Dynamics of self-propelled colloids and their application as active matter
Choudhury, Udit

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2019

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
3 : Active colloidal propulsion over a crystalline surface
This chapter is largely based on the journal paper “Active colloidal propulsion over a crystalline surface” Udit Choudhury, Arthur V Staube, Peer Fischer, John G. Gibbs and Felix Hofling in *New Journal of Physics* 19, 125010 (2017).¹

The author performed the measurements, including video tracking and analysis. The author was assisted by Cornelia Miksh in preparing the surfaces. The theory underlying the experimental work of the author was developed by A.S. and F.H.

### 3.1 Introduction

The motion of self-propelled colloids differs from simple Brownian motion, because active particles interact hydrodynamically and chemically with each other and walls. For instance, the distribution of reaction products is affected by the presence of a wall, which breaks symmetry and directs the particle. It is therefore of interest to observe the dynamics of self-propelled particles near a complex boundary and the interaction with a more complicated topography is thus expected to play a major role to determine the dynamics of an active colloid. Here, a model system is considered and the dynamics of chemically self-propelled Janus colloids moving atop a two-dimensional crystalline surface is studied.

The surface is a hexagonally close-packed monolayer of colloidal particles of the same size as the mobile one. The dynamics of the self-propelled colloid reflects the competition between hindered diffusion due to the periodic surface and enhanced diffusion due to active motion. The propulsion strength determines which contribution dominates and can be systematically tuned by changing the concentration of a chemical fuel. The mean-square displacements (MSDs) obtained from the experiment exhibit enhanced diffusion at long lag times. The MSD describing the crossover from free Brownian motion at short times to active diffusion at long times are fitted to an approximate analytical model to describe the diffusion coefficients.

### 3.2 Motivation

The non-equilibrium behavior of active and passive particles ranging from microorganisms such as bacteria and artificial microswimmers to passive colloidal particles is an area of intense research in the last decade.²⁻⁵ Biological microswimmers move by means of body
shape changes driven by flagella and cilia. On the other hand, synthetic active particles are engineered to cause self-propulsion without any body shape changes. Typically, they have a catalytic patch on their surface that can consume fuel present in the fluid. This creates a local field gradient via a self-diffusiophoresis mechanism as has been discussed in Chapters 1 and 2 of this thesis.

Confining external potentials can substantially influence the dynamics of particles. For instance, the transport properties of passive particles changes when driven over one- and two-dimensional spatially periodic or random potential landscapes or in time-dependent potentials. This manifests in control over speed of particles, the strength of diffusion and also in appearance of transport anomalies. For active colloids, one also expects changes in their dynamics and indeed those confined by external potentials, behave similarly to passive particles with an elevated effective temperature or subject to an effective potential. Furthermore, simulation studies of microswimmers exploring a heterogeneous, random landscape suggest a rich phenomenology due to the interference of the landscape with the trajectory of the swimmer.

Hydrodynamic coupling with a confining boundary can also significantly affect the motion of a particle moving through fluids. In case of a passive particle dragged or rotating near a plane wall, its mobility is significantly suppressed. In case of active motion near plane, the situation is, however, further complicated by swimmer–wall interaction forces. For instance, the concentration of chemical fields near self-phoretic swimmers can be modified by the presence of a surface. Moreover, active colloids tend to accumulate at surfaces, even in the absence of direct, e.g. attractive electrostatic interactions between the swimmer and the surface. In these cases a description based on an effective temperature is likely to be too simplistic.

In this study, the interplay of active propulsion and a periodic confining potential is investigated. Experimentally, active colloidal micro-spheres are moving over a periodic surface realized as a hexagonal close-packed (HCP) monolayer of colloidal particles. The particles’ activity is controlled by changing the concentration of a chemical
fuel. Theoretically, the three-dimensional motion of an active colloid over the crystalline surface is treated as active Brownian motion in a two-dimensional energy landscape, while also accounting for the particles’ rotational diffusion. An intricate interplay between confinement effects and active motion is observed which leads to non-trivial dependencies on the long-time diffusion coefficients and crossover timescales.

