

Size dependence of the propulsion velocity for catalytic Janus-sphere swimmers

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The propulsion velocity of active colloids that asymmetrically catalyze a chemical reaction is probed experimentally as a function of their sizes. It is found that over the experimentally accessible range, the velocity decays as a function of size, with a rate that is compatible with an inverse size dependence. A diffusion-reaction model for the concentrations of the fuel and waste molecules that takes into account a two-step process for the asymmetric catalytic activity on the surface of the colloid is shown to predict a similar behavior for colloids at the large size limit, with a saturation for smaller sizes.

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Introduction. The motion of colloids under the influence of externally imposed solute concentration gradients in solutions, known as diffusiophoresis [1], is an interesting nonequilibrium phenomenon [2,3] that has recently been used for a number of applications, such as manipulating colloids in microfluidic systems [4]. If a colloid is equipped with a mechanism to generate and maintain a concentration gradient around itself, e.g., by having an asymmetric coating of a catalyst on its surface [5], then the self-diffusiophoresis provides a mechanism that propels the colloid as long as the *fuel* molecule—that the catalyst breaks down—is available in the solution, without the need to impose an external gradient or other forms of driving [6,7]. In addition to providing a mechanism for making artificial micro- and nanoscale swimmers, which is an active multidisciplinary area of research [8], self-diffusiophoresis has also been suggested to play a role in biological systems with catalytic motility, such as *Listeria* [9], where the phenomenon needs to be formulated in the advection-dominated limit [10]. The mechanism has also been demonstrated to work in critical binary fluid mixtures [11].

Recent studies have revealed very interesting properties for self-diffusiophoretic colloids under a variety of circumstances. These studies examined the effects of solute density fluctuations (and the resulting anomalous nature of colloidal fluctuations) [12], confinement [13], geometrical features [14], attachment of polymer tether [15] and cargo [16], external shear flow [17], and gravity [18], as well as the efficiency of the catalytic propulsion mechanism [19]. Other studies have focused on the characteristics of the motion such as the direction of propulsion in the Janus-sphere system [20], as well as making more complicated geometries such as dumbbells with a variety of catalytic patterns [21,22].

While knowing the characteristics of such active colloids could help us determine how feasible this mechanism is as a means of making catalytic swimming devices, it also provides an opportunity to systematically probe the statistical physics of a well-defined nonequilibrium model system. This could be of particular significance when there are rival

theoretical formulations with conflicting predictions about the dependency on certain parameters. As a recent example, we note the controversies surrounding the size dependence of the thermophoretic response of colloids [23]. It is natural to expect that size could also provide such a testing ground for self-diffusiophoresis.

Here we study, both experimentally and theoretically, the effect of size on the propulsion velocity of spherical colloidal swimmers that have a hemispherical coating of catalyst. We have made Janus particle swimmers with well-defined sizes ranging from 250 nm to 5 μm in radius (R), and have analyzed their trajectories to determine their intrinsic velocities, keeping other parameters known to alter velocity—such as catalyst coating, thickness, and fuel concentration—constant. We find that the velocity is extremely sensitive to the size of the Janus particle, exhibiting a decrease that is compatible with a $1/R$ dependence in the range of our observations, as Fig. 1 shows. We use a simple model to study the reaction-diffusion process of the fuel and the waste molecules that involves a two-step process for the catalytic breakup of the fuel on the surface of the Janus particle. Our model predicts a crossover for the swimming velocity from a size-independent form at small R to an asymptotic form in the large R limit as

$$V \simeq 0.3 \frac{k_B T \lambda_{\text{eff}}^2 C_\infty}{\eta R}, \quad (1)$$

where $k_B T$ is the thermal energy scale, η is the viscosity of water, C_∞ is the concentration of the fuel molecules far away from the sphere, and λ_{eff} is an effective Derjaguin length (see below for definition). As seen in Fig. 1, this scaling form appears to fit reasonably well with the measured velocities in the range covered by our experiments.

