

Supplementary information for “Slip length dependent propulsion speed of catalytic colloidal swimmers near walls”

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I. EXPERIMENTAL DETAILS

A. Particle preparation

Synthesis of TPM colloids: 2.7 μm carboxylated 3-(trimethoxysilyl)propyl methacrylate (TPM) colloidal spheres with polydispersity in size 2.37% were prepared following a one-pot surfactant-free synthesis protocol extended from Ref. [1]. In short, itaconic acid (ITA, Sigma Aldrich) was weighed into a plastic beaker. 30g of MilliQ water (18.2 M Ω cm resistivity, obtained using a Millipore Filtration System Milli-Q Gradient A10) was added and the pH was adjusted to 10.8 with NH_3 (28-30%). The solution was stirred at 300 rpm until ITA was fully dissolved. 900 μL TPM oil (Sigma Aldrich, 98%) was rapidly injected into the stirred solution, which was then covered with parafilm. After 4 h, 100 mg azobis(isobutyronitrile) (AIBN, Sigma Aldrich, $\geq 98\%$) was added. In total the emulsion was stirred for 5 h prior to heating in an oil bath at 80 $^\circ\text{C}$ under rotation at 50 rpm for 2.5 h. The colloids are washed and stored in MilliQ. The resulting spheres have a zeta potential of -70 ± 2 mV in MilliQ (pH 5.5). Their density is 1.31 kg/L [1].

Pt/TPM colloids: TPM spheres were spin coated from ethanol on glass slides at sub-monolayer concentrations and subsequently sputter coated from above with a 4.9 nm Pt/Pd (80/20, MicroNano70-PPS708) layer via physical vapor deposition using a standard sputter coating system (Cressington 208HR High Resolution Sputter Coater). During deposition, the stage was rotated at a constant speed to ensure even Pt distribution. The Pt/TPM colloids were redispersed in 5 mM NaOH by 5 min sonication and were subsequently washed and stored in MilliQ water. This method produced single particles. All colloids were prepared in one batch. The resulting Pt/TPM spheres have a zeta potential of -54.6 ± 1.5 mV in MilliQ water.

B. Substrate preparation

Glass substrates were purchased from VWR (631-1584 25mm No1) and were used as received unless stated otherwise. They are made of borosilicate glass and are subsequently coated with a Schott's D263M coating. According to the supplier, these cover glasses are more hydrophobic than typical soda lime glasses. The contact angle for 10% H_2O_2 on these cover glasses is $44^\circ \pm 9^\circ$.

Hydrophilic glass (clean glass) was prepared by sonicating the glass substrates for 20 min in acetone, followed by 30 min sonication in ethanol and drying in a preheated oven at 80 $^\circ\text{C}$ for 10 min. The contact angle for 10% H_2O_2 is $30^\circ \pm 3^\circ$.

Highly hydrophilic glass was prepared by immersing the glass substrates in a 1:1 mixture of methanol and hydrogen chloride (37%) for 30 min, followed by thoroughly rinsing with MilliQ water and drying with N_2 [2]. The contact angle for 10% H_2O_2 is $13^\circ \pm 4^\circ$.

Hydrophobic glass was prepared by first immersing glass substrates in 2% Hellmanex while stirring for 30 min. The substrates were then rinsed with MilliQ water and immersed in ethanol for 20 min and dried in the oven at 150 $^\circ\text{C}$ for 30 min. The dried glasses were then immersed for 20 s in 50 g xylene and 2.9 mL surfasil, for 20 s in xylene and for 60 s in methanol and were dried in the oven at 150 $^\circ\text{C}$ for 30 min. The contact angle for 10% H_2O_2 directly after preparation is $68^\circ \pm 5^\circ$.

