed by the sessile drop method using the drop shape analysis technique (DSA100, Krüss, Germany).

Figure A1. Experimental setup and active trajectories. Microswimmers self-propel due to the catalytic decomposition of H2O2 at the Pt-coated hemisphere. Their self-phoretic motion is measured both (a) above a glass slide after sedimentation and (b) at the interface between two immiscible fluids (H2O2 aqueous solution and hexadecane). (c–d) Active trajectories for three H2O2 concentrations. At the water–oil interface, we observe two populations of active particles with very different persistency and effective diffusivity (two examples reported for each [H2O2]). All trajectories last 40 s. See also the supplemental movies S1 and S2.
In a typical experiment, a water droplet of 5 μl is formed on the substrate. To ensure that the sessile drop is at equilibrium, the analysis is started when no contact angle evolution is observed.

Numerical simulations

The motion of the microswimmers is simulated using Brownian dynamics based on the active Brownian particle (ABP) model [13]. An ABP is a spherical colloidal particle that performs (both translational and rotational) Brownian motion and is propelled along a direction fixed with respect to the particle body [1]. We consider two models: one where the ABP rotational diffusion occurs in three dimensions (ABP-3D) and one where it occurs in two dimensions (ABP-2D). As we have seen in the text, the ABP-2D model better describes the results of the experiments because of the pinning of the contact line of the Janus particle at the interface, which restricts its reorientation possibilities. The corresponding stochastic differential equations for ABP-2D are:

\[
\begin{align*}
\dot{x} &= V \cos(\varphi) + \sqrt{2D_R} \xi_x, \\
\dot{y} &= V \sin(\varphi) + \sqrt{2D_R} \xi_y, \\
\dot{\varphi} &= \sqrt{2D_R} \xi_\varphi,
\end{align*}
\]  

(A.3)

where \((x, y)\) is the particle position, \(\varphi\) is the particle orientation, \(D_R\) the effective rotational diffusion and \((\xi_x, \xi_y, \xi_\varphi)\) are independent delta-correlated white-noise stochastic processes with a zero mean. In the case of ABP-3D, the particle orientation is described by the polar and azimuthal angles, which perform a Brownian motion on the unit sphere. For simplicity, we assume the effective viscosity to be the average of the water and oil viscosity as if the particles were sitting at the interface with a 90° contact angle. In a very good first approximation, the friction coefficient depends mostly on the size of the particle and only very weakly on its surface properties and contact angle (see section 'Discussion and conclusions' of the article).

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