3.3 Results

3.3.1 Experimental setup

First, the experimental system and tuning of particle activity by changing the concentration of a chemical propellant\textsuperscript{10,11,51} is described. An HCP monolayer consisting of spherical silica (SiO\textsubscript{2}) microbeads (average diameter d = 2.07 µm with a coefficient of variation of 10\%-15\%, Bangs Laboratories) forms the periodic surface upon which the active colloids move. The lattice constant of the crystal is set by the particle diameter. The HCP monolayer was prepared with a Langmuir–Blodgett (LB) deposition technique\textsuperscript{52} and covered an entire silicon wafer. A scanning electron microscope (SEM) image of the monolayer can be seen in Figure 3.1 b, and the actual topography of the surface is inferred from the atomic force microscope (AFM) image in Figure 3.1d. The silica microspheres were first functionalized with allyltrimethoxysilane, to facilitate LB deposition, then dispersed in chloroform. This colloidal suspension was then distributed over the air–water interface of an LB trough. A cleaned silicon wafer is dipped into the trough and, upon slowly pulling out the wafer, the monolayer is compressed to form a close-packed assembly. This process transfers the monolayer from the air–water interface to the silicon wafer. The wafer is then dried and treated with air plasma to remove any organic impurities before the experiments. While the LB technique yields large area HCP monolayers of silica beads, microscopic line defects can result from the lattice mismatch between adjacent self-assembled colloidal crystals. In order to ensure consistency of the underlying substrate topography, the lattice experiments were carried out on the same piece of wafer by varying the peroxide concentration for the same batch of particles. The active Janus colloids were fabricated by evaporating a 2 nm Cr adhesion layer followed by 5 nm of Pt onto microbeads of the same type as used for the monolayer; see Figure 3.1 a for an SEM image. The Janus spheres were
then suspended into H₂O₂ and subsequently pipetted onto an HCP lattice surface (Figure 3.1c). The Pt on the Janus particle catalyzes the decomposition of hydrogen peroxide (H₂O₂) and gives rise to self-propulsion. The strength of the propulsion was altered by adding different concentrations of aqueous H₂O₂ to the colloidal suspension, covering concentrations between 0% and 6% (v/v). For each concentration, trajectories from 10 randomly chosen Janus particles were recorded for 100 s at a frame rate of 10 fps with a Zeiss AxioPhot microscope in reflection mode with a 20× objective coupled to a CCD camera (pixel size 5.5 µmx 5.5 µm, resolution 2048 × 1088).

3.3.2 Data Analysis

Time-averaged mean-square displacements (MSDs) of 10 trajectories for each H₂O₂ concentration were computed, and by averaging the MSDs at each lag time the averaged MSD and its standard error was obtained. Data fitting was performed with the software OriginLab (OriginLab Corp., Northampton, MA) using a Levenberg–Marquadt iteration algorithm. Due to the linearly spaced time grid, the data points accumulate in the double-logarithmic representation at large times. To account for the different density of data points at short and long lag times on logarithmic scales, a 1/t weighting factor was used. The fits to eqns. (2) and (4), respectively, were then performed simultaneously for all 10 data sets of each concentration such that the different scatter of the data points enters the error estimate of the fit parameters. The free diffusivity D₀ was fixed initially to its value for the passive particle moving over a smooth surface and was slightly adjusted afterwards for each H₂O₂ concentration to obtain the best match with the averaged MSD curves.

3.3.3 Height of the potential barrier

Under gravity the Janus particles settle onto the substrate; once settled and in the absence of any fuel, Brownian motion leads to effectively two-dimensional diffusion in the gravitational potential imposed by the surface. The potential exhibits a periodic, hexagonal structure of potential wells with adjacent energy minima separated by a distance d/√3. In the presence of fuel a series of 'hops' are observed between adjacent wells (energy minima), or in analogy to surface diffusion, adjacent ‘adsorption sites’. Figure 3.2a
schematically demonstrates a single hop from one minimum to an adjacent one. A successful hop requires the Janus particle to overcome an energy barrier as depicted in Figure 3.2b. The gravitational potential $U(x) = \Delta mgz(x)$ is given by

Figure 3.1 Experimental setup (a) Scanning electron microscope (SEM) image of a single half-coated Janus particle; inset: dark-blue shows the location of the Pt cap. (b) Top-view SEM image of an HCP monolayer of SiO$_2$ microbeads. (c) An oblique-view schematic of Janus particle situated on the periodic, two-dimensional lattice, giving a sense of the corrugated, periodic morphology of the surface. (d) Atomic force microscope (AFM) image exhibiting the topography of the surface, color indicates the height in μm. Image taken from Ref 1.
the buoyant mass $\Delta m$ of the Janus particle, the acceleration $g$ due to gravity, and the height profile $z(x)$ at the two-dimensional position $x$.