PDMS substrates were prepared similarly to [3] using the PDMS kit Sylgard-184 by Dow Corning. The base silicon elastomer and curing agent were mixed at a 5:1 ratio. The mixture was placed in a vacuum desiccator for 1 h to remove trapped bubbles due to agitation, and was then drop cast and flattened on glass. After 45 min in the desiccator, the substrates were dried in the oven at 120 $^\circ\text{C}$ for 3 h. We verified that the contact angle for water on these substrates was 100° , as stated by the supplier and has also been measured elsewhere [4]. The contact angle for 10% H_2O_2 is $100^\circ \pm 3^\circ$.

Hydrophilic PDMS was prepared by UV-ozone treatment of the PDMS substrates [3, 5] for 60 min using a UVO cleaner (Jelight Company Inc. No 42A-220). This treatment converts the PDMS surface into a silica-like surface,

see Ref. [3] for a detailed study on surface properties. The resulting contact angle for water after 60 min treatment was $37^\circ \pm 7^\circ$, close to values measured in the literature after similar treatment [5], and indeed close to the contact angle of $30^\circ \pm 3^\circ$ that we measured here for water on clean glass. We note that we perform our experiments within 1 h after surface treatment during which time the substrates remain hydrophilic, see Ref. [5] for the timescale of the hydrophobic recovery of PDMS.

PE substrates were purchased from ibidi GmbH (μ -slide 8 Well ibiTreat No 80826) and were used as received. These substrates are made from a polyethylene derivative and are subsequently plasma treated by the supplier. The supplier stated that the plasma treatment leads to a permanent change in the substrate properties, however there may be some surface inhomogeneities. The contact angle for 10% H_2O_2 is $51^\circ \pm 3^\circ$.

PS petri-dishes were purchased from Sarstedt and were used as received. The supplier has introduced hydrophilic groups into the surface via a special treatment of the PS. The contact angle for 10% H_2O_2 is $46^\circ \pm 6^\circ$.

C. Imaging and Tracking

TPM/Pt colloids were dispersed in 10% H_2O_2 in MilliQ water at dilute particle concentration ($\approx 10^{-7}$ v/v). Their motion was recorded with a 60x ELWD air objective (NA 0.7) mounted on an inverted Nikon Eclipse Ti microscope. 25 s movies were acquired over the xy plane at 18.92 frames per second. All measurements were performed in the dark and within the first hour after sample preparation to avoid photocatalytic decomposition of the H_2O_2 [6] and potential changes in the slip of the substrate due to reaction with H_2O_2 . At least 70 colloids were imaged and analyzed for all substrates considered in Figures 2 and 3 of the main text. Additional 30 s movies of the TPM/Pt colloids were taken at 18.92 frames per second in water, and water containing 1 mM NaCl. Tracking was performed using the python tracking algorithm trackpy that is available online [7].

D. Data Analysis

The translational diffusion coefficient, D_T , of each TPM/Pt colloid in water above each substrate was extracted by fitting its mean squared displacement (MSD) with $\Delta r^2 = 4D_T\Delta t$, for lag times smaller than 1 s. The diffusion coefficients were then averaged to obtain the corresponding D_T above each substrate, see SI Table I. The error reported in SI Table I is calculated from the standard deviation of the corresponding D_T divided by $\sqrt{N-1}$, where N is the number of colloids considered for each substrate. The diffusion coefficient in bulk is $0.17 \mu\text{m}^2/\text{s}$, obtained from $D_{\text{bulk}} = \frac{k_B T}{6\pi\eta\alpha}$.

Colloid velocities in the active state were extracted from fitting particles' MSDs in H_2O_2 with the expression $\Delta r^2 = 4D\Delta t + V^2\Delta t^2$ following Ref. [8], which holds for short-time scales $\Delta t \ll \tau_R$; with τ_R the characteristic time scale for the particle to undergo rotational diffusion obtained from $\tau_R = 1/D_R$, where D_R the rotational diffusion coefficient $D_R = \frac{k_B T}{8\pi\eta\alpha^3}$. We fit the first seven data points of the MSDs, corresponding to lag-times Δt of 0.4 s. Examples of three individual colloid MSDs above three different substrates are shown in SI FIG. 1A. To obtain the velocity for each colloid, we first fit all colloid MSDs above a specific substrate with both D and V as open parameters. We then use the averaged D value for the substrate as a fixed parameter to obtain V for each colloid. We note that even though the high frame rate allows us to access the short-time behavior, due to the relatively short time duration of our measurement the long-time behavior or else the enhanced diffusion regime is not recovered from our datasets.