Experiment. Janus particle swimmers are made by evaporating platinum metal onto a monolayer of polystyrene beads with a well-defined size distribution, purchased from Thermo Scientific. As the thickness of the platinum coating affects the propulsion velocity, the differently sized spheres were codeposited onto the same substrate, to ensure they received an equivalent coating. After manufacture, the assorted Janus beads were suspended into aqueous solutions containing 10% H_2O_2 fuel. The active colloids have a propulsive component in addition to their passive Brownian motion, which is controlled

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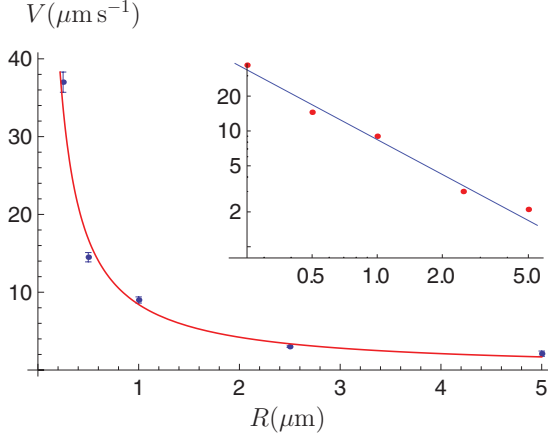


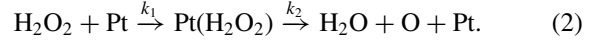
FIG. 1. (Color online) Experimental results for the swimming velocity as a function of the radius of the colloidal sphere. The solid line is a plot of Eq. (1) with $T = 293$ K, $\eta = 1.0 \times 10^{-3}$ Pa s, $C_\infty = 3.0$ M (10% w/v), and $\lambda_{\text{eff}} = 0.62$ Å (the only fitting parameter). Inset: The same results in log-log form.

by the translational diffusion coefficient $D = k_B T / (6\pi\eta R)$. The persistence in the orientation of the propulsion decays after the rotational diffusion time $\tau_R = 8\pi\eta R^3 / k_B T$. Videos of 30-s duration of many different Janus particles for each diameter were recorded using a Nikon microscope. The trajectory of each particle was subsequently determined using custom-built LABVIEW image analysis software, and the resulting quantitative mean-square displacements (ΔL^2) as a function of the time step (Δt) were analyzed to determine the intrinsic propulsion velocities (V) [24]. This was achieved by fitting the mean-square displacement data to an approximate quadratic expression for swimmer displacements $\Delta L^2 = 4D\Delta t + V^2\Delta t^2$, which is valid while $t \ll \tau_R$ [7]. The Δt ranges fitted were adjusted as far as experimentally possible to ensure this latter condition was satisfied (radius, fitted range, and percentage of τ_R : 0.25 μm ; $\Delta t = 0.022$ s, 22.7%; 0.5 μm ; $\Delta t = 0.133$ s, 17.2%; 1 μm ; $\Delta t = 0.133$ s, 2.1%; 2.5 μm ; $\Delta t = 1$ s, 1%; 5 μm ; $\Delta t = 4$ s, 0.51%). For small particles, a maximum video frame capture rate of 66 Hz imposed a limit on the shortest time period that could be fitted. Theoretical values for D were used to constrain the fits. We note that the majority of the data was taken in the solution with the focal plane situated in the middle of a 1-mm path-length cuvette.

The resulting swimming velocities obtained by performing a trajectory analysis for Janus particles half coated with a platinum catalyst in 10% H_2O_2 with radii in the range of 0.25–5 μm are shown in Fig. 1. We observe that the velocity of the active colloids decreases as their size increases. This appears to contradict the expectation that the velocity of self-diffusiophoretic swimmers is independent of size, and is only controlled by the *activity*, which is a measure of the effective rate of activity for the catalytic reaction, the *mobility*, which is controlled by the interaction of the solute molecules with the surface of the colloid, and the diffusion coefficient of the solute [5]. This is, however, only a statement about the contribution of size to the swimming velocity due to hydrodynamics. The key to resolving this apparent contradiction is to realize that the activity, which is taken as an effective rate of particle production per unit area, is itself

the result of a complex catalytic reaction-diffusion process and might depend on size. To calculate this effective rate we need to properly understand the kinetics of the reaction by taking into account all of the molecular species involved in the reaction, their asymmetric and localized catalytic activities on the surface of the colloids, as well as their diffusion in the bulk. This is what we set out to do next.

Reaction-diffusion process of the fuel molecules. We consider the simplest kinetic route for the chemical reaction that involves an intermediate process in which hydrogen peroxide forms a complex with the platinum:



Assuming a separation of time scale between the solute diffusion and the motion of the sphere [12], we can treat the reaction-diffusion process of the molecules in the stationary limit. Using the notation $C_{\text{hp}} \equiv [\text{H}_2\text{O}_2]$ and $C_o \equiv [\text{O}]$, and ignoring advection (see below), the solutes satisfy the diffusion equations $\nabla^2 C_{\text{hp}}(r, \theta) = 0$ and $\nabla^2 C_o(r, \theta) = 0$ in the bulk, subject to the boundary conditions

$$-D_{\text{hp}}\partial_r C_{\text{hp}}|_{r=R} = -k_1 C_{\text{hp}}(R, \theta) p_{\text{fr}}(\theta) K(\theta), \quad (3)$$

$$-D_o\partial_r C_o|_{r=R} = k_2 p_{\text{cx}}(\theta) K(\theta), \quad (4)$$

at the surface of the sphere, where D_{hp} and D_o are the diffusion coefficients for hydrogen peroxide and oxygen, respectively. Here, $K(\theta)$ is the “coverage” function

$$K(\theta) = \begin{cases} 1, & 0 < \theta < \frac{\pi}{2}, \\ 0, & \frac{\pi}{2} < \theta < \pi, \end{cases} \quad (5)$$

which describes the angular pattern of the platinum patch on the surface of the Janus particle, $p_{\text{cx}}(\theta)$ is the probability of a $\text{Pt}(\text{H}_2\text{O}_2)$ complex forming at the surface, and $p_{\text{fr}}(\theta)$ is the probability that platinum is free. Naturally, the two probabilities satisfy $p_{\text{cx}} + p_{\text{fr}} = 1$. The stationary state for the two stages of the reaction of Eq. (2) requires

$$k_1 C_{\text{hp}}(R, \theta) p_{\text{fr}}(\theta) = k_2 p_{\text{cx}}(\theta), \quad (6)$$

which could be used to solve for the probabilities. Equation (6) puts a constraint on the two concentrations as $D_{\text{hp}} C_{\text{hp}}(r, \theta) + D_o C_o(r, \theta) = D_{\text{hp}} C_\infty$, such that there is only need to solve for one of the concentrations, namely, hydrogen peroxide, which will now be subject to the nonlinear boundary condition $-D_{\text{hp}}\partial_r C_{\text{hp}}|_{r=R} = -k_2 k_1 C_{\text{hp}}(R, \theta) K(\theta) / [k_2 + k_1 C_{\text{hp}}(R, \theta)]$. The solution of the Laplace equation for the concentration of hydrogen peroxide in terms of Legendre polynomials reads $C_{\text{hp}}(r, \theta) = C_\infty [1 - \sum_\ell B_\ell (\frac{R}{r})^{\ell+1} P_\ell(\cos \theta)]$, which can be inserted in the boundary condition to give the self-consistent equation for the coefficients B_ℓ as

$$\sum_\ell B_\ell (\ell + 1) P_\ell = \frac{(\frac{k_1 R}{D_{\text{hp}}}) [1 - \sum_\ell B_\ell P_\ell] K(\theta)}{1 + (\frac{k_1 C_\infty}{k_2}) [1 - \sum_\ell B_\ell P_\ell]}. \quad (7)$$

These coefficients will determine the concentration profiles of all the solute molecules, from which we can deduce the diffusiophoretic slip velocity as $\mathbf{V}_s = (\mathbf{I} - \mathbf{nn})[\mu_{\text{hp}} \nabla C_{\text{hp}} + \mu_w \nabla C_w + \mu_o \nabla C_o]$ just outside the surface of the Janus sphere, where w denotes water and \mathbf{n} is the surface normal unit

vector [2]. Here the surface mobility for the solute species j is defined as $\mu_j = \frac{k_B T}{\eta} \int_0^\infty dz z [1 - e^{-W_j(z)/k_B T}]$ in terms of the interaction potential $W_j(z)$ between the diffusing molecules and the surface of the colloid. Note that $\mu_w = 0$, since we have a special case in which one of the products of the reaction is the same as the solvent. Averaging over the surface of the sphere (using integration over the solid angle Ω), we can obtain the swimming velocity of the Janus sphere as $\mathbf{V} = -\frac{1}{4\pi} \int d\Omega \mathbf{V}_s$, which yields

$$V = \frac{2}{3} \left(\frac{k_B T \lambda_{\text{eff}}^2}{\eta} \right) \frac{C_\infty}{R} B_1 \left(\frac{k_1 R}{D_{\text{hp}}}, \frac{k_1 C_\infty}{k_2} \right), \quad (8)$$

where the effective Derjaguin length [1] is calculated as $\lambda_{\text{eff}}^2 = \int_0^\infty dz z \left\{ \frac{D_{\text{hp}}}{D_o} [1 - e^{-W_o/k_B T}] - [1 - e^{-W_{\text{hp}}/k_B T}] \right\}$. The propulsion velocity depends on the concentration of the fuel and the size of the sphere through the coefficient B_1 , which needs to be solved for using Eq. (7).