The energy barrier between adjacent potential minima is thus $E_a = \Delta mg\Delta z$, where $\Delta z$ follows from elementary geometry as shown in Figure 3.2c for the configurations of maximal and minimal height. At the barrier maximum (left column of Figure 3.2c), the centers of two substrate particles and the mobile one form an equilateral triangle. The Janus particle is thus elevated by $z_{\text{max}} = \sqrt{3}d/2$ above the centers of the substrate particles. If the Janus particle is found in a potential minimum, the centers of three substrate particles and the mobile one form a regular tetrahedron, thus $z_{\text{min}} = \sqrt{6}d/3$. For a successful hop, the particles must overcome a geometric barrier of height $\Delta z = z_{\text{max}} - z_{\text{min}} \approx d/20$, which evaluates to $\Delta z \approx 100 \text{ nm}$ for $d = 2 \mu\text{m}$. This is consistent with the surface’s height profile obtained from AFM as shown in Figure 3.1d.

The second ingredient to the energy barrier $E_a$ is the total force on the Janus particle, which results from the competition of gravity and buoyancy, i.e. the energy barrier is also a function of the material from which the Janus particle is made. Let us first consider a silica sphere without a metal coating. Then the buoyant mass is $\Delta m = \Delta \rho V_{\text{SiO}_2}$, where $\Delta \rho = \rho_{\text{SiO}_2} - \rho_{\text{H}_2\text{O}}$ is the difference in density between SiO$_2$ and H$_2$O, and $V_{\text{SiO}_2} = (4/3)\pi a^3$ is the volume of the fluid displaced by the particle of radius $a = d/2$. For a bare SiO$_2$ bead of 2 $\mu\text{m}$ diameter, this yields $E_a = 1.7k_BT$.

In the case of the Janus particle, the asymmetric distribution of the metallic coating needs to be taken into account. Even though the volume of the cap is small in comparison to that of the bead, it has a significant effect on $E_a$ due to the higher density of Pt. Following Ref. [53], the hemispherical cap was modeled as ellipsoidal in shape; the thickness $\Delta a$ of the deposited metal is largest at the top of the sphere and tapers to zero at the equator. This assumption is justified from the deposition process, which delivers the atoms in the vapor plume ballistically to the top surface of the sphere while the sides along the equator remain shadowed and consequently have a thinner metal coating. The volume of the cap can be estimated as $V_{\text{Pt}} = [4/3\pi a^2(a + \Delta a) - 4/3\pi a^3]/2 = 2/3\pi a^2\Delta a$ and with this, the buoyant mass of the Janus particle is $\Delta m = (\rho_{\text{SiO}_2} - \rho_{\text{H}_2\text{O}}) V_{\text{SiO}_2} - (\rho_{\text{Pt}} - \rho_{\text{H}_2\text{O}}) V_{\text{Pt}}$. Adopting a value of $\Delta a = ...
5 nm as the maximal thickness of the Pt cap and using $\rho_{Pt} = 21.4 \text{ g/cm}^3$, one can estimate $E_a = \Delta m g \Delta z \approx 2.1 k_B T$ for the energy barrier of the Janus particle including the metal cap.

### 3.3.4 Distance from top of surface

For the Janus particle moving passively over a smooth plane, the translational diffusion constant $D_0$ is 0.13 $\mu m^2/s^{-1}$, which implies a translational (hereafter indicated by the subscript ‘T’) hydrodynamic friction of $\zeta_T = k_B T/D_0 = 3.2 \times 10^{-8} \text{ Pa-s/m}$ at $T=298 K$. As expected, the presence of a surface increases the hydrodynamic friction compared to unbounded motion: comparing with the Stokes friction $\zeta^{St}_T = 6\pi \eta a \approx 1.74 \times 10^{-8} \text{ Pa-s-m}$ in H$_2$O ($\eta = 0.89 \text{ mPa-s}$), one finds $\zeta_T \approx 1.8 \zeta^{St}_T$. For a planar surface, the friction coefficient $\zeta_T$ of a sphere of radius $a$ dragged parallel to the surface at a distance $h$ from the sphere center obeys Faxén’s famous result