The velocity distributions on the different substrates are asymmetric (tail on the right), see SI FIG. 1B as an example of the probability density function (PDF) of the velocity obtained from 50 individual colloid velocities on hydrophilic glass. We fit the distributions with a log-normal distribution following Goldstein, Lauga, and collaborators [10]. We first performed a Kolmogorov-Smirnov (K-S) test for the goodness of fit, using the statistics package that is build in Python's scipy. From the obtained p-values and the observed agreement between theoretical fit and data, we concluded that the log normal fits the data adequately well. From the fit we obtain the moments of the distributions, see summary of those values in SI Table II, which we use to determine parameters of the distributions, such as the standard deviation. Due to the distributions being asymmetrical, the peak corresponds to the most frequent value

Substrate	Glass	PDMS	PE	Glass H/philic	PDMS H/philic	Glass H/phobic	Glass Highly H/philic	PS
D_T ($\mu\text{m}^2/\text{s}$)	0.099	0.105	0.098	0.096	0.091	0.098	0.090	0.110
Standard Error ($\mu\text{m}^2/\text{s}$)	0.005	0.005	0.008	0.006	0.003	0.007	0.003	0.003

TABLE I: Translational diffusion coefficient D_T of the Janus colloids above each substrate in water. The diffusion coefficient D_{bulk} is $0.17 \mu\text{m}^2/\text{s}$.

Substrate	Glass	PDMS	PE	Glass H/philic	PDMS H/philic	Glass H/phobic	Glass Highly H/philic	PS
Shape	0.68	0.56	1.09	0.45	0.67	0.61	0.37	1.03
Location	0.49	0.08	0.71	0.35	0.51	0.44	0.22	0.28
Scale	0.87	3.75	0.46	0.52	0.26	1.24	0.41	0.87

TABLE II: Moments of the velocity distributions on all substrates as obtained from the log-normal fit.

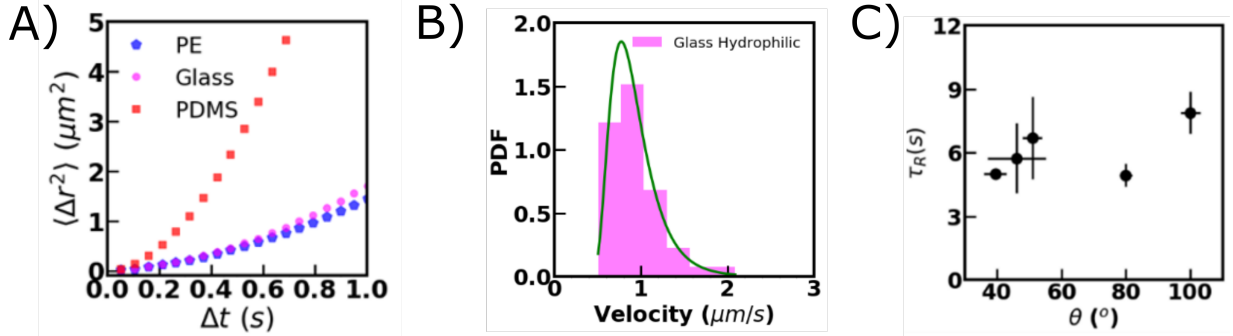


FIG. 1: A) Typical MSD examples from three individual colloids measured on PE, Glass and PDMS in H_2O_2 . B) PDF of the velocity on hydrophilic glass as obtained from 50 individual colloid velocities. The data is fitted with a log-normal distribution. The moments of the distribution as obtained from the fit are shown in Table II. Using those moments, we determine the variance (0.078) and therefore the standard deviation (0.28 $\mu\text{m/s}$). The most frequent velocity value is obtained from the fitted peak position (0.8 $\mu\text{m/s}$). C) Averaged τ_R as extracted from the decorrelation of the velocity vector for individual colloids following [9] as a function of contact angle θ .