Different scaling regimes. We can extract the different asymptotic forms of the coefficient B_1 by examining the behavior of Eq. (7) in various limits. In the large size limit when $R \gg D_{\text{hp}}/k_1$ and $R \gg D_{\text{hp}}C_\infty/k_2$, Eq. (7) requires $[1 - \sum_\ell B_\ell P_\ell]K(\theta)$ to nearly vanish, which can be achieved via $1 - \sum_\ell B_\ell P_\ell = \alpha[1 - K(\theta)]$, where α is a constant of proportionality that can be determined numerically. Using the expansion of the coverage function in Legendre polynomials $K(\theta) = \frac{1}{2} + \frac{3}{4}P_1(\cos\theta) - \frac{7}{16}P_3(\cos\theta) + \dots$, we can read off the coefficients in this limit. In particular, we find $B_1 \simeq \frac{3}{4}\alpha$, which yields Eq. (1), using the numerically determined $\alpha = 0.6$ (see below). When $R \ll D_{\text{hp}}/k_1$ and $C_\infty \ll k_2/k_1$, Eq. (7) yields $B_1 \simeq \frac{3}{8}(\frac{k_1 R}{D_{\text{hp}}})$, which gives the swimming velocity $V \simeq k_B T \lambda_{\text{eff}}^2 k_1 C_\infty / (4\eta D_{\text{hp}})$. Similarly, when $R \ll D_{\text{hp}}/k_1$ and $C_\infty \gg k_2/k_1$, we obtain $B_1 \simeq \frac{3}{8}(\frac{k_2 R}{D_{\text{hp}} C_\infty})$, which yields $V \simeq k_B T \lambda_{\text{eff}}^2 k_2 / (4\eta D_{\text{hp}})$. These results are summarized in Fig. 2. We have numerically solved Eq. (7) to find B_1 as a function of the size and fuel concentration. The result is shown in Fig. 3, and agrees with the above asymptotic analysis. The plateau value of $B_1 = 0.45$ in Fig. 3 yields $\alpha = 0.6$.

Comparison with experiment. The strong size dependence of the measured velocities (presented in Fig. 1) suggests that in the current experiment the system must correspond to region III in the diagram in Fig. 2. In this regime, the swimming velocity could be approximately described by Eq. (1), which is independent of the two reaction rates (that are generally very difficult to ascertain and could be very variable), and only depends on the Derjaguin length (in addition to other known quantities), which we expect to be in the range of an angstrom. The solid line in Fig. 1 shows that, in addition to the general behavior, Eq. (1) also predicts the right order of magnitude for the swimming velocity, with a choice of $\lambda_{\text{eff}} = 0.62 \text{ \AA}$ for the Derjaguin length.

The $1/R$ behavior is expected to saturate when $R \ll D_{\text{hp}}/k_1$ for $C_\infty \ll k_2/k_1$, or $R \ll D_{\text{hp}}C_\infty/k_2$ for $C_\infty \gg k_2/k_1$ (see Fig. 2). Since we do not observe this saturation even for $R = 250 \text{ nm}$ (and using $D_{\text{hp}} = 1.4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$), we can estimate that in the current experiment $k_1 > 3.4 \times 10^{24} \text{ M}^{-1} \text{ m}^{-2} \text{ s}^{-1}$, or in units where concentration is in percentage (as in Ref. [7]) $k_1^y > 1.0 \times 10^{14} \mu\text{m}^{-2} \text{ s}^{-1}$.

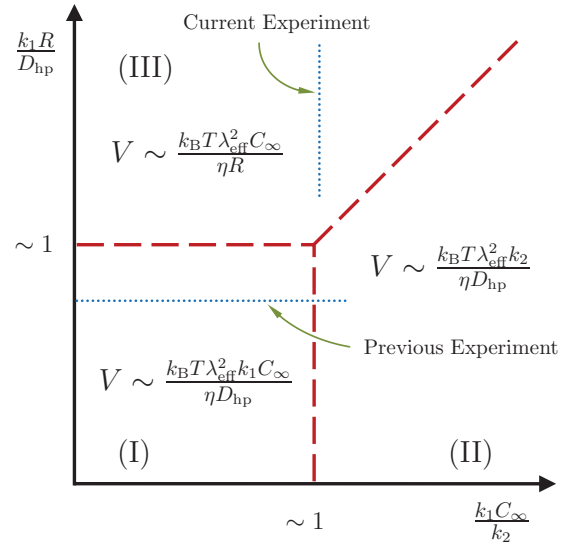


FIG. 2. (Color online) Three different scaling regimes for the swimming velocity as a function of the size and fuel concentration. The dashed lines show the crossover boundaries between the different regimes. The dotted lines show the locations in this diagram corresponding to the current experiment and the previous experiment of Ref. [7].