$$\frac{\zeta^{St}_T}{\zeta_T} \approx 1 - \frac{9}{16} \frac{a}{h} + \frac{1}{8} \left( \frac{a}{h} \right)^3 - \frac{45}{256} \left( \frac{a}{h} \right)^4 - \frac{1}{16} \left( \frac{a}{h} \right)^5, \quad a \ll h, \quad (1)$$

Inserting the above experimental value for $\zeta_T$ and solving for $h$ with $a = 1 \mu m$, $h \approx 1.3 \mu m$ leaving a gap of $h-a \approx 0.3 \mu m$ between the two surfaces of the Janus particle and the planar substrate. Note that Faxén’s calculation relies on a far-field expansion of the flowfield and is justified only for small ratios $a/h$. As can be seen $a posteriori$, $a/h \approx 0.8$, implying slow convergence. Indeed, truncating after the 3rd order in $a/h$ yields an unphysical $h<a$, which is fixed by the 4th order term. The 5th order term contributes merely a relative correction of 2%, which suggests convergence of the series. Furthermore, this far-field estimate is compared with the predictions from lubrication theory$^{54}$ and a rigorous series expansion$^{55}$ accurate at all separations of the particle and the surface, including the singular limit of close approach. This cross-check shows that the present experimental situation is still outside the lubrication regime and equation (1) should provide very good estimates of the friction coefficient and the elevation $h$. In the following, it is assumed that the translational friction $\zeta_T$ does not change appreciably for the range of H$_2$O$_2$ concentrations used, although it may be modified for active motion due to altered boundary conditions at the colloid’s surface.
Figure 3.2 Topology of crystalline substrate. (a) Top-view schematic of a single hop from one potential well to an adjacent one. (b) Side-view schematic of an active particle situated in an energy minimum. (c) A cross-sectional representation of the Janus sphere traversing the energy barrier as it moves from one adsorption site to an adjacent one. The center of the sphere follows the black curved arrow, which is a section of a circle of radius \( h + a \), where \( h \) is the “elevation” above the crystalline surface. The maximum position corresponds to the dashed light-blue circle in the top-center portion of the figure. (d) Geometry of the barrier between adjacent potential wells due to the HCP lattice substrate. Top row: side-view of the mobile particle (blue circle) at its highest and lowest out-of-plane positions, \( z_{\text{max}} \) and \( z_{\text{min}} \) on the left and right columns, respectively. Bottom row: corresponding top-views, representing the in-plane positions of the mobile particle with respect to the location of the substrate particles (black circles). Image taken from Ref. 1.
3.3.5 Active motion on a plane and enhanced diffusion

In order to control the activity, the H$_2$O$_2$ concentration dependence of active motion as previously seen in catalytic chemical self-propulsion is utilized. On a flat, planar surface, the MSD after a lag time $t$ is given by

$$\Delta R^2(t) = 4 \left( D_0 + \frac{v^2 \tau_{rot}}{2} \right) t + 2 v^2 \tau_{rot}^2 \left( e^{-t/\tau_{rot}} - 1 \right),$$  \hspace{1cm} (2)

which follows upon assuming independence of translational diffusion of the colloid center and rotational diffusion of the Pt cap orientation; here $D_0$ is the diffusion coefficient for passive Brownian motion over a smooth plane, $v$ the root-mean-square propulsion velocity in the plane, and $\tau_{rot}$ the persistence time of the propulsion direction. The subscripts 'a', 'p' are used to distinguish between the active and passive motion and 'p' refers to the case of planar surface. Qualitatively, equation (2) implies that the active colloid undergoes passive diffusion for $t \ll \tau_0 = 4D_0/v^2$; ballistic motion for $\tau_0 \ll t \ll \tau_{rot}$, and enhanced diffusion for $t \gg \tau_{rot}$. In the latter regime, the MSD grows linearly with time with an increased diffusion coefficient $D_{a,p} = D_0 + v^2 \tau_{rot}/2$. Thus at long times, the motion of the active particle displays an enhanced diffusion relative to the motion of the passive particle ($v = 0$).