and is therefore representative of the distributions at hand. We therefore determine the fitted peak position of the velocity, which takes into account the full shape of the distribution. The corresponding peak values are plotted in Figure 2 of the main text. The reported error corresponds to the standard error $\frac{\sigma}{\sqrt{N-1}}$, with σ the standard deviation of the distribution and N the number of colloids. We note that on all substrates a few percent of the particles irreversibly adsorbed, except for the PS and highly hydrophilic glass where about 30% and 80% of the particles adsorbed, respectively. Only velocities from colloids with non-zero velocities are included in the PDFs. Moreover, only colloids that do not interact with other colloids are included in the PDFs, since solute gradients in such case may interact and affect the velocities. In addition, colloids with chiral trajectories are not included in the analysis; such colloids are rarely encountered in our samples. We note that for the salt experiments it is hard to obtain sufficient trajectories because sticking of particles increases considerably for all samples/substrates; moreover, Brownian colloids, which also increase with salt, are excluded. Due to having fewer active particles, we cannot plot velocity distributions, and therefore report average velocities from arithmetic means in Figure 3 of the main text. However, the K-S test that we perform on the biggest data set gives a p-value of 0.83, showing that the log-normal distribution in principle still fits the data also in salt.

We extract the characteristic time scale for rotation τ_R from the velocity autocorrelation function following Ref. [9]. We find no correlation between τ_R and the solution contact angle on the different substrates, see SI FIG. 1C.

E. Surface Zeta Potential

Zeta potential measurements were performed with a Malvern Zetasizer Nano ZS, which measures electrophoretic mobility of colloidal particles with laser doppler micro-electrophoresis. The zeta potential of the colloids under study was measured in water as well as in acidic pH conditions. In short, we insert a dilute solution of charged colloids in a cell that has an electrode at each end and apply a voltage, causing the colloids to move to the oppositely charged electrode. The resulting phase shifts of the laser light due to the colloid motion are measured by a laser interferometric technique called Phase Analysis Light Scattering, yielding the colloid velocity and electrophoretic mobility. The zeta potential is obtained from the electrophoretic mobility using the Henry equation and the Smoluchowski approximation $\mu = \frac{\epsilon_r \epsilon_0}{\eta} \zeta$, which are incorporated in the Zetasizer.

To measure the substrate zeta potential, the substrates under study were mounted on a planar cell custom made by Malvern for surface measurements. We measured the electrophoretic mobility of charged tracer particles at various distances from the substrate upon applying an electric field. From the tracer electrophoretic mobilities as a function

of displacement, the corresponding zeta potentials were obtained through Smoluchowski's equation as a function of displacement, and thereby the zeta potential at zero displacement (intercept) was extrapolated. The substrate zeta potential ζ_s was then obtained according to Ref. [11] from $\zeta_s = -\text{intercept} + \zeta_{\text{tracer}}$. Those measurements were performed using $1\ \mu\text{m}$ carboxylated polystyrene colloids as tracers, prepared following a surfactant-free dispersion polymerization protocol, see Ref. [12]. Due to bubble formation at the electrodes in the presence of H_2O_2 , all experiments were performed in aqueous HCl. The control experiments for the zeta potential of glass as function of pH are shown in SI FIG. 2, and were performed in aqueous HCl with pH values equivalent to those at experimental conditions of 0.5-10% H_2O_2 . After obtaining good agreement with streaming zeta potential measurements, we performed the zeta potential measurements of PDMS and PDMS hydrophilic, the values of which are found in the main text.