In the previous experiment [7], where we changed the concentration of hydrogen peroxide and not the size of the beads, we had two constraints in our fitting for the three parameters of λ_{eff} , k_1^y , and k_2 , and therefore we could not determine the values of these parameters unambiguously. We assumed a value of $\lambda_{\text{eff}} = 5 \text{ \AA}$ based on its expected order of magnitude, and reported the values of $k_1^y = 4.4 \times 10^{11} \mu\text{m}^{-2} \text{ s}^{-1}$ and $k_2 = 4.8 \times 10^{10} \mu\text{m}^{-2} \text{ s}^{-1}$ from the fitting [7]. If we use $\lambda_{\text{eff}} = 0.62 \text{ \AA}$ as suggested by the current experiment, we need to rescale both reaction rates by a factor of $(5/0.62)^2 \simeq 65$, which yields $k_1^y = 2.9 \times 10^{13} \mu\text{m}^{-2} \text{ s}^{-1}$ and $k_2 = 3.1 \times 10^{12} \mu\text{m}^{-2} \text{ s}^{-1}$. Using $R = 801 \text{ nm}$ and the new value for k_1^y , we can estimate that $k_1 R / D_{\text{hp}} = 0.5$ in the experiment of Ref. [7], suggesting that it corresponded

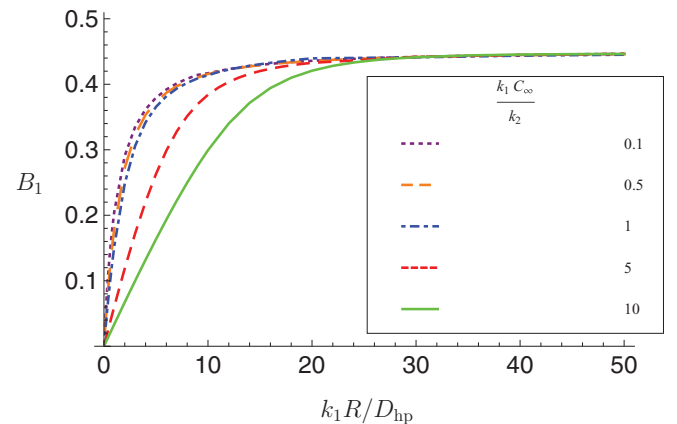


FIG. 3. (Color online) The coefficient B_1 that determines the swimming velocity as shown in Eq. (8) as a function of size and fuel concentration.

to a crossover from region I to region II, as shown in Fig. 2. Note that using the estimate for λ_{eff} obtained in the current experiment for the previous one is a crude approximation, as we expect the variability in the coating to affect this parameter. However, we expect our estimate to represent the order of magnitude of the parameter better than the originally presumed value.

Discussion. In our analysis, we have made a number of simplifying assumptions. The kinetics of the breakup of hydrogen peroxide catalyzed by platinum could in reality be more complicated than Eq. (2). However, we expect that more complicated intermediate steps will not change the main qualitative features of our results. Another assumption in our calculations is that the advection term can be neglected in the reaction-diffusion equation for the solutes. This might appear unjustified as the Peclet number for our swimmers could be rather large, reaching, for example, $Pe = 83$ for the $5\text{-}\mu\text{m}$ bead. However, in diffusiophoresis the condition that advection could be neglected is not $Pe \ll 1$, but rather $Pe \ll R/\lambda_{\text{eff}}$ (in the limit $\lambda_{\text{eff}} \ll R$) [25], which is always the case in our experiments. Using Eq. (1), we can calculate the Peclet number in the large R limit as $Pe \equiv \frac{VR}{D} \simeq 3\pi\lambda_{\text{eff}}^2 C_\infty R$. Hence, we find that advection can be neglected provided

$C_\infty \ll 1/\lambda_{\text{eff}}^3$, which is interestingly independent of the size of the swimmer.

It would be desirable to experimentally probe the entire parameter space as presented in Fig. 2. There are, however, experimental limitations on the practical range of size and fuel concentration, if we are to use a consistent protocol based on particle tracking and stay within the regime where self-diffusiophoresis is expected to be the dominant propulsion mechanism. Smaller sizes would require the use of scattering methods, due to the optical limit, which would no longer allow direct determination of individual swimmer velocities. Increasing the fuel concentration or using larger particles will lead to the local production of oxygen concentrations too large to dissolve, causing bubble release. The bubbles contribute to propulsion and do not allow systematic probing of self-diffusiophoresis.

In conclusion, we have shown that the size dependence of the propulsion velocity of catalytic Janus beads could be used to shed more light on the nature of the nonequilibrium activity of such colloids.

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