Figure 3.3 shows the experimental results for active motion on a smooth, planar surface for the six H$_2$O$_2$ concentrations investigated, from which the enhanced diffusion was obtained. The solid curves in Figure 3.3 are fits to equation (2), following the procedure in section 1.3.2, with the obtained parameters given in Table 3.1. In the inset of Figure 3.3, the MSD is rectified by dividing by the time lag $t$. This way, the crossover from Brownian diffusion $D_0$ at short times to enhanced diffusion $D_{a,p}$ at long times can be inferred more easily, and this representation serves also as a sensitive test of the fit quality. The short-time diffusivity $D_0$ was varied between 0.14$\mu$m$^2$/s and 0.18$\mu$m$^2$/s to obtain the best match with the averaged MSD curves. The small variability of the background diffusivity may be attributed to the sparseness of data points at short timescales, but it may also reflect possibly altered boundary conditions at the surface due to the catalytic reaction. The propulsion velocity $v$ measured this way (Table 3.1) increases monotonically with the H$_2$O$_2$ concentration $c$. 

44
Figure 3.3: Experimental MSDs of the active particles moving over a planar surface for six H₂O₂ concentrations. Solid lines are fits to eq. (2). Inset: rectification plot of the same data showing $\Delta R^2(t)/t$ vs. $t$ in order to more clearly expose the crossover from Brownian to enhanced diffusion. It also serves as a test of the fit quality. Between adjacent energy minima, or in analogy to surface diffusion, adjacent 'adsorption sites'. Image taken from Ref 1.
Table 3.1. Parameters obtained from fitting eq. (2) to the MSD data for active motion atop a planar substrate, shown in Figure 3.3. The long-time diffusion coefficient $D_{a,p}$ was calculated from $D_{a,p} = D_0 + v^2 \tau_{rot}/2$. The indicated uncertainties are standard errors of mean as obtained from the fitting procedure.

<table>
<thead>
<tr>
<th>$c$(%v/v)</th>
<th>$D_{0,p}$(μm²/s)</th>
<th>$D_{a,p}$(μm²/s)</th>
<th>$\tau_{rot}$(s)</th>
<th>$v$(μm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.13</td>
<td>0.13±0.0</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>0.1</td>
<td>0.16</td>
<td>0.35±0.1</td>
<td>11±3</td>
<td>0.18±0.0</td>
</tr>
<tr>
<td>0.5</td>
<td>0.14</td>
<td>0.7±0.2</td>
<td>12±3</td>
<td>0.30±0.0</td>
</tr>
<tr>
<td>2</td>
<td>0.16</td>
<td>1.4±0.5</td>
<td>4.2±0.7</td>
<td>0.77±0.0</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
<td>3.6±0.8</td>
<td>7.9±1.2</td>
<td>0.93±0.0</td>
</tr>
<tr>
<td>6</td>
<td>0.14</td>
<td>8.0±1.6</td>
<td>2.3±0.6</td>
<td>2.6±0.3</td>
</tr>
</tbody>
</table>

The long-time diffusivity $D_{a,p}$ also grows progressively with an increase in $c$ and is enhanced over $D_0$ for all concentrations $c>0$ studied, in accordance with equation (2). Further, since $v$ and $D_{a,p}$ for $c = 6\%$ v/v are significantly larger than the corresponding values for $c=4\%$ v/v, suggesting that additional effects become important for the propulsion mechanism at this high concentration. Finally, a large, non-monotonic variation of $\tau_{rot}$ is observed signifying that the rotational motion is non-trivially altered by the activity. This may be attributed to imperfections in the Janus particle, causing deviations from axisymmetric symmetry and thus the possibility of a residual active angular velocity on the particle.