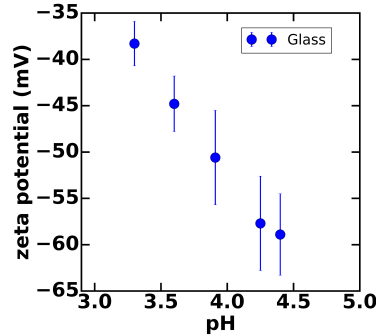


FIG. 2: Zeta potential of the glass substrates under study at various acidic pH conditions.

F. Atomic Force Microscopy

Measurements were performed with a JPK Nano Wizard 3 (Ultra Speed) AFM in air, using Opus 240AC-NA probes. The measured frequency and stiffness of the probes were respectively 75 kHz and 1.3 N/m. Images of the glass and PS substrates were acquired in AC mode, a dynamic contact mode otherwise known as tapping mode. A typical image of a glass substrate used in this work is shown in SI FIG. 3: we presume that the spherical nanoparticles seen on the glass are part of the coating applied by the supplier, see Section II B. A typical image of the PS surface is also shown in SI FIG. 3: we presume that the fiber-like surface is either a coating as part of the special treatment that the supplier uses to render PS hydrophilic, or polishing marks/scratches on the surface to make it flat during the preparation. To avoid harming the surface, images of PDMS were acquired in QI mode (quantitative imaging mode), which allows better vertical force control than AC mode and applies no lateral forces on the sample. This is a force curve based mode that provides three dimensional images by measuring the interaction between tip and surface while the tip moves vertically towards the surface providing an approach and a retract force curve pixel by pixel. For these reasons QI mode is more suited for softer samples. From the 3-dimensional images and height profiles, the Ra roughness was directly extracted using the JPK data-processing software version 6.1. The Ra roughness values for glass and PDMS are found in the main text. The Ra roughness for PS is 2.5 nm. The Ra is defined as the arithmetic mean of the deviations in height from the roughness mean value and is given by $Ra = \frac{1}{n} \sum_{i=1}^n |y_i|$, where y is the vertical distance from the mean. In air and with the same probe we observed from the shape of the approach curves that the stiffness increases from PDMS to glass. However, the stiffness of the PDMS should not be affected by the surface treatment that yields it hydrophilic. Therefore, if substrate stiffness had a strong effect on the velocities, velocities on PDMS and hydrophilic PDMS would not be as different.

G. Contact Angle Measurements

Images were taken with a Canon EF-S 60mm f/2.8 Macro USM lens mounted on a Canon EOS 500D Digital SLR Camera with backlighting. Water droplets with volumes between 1 and 10 μL were placed on the various substrates. To determine the variation of contact angle for a specific surface, multiple droplets were imaged on the surface. To determine the spread in the contact angle for a certain material, droplets were imaged on different surfaces. These processes were repeated also for droplets containing 10% H_2O_2 , 1 mM NaCl, and 10% H_2O_2 with 1 mM NaCl. All images were taken within seconds after droplet placement. The static contact angles were determined using ImageJ.

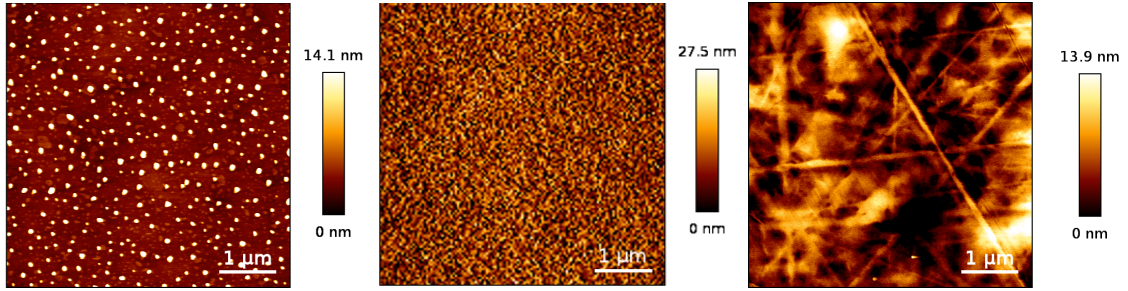


FIG. 3: From left to right: AFM images of the glass, PDMS and PS substrates under study.