3.3.6 Active motion on crystalline surface

Figure 3.4a shows the averaged MSD data of Janus particles being actively propelled atop the crystalline surface for six H₂O₂ concentrations. As expected, increasing the H₂O₂ concentration leads to higher observed propulsion speeds and higher long-time diffusion. The latter can be directly inferred from the rectification $\Delta R_{a,c}^2(t)/t$ displayed in the inset of Figure 3.4a. The data suggest further a monotonic dependence on time, either decreasing or increasing depending on the concentration of fuel, which can be interpreted as a
competition of the suppression of diffusivity due to the potential landscape with the enhancement due to active motion. The mean squared displacement of an active colloid on crystalline surface can be derived as (See Appendix 3.6)

\[ \Delta R_{a,c}^2 = 4 \left( D_{0p} - \Delta D_c + \frac{v^2 \tau_{rot}}{2} \right) t - 4 \Delta D_c \tau_s \left( e^{-t/\tau_c} - 1 \right) + 2 v^2 \tau_{rot}^2 \left( e^{-t/\tau_{rot}} - 1 \right). \] (3)

Fitting Eqn.(3) to the experimental MSD data would, in principle, provide an estimate for the parameters \( \Delta D_c, v, \tau_c, \tau_{rot} \). Following this approach, it turned out all of the parameters depend on the H\(_2\)O\(_2\) concentration. Specifically, fixing the values of \( v \) and \( \tau_{rot} \) to those from the experiments with the planar surface does not produce satisfying fits. Further, the four-parameter fits suggest similar values for \( \tau_c \) and \( \tau_{rot} \), which motivated us to merge both timescales into a single parameter, \( \tau \). This is consistent with the absence of any minimum or maximum at intermediate lag times in the data for \( \Delta R_{a,c}^2(t)/t \), which would be supported by Eqn.(3). However, \( \tau_c \approx \tau_{rot} \) implies that the parameters \( \Delta D_c \) and \( v \) are no longer independent, merely the combination \( \Delta D = \Delta D_c - v^2 \tau/2 \) can be obtained. Thus, Eqn.(3) reduces to a simplistic, effective model of the MSD of a self-propelled particle atop a periodic surface,

\[ \Delta R_{a,c}^2(t) \approx 4D_{a,c} t + 4(D_{a,c} - D_0) \tau \left( e^{-t/\tau} - 1 \right). \] (4)

By construction, this result has the same form as Eqn.(2) but the interpretation of the parameters is different in each case. For long times \((t>>\tau_c, \tau_{rot})\), the MSD increases linearly, and the combination \( D_{a,c} = D_0 - \Delta D_c - D + v^2 \tau/2 \) is the long-time diffusion coefficient on the crystalline surface. Eqn.(4) is used to fit the MSD data with \( D_0, D_{a,c}, \) and \( \tau \) as free parameters. The results obtained for each concentration are given in Table 3.2 and the fits shown as solid curves in Figure 3.4 provide a consistent description of the data. A slight variability of \( D_0 \) is obtained and a strong dependence of \( \tau \) on the H\(_2\)O\(_2\) concentration.
The enhancement of the long-time diffusivity $D_{ac}$ with increasing $\text{H}_2\text{O}_2$ concentration is much less pronounced compared to the case of a planar surface ($D_{ap}$ in Table 3.1), which is a direct consequence of the trapping potential.

Figure 3.4b shows effective diffusion coefficients on the crystalline and plane surfaces, $D_{ac}$ and $D_{ap}$, respectively, against the fuel concentration $c$. Strong deviations from one another at high concentrations are observed. At low concentrations of fuel, the particles move over the periodic surface by a hopping mechanism, probing the shape of the potential wells. Essentially, it appears there is a transition from a periodic landscape of high potential barriers at low concentration to a free particle system without any barrier, and therefore, the motion is similar to what is seen for a free active particle on a planar surface, but with a reduced diffusion coefficient. The experimental values for the ratio $D_{ac}$ to $D_{ap}$ vary between 0.7 and 0.19 and suggest a decrease towards higher concentrations $c$.