The contact angle for a specific drop is typically determined with an error of less than 1° . Values reported in the main text, Figure 2 of the main text, and Section I B correspond to averaged values from several individual water droplets containing 10% H_2O_2 , with the error denoting the standard deviation. Values reported in Figure 3 of the main text correspond to water droplets containing 10% H_2O_2 and 1 mM NaCl, with the error denoting the standard deviation.

II. THEORY ON OSMOTIC COUPLING INDUCED SPEED VARIATION

Understanding the effect of the wetting properties of the wall on the motion of a catalytically propelled swimmer is non-trivial. However, we shall show here that osmotic coupling leads to $V \propto (1 + \cos \theta)^{-3/2}$, under certain conditions, and thus provides a plausible explanation for our experimental result. We will also discuss other potential mechanisms and explain why these are less likely to account for the significant effect of the wall, as reported in the main text.

A. Slip and Contact Angle

Before we proceed with our analysis, it is convenient to (re)introduce the concept of slip and contact angle from our main text. A hydrodynamic slip boundary condition on a wall (at $z = 0$) is defined as

$$b \frac{\partial}{\partial z} \mathbf{u}_i(x, y, z = 0) = \mathbf{u}_i(x, y, z = 0), \quad (1)$$

where z measures distance normal to a wall, and x and y are orthogonal co-planar coordinates. The fluid velocity is given by $\mathbf{u}$ and the subscript $i = x, y$ indicates that the boundary condition is applicable to the co-planar components of the flow vector. Finally, b denotes the slip length, which is zero for a no-slip surface and divergent for a full-slip surface. Regardless of the value of b , the fluid velocity normal to the boundary is characterized by a no-penetration condition: $\mathbf{u}_z(x, y, z = 0) = 0$. We do not consider patterned surfaces here, in line with our AFM measurements of the experimental surfaces, see Section I F, which means that we can use a single slip value that is homogeneous along the surface.

Huang *et al.* [13] have argued that the following quasi-universal relation between slip and contact angle holds:

$$b \propto (1 + \cos \theta)^{-2}, \quad (2)$$

with θ the contact angle, which is defined as the angle between the surface and a wetting droplet of water in air. The no-slip condition is implied to hold at $\theta = 0$, and the prefactors of the proportionality may be appropriately chosen to achieve this [13].

B. Diffusion coefficient near surfaces

The surface-to-surface separation between the colloid and the wall δ is important for hydrodynamic and chemical coupling. We therefore analyze its value in this section. It is natural to think that a variation in swim speed stemming from modifying the wall properties may be caused by associated height variations. Such a height change could be a secondary effect of changing the wall's chemical properties, for instance, through changing the electrostatic repulsion. However, it will turn out that this idea does not match with our experimental results.

We find that the separation δ is comparable to the particle radius α . We gain this insight from the experimentally measured diffusion coefficient of our Pt-coated particles in water, see Section IC and ID for experimental details and values. The diffusion coefficients are similar within error above all substrates and therefore similarly different from the diffusion coefficient for free diffusion in the bulk, see also Section ID. Our results are in agreement with predictions, see for example Ref. [14] on the hydrodynamic mobility of a passive particle moving close to a no-slip wall. We use Faxen's theoretical prediction for the near-wall in the plane parallel to the wall diffusion, which has been experimentally proven in Ref. [15] and [16], given by $\frac{D}{D_{\text{bulk}}} = 1 - \frac{9}{16}\gamma + \frac{\gamma^3}{8} - \frac{45\gamma^4}{256}$ with $\gamma = \frac{\alpha}{h+\alpha}$ and h the colloid-wall separation. Faxen's law applies to a no-slip condition, however we are still probing here small departures in terms of slip from this condition. The contact angles that we measure are in the range between 15° and 100° , implying that the corresponding slip lengths, calculated by Eq. 2, change by roughly a factor of 5. The measured translational diffusion coefficients remain constant upon a variation in slip of that order, and show a reduction of roughly a factor of 2 compared to free diffusion in bulk. Figure 3.1 in Ref. [17], shows the effect of the slip on the force acting on a translating sphere as function of separation distance; the effect on the diffusion coefficient is directly related to the effect on the force, therefore this figure can be used to gauge the effect of the slip on the diffusion coefficient as function of separation distance. To understand the changes in the distance with slip, we look horizontally in the above-mentioned figure — for the here constant diffusion coefficient — and read the separation gap size that would correspond to the changes in separation distance based on the conditions that follow from our measurements. We conclude that for a factor of 2 reduction compared to the bulk value, in combination with the factor 5 change in slip, the variation in the separation will be minimal. Since diffusion coefficients are similarly reduced, we use the average value above the various substrates ($0.098 \mu\text{m}^2/\text{s}$) and find that the separation δ in the brownian state is $0.5 \mu\text{m}$, which corresponds to $\delta \sim 0.4\alpha$. Our experiments in 1 mM salt showed that the diffusion coefficient is further reduced by salt. We find that the separation for the brownian state in salt is $0.3 \mu\text{m}$ which corresponds to $\delta \sim 0.2\alpha$. In summary, the measured constancy of the passive diffusion coefficients with θ is an indicator that there is limited variation in δ with changes to the wall properties.

C. Osmotic Coupling

Osmotic coupling can directly affect the speed upon changing the wall, even for fixed δ . We will focus on this mechanism and discuss how such a coupling may give rise to the observed trend. We assume, for convenience, neutral self-diffusiophoresis and homogeneous surface properties for both the wall and the colloid. The properties of the wall and swimmer may be different and we will distinguish these by subscripts w and s , respectively. The discussion is analogous for self-electrophoretic mechanisms, with the minor exception that the Debye length is typically considerably larger than the one associated with non-electrostatic molecular interactions.

Uspal *et al.* [18] have investigated osmotic coupling near a no-slip wall. However, adopting their result is not entirely trivial, as the derivation therein makes explicit use of the fundamental hydrodynamic solutions near a no-slip wall. It is relatively straightforward to compute the Stokeslet for a full-slip wall [19]. However, this limit is problematic for other reasons, as ξ_w will turn out to diverge, due to its dependence on θ ; we will return to this shortly. The expressions for the Greens functions near wall with intermediate values of slip are convoluted [20] and do not provide significant additional insight beyond what can be obtained through scaling arguments.

Referencing [18], we observe that the osmotic contribution to the speed $\propto (a + \delta)^{-3}$ for no-slip surfaces; this scaling will hold even for partial or full slip. Thus, we may write

$$V \approx V_{\text{other}} + \frac{\alpha^3}{(\alpha + \delta)^3} V_{\text{osm.}}, \quad (3)$$

where $V_{\text{osm.}}$ is a proportionality constant that measures the impact of osmotic flow along the wall on the speed of the swimmer above it. The velocity V_{other} accounts for confinement effects and is assumed constant here, with variation of θ , because the height is assumed constant. Both V_{other} and $V_{\text{osm.}}$ depend on α , however, only $V_{\text{osm.}}$ is strongly dependent on θ . Applying the standard diffusiophoretic theory [21], we have that $V_{\text{osm.}} \propto \xi_w/D_{\text{sol.}}$ with $D_{\text{sol.}}$ the solute diffusion coefficient. Ajdari and Bocquet [22] have shown that for a partial-slip wall the coupling parameter may be written as

$$\xi_w = (k_B T / \mu) \lambda_w \gamma_w (1 + b_w / \lambda_w), \quad (4)$$

with k_B Boltzmann's constant, T the temperature, λ_w a length scale for the solute-surface interactions, γ_w a length measuring the solute excess, and b_w the hydrodynamic slip length of the wall. This expression reduces to the no-slip result for $b_w = 0$. It should be noted that typically $b_w \gg \lambda_w, \gamma_w$ [22], implying that the dominant effect of changing the wall comes from the hydrodynamic slip this induces. The value λ_w is left relatively unaffected by changes in the

wall, as the interaction length scale is molecular $\approx 1 \text{ \AA}$ for neutral solutes. However, γ_w will vary, as it depends on details of the molecular interactions between the solutes and wall, which are key to determining wetting (and slip). Following Huang *et al.* [13], we have

$$\gamma_w \propto \sqrt{1 + \cos \theta}, \quad (5)$$

and for b_w we can use Eq. (2). Isolating the dominant dependence on θ , we obtain the following proportionality

$$V \propto V_{\text{osm.}} \propto \frac{1}{(1 + \cos \theta)^{3/2}}, \quad (6)$$

whenever $b_w \gg \lambda_w, \gamma_w$, such that the slip-length term dominates.

D. Discussion

Equation (6) has some interesting consequences and caveats in relation to our experimental data:

- The presence of the factor 1 in the numerator to Eq. (6) allowed us to capture the finite (extrapolated) velocity at $\theta = 0$ and the global trend well without requiring an offset to Eq. 6. That is, a nearly negligible offset best fits the experimental data. The implication is that the prefactors and separation δ in Eq. (3) are such that for a no-slip, fully-wetting surface there is some (fortuitous) cancellation of terms that eliminate the U_{other} contribution to the speed. This could be an expression of a competition between confinement, bulk, and osmotic effects, which may have opposite signs. It is difficult to make strong statements in this regard, without knowing more about the specifics of the self-propulsion mechanism.
- The most interesting feature of Eq. (6) is the potential for a divergence of the velocity of a self-propelled particle near a full-slip surface. This is counter intuitive, as for a dragged passive sphere the mobility enhancement with respect to bulk is only a factor 1.37 [17, 23] in the full-slip case. The reason for this is that the surface velocity generated by the osmotic coupling can become very significant, as there is a divergent separation in length scales between the atomic interactions that force the fluid λ_w and the hydrodynamic slip length b_w as θ approaches 180° . Such a divergence does not occur in a real system as the effect of enhanced surface speed would either push the solute concentration out of the low-Péclet regime — solute diffusion dominates its advection by the fluid — or modulate the height of the swimmer. Both effects being self-limiting in nature.

Lastly, we wish to discuss other arguments for describing our findings:

- Purely hydrodynamic coupling, *i.e.*, modification of the (bulk) flow field around the swimmer through the presence of the wall, but in absence of the osmotic effect. This type of coupling has been investigated in detail for simple swimmer models, *e.g.*, see Ref. [24]. Flow-mediated interactions give rise to attraction and repulsion for pusher and puller swimmers, respectively, and may also lead to swimmer reorientation [24–26]. At a constant, yet small value of $\delta \lesssim a$, hydrodynamic slip can modify the mobility of a passive particle substantially [17, 23]. Nonetheless, a purely hydrodynamic effect is unlikely to describe our experiment. This is because at a fixed value of δ , boundaries perturb the parallel motion of an active particle less than that of a passive one. The former has a leading-order dipolar flow-field decay [24], while the latter has a leading-order monopolar decay, explaining the difference. It is straightforward to demonstrate that within far-field theory the effect is less than 10% of the bulk speed for a squirmer-type swimmer [27, 28] moving parallel to the wall, even for small separations.
- Solute-species confinement in the gap between wall and swimmer, which perturbs concentration gradients along the colloid surface. This affects the swimmer’s slip velocity and, in turn, its speed. Note that this effect comes on top of any purely hydrodynamic change of the velocity. This coupling has been extensively studied [29–33]. However, under the assumption that height remains fixed by modifying the nearby wall surface properties, the effect of this mechanism should be limited. This is because typically the Péclet number is small and the solute species are not substantially impacted by changes in the hydrodynamic flow field, due to wall modification.

Considering the above, we believe that the osmotic coupling scenario is the most likely candidate for describing our experimental observations.

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