Table 3.2. Parameters estimates from fitting eq. (4) to the MSD data shown in Figure 3.4a

<table>
<thead>
<tr>
<th>$c$(%v/v)</th>
<th>$D_{0,p}$(μm²/s)</th>
<th>$D_{ac}$(μm²/s)</th>
<th>$\tau$(s)</th>
<th>$D_{ac}/D_{ap}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.14±0.0</td>
<td>0.05±0.0</td>
<td>0.4±0.0</td>
<td>0.38</td>
</tr>
<tr>
<td>0.1</td>
<td>0.17±0.0</td>
<td>0.25±0.0</td>
<td>6.3±2.9</td>
<td>0.71</td>
</tr>
<tr>
<td>0.5</td>
<td>0.18±0.0</td>
<td>0.29±0.0</td>
<td>5.4±2.2</td>
<td>0.41</td>
</tr>
<tr>
<td>2</td>
<td>0.14±0.0</td>
<td>0.56±0.0</td>
<td>2.3±0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>4</td>
<td>0.14±0.0</td>
<td>0.8±0.5</td>
<td>3.2±0.1</td>
<td>0.22</td>
</tr>
<tr>
<td>6</td>
<td>0.14±0.0</td>
<td>1.5±0.4</td>
<td>1.5±0.4</td>
<td>0.19</td>
</tr>
</tbody>
</table>
Figure 3.4 Active diffusion on a crystal surface. a) MSDs of the active particles moving atop the crystalline surface for six H$_2$O$_2$ concentrations. The solid lines are fits to eq. (4). Inset: rectification of the same data by plotting $\Delta R^2(t)/t$ vs $t$. b) Longtime diffusion coefficients on plane ($D_{a,p}$) and lattice ($D_{a,c}$) from Table 3.1 and Table 3.2 plotted against H$_2$O$_2$ concentrations. Image 3.4a taken from Ref 1.
This observation becomes more transparent when looking at lag times $t \ll \tau_{\text{rot}}$. Under these conditions, the propulsion direction is essentially fixed, and the active motion can be absorbed into an effective potential, $U_{\text{eff}}(x) = U(x) - \zeta_T v x$ which attains the shape of a tilted washboard. In this case and specializing to one dimension, Eqn. (4) reduces to a stochastic Adler equation, similar to the case of paramagnetic colloids driven over a periodic potential by a constant force$^{17,18}$. At relatively small velocities, $v < v_c$, the particle can escape the periodic minima of $U_{\text{eff}}(x)$ only by diffusion, and these minima vanish for velocities above a critical value, $v > v_c = E_a/\pi\zeta_T L \approx 1 \mu m/s$, assuming a period length $L = d/\sqrt{3}$ of $U(x)$. This can be compared to an active colloidal particle on plane that propels with a velocity of 0.93 $\mu m/s$ in a concentration of 4% H$_2$O$_2$ (see Table 3.1).

### 3.4 Discussions

The problem of propulsion of an active colloidal particle above a crystalline surface by a combination of experiment and theory, was studied in this chapter. The experimental system consists of catalytically driven colloidal Janus spheres sedimenting due to gravity on top of a periodic substrate. The strength of self-propulsion is controlled by changing the concentration of the chemical fuel, H$_2$O$_2$. Due to a relatively heavy cap, the center of mass of the nearly spherical active particle is slightly displaced from its center, which makes it bottom heavy. The substrate is realized by an HCP colloidal monolayer made of passive stationary colloidal particles of similar size and material. MSD of the Janus particle were investigated and parameters were extracted characterizing different regimes of motion. In particular, the behavior long-time diffusion coefficient was investigated showing how it changes relative to the free diffusivity and how it develops from the Brownian motion at short timescales. Two limiting cases were considered, which permit comparably simple interpretations, and finally their interplay was studied. First, active propulsion above a planar surface was studied, which shows an enhanced long-time diffusion constant and is in agreement with previously known results. Fitting the full time dependence of the MSDs provides additional details on how activity modifies the rotational diffusion. Second, the case of passive diffusion above a crystalline surface was investigated, which plays the role of a trapping potential and results in the suppression of the particle diffusivity. Third, the interplay of these two factors was studied, which have opposite effects on the diffusion
constant. It was found that depending on the strength of the activity relative to the strength of the trapping potential, the long-time diffusion constant can be either lower (weak activity) or higher (strong activity) relative to free diffusion. In all instances studied, the diffusion constant of an active particle remains larger than that of a passive particle. These findings are expected to apply to a broad class of self-propelled colloids and microswimmers moving on complicated topography where hydrodynamic coupling phenomena in the lubrication regime\textsuperscript{48} are relevant. Further, analogies with this model colloidal system with adatom diffusion on surfaces can also be investigated.
3.5 References


3.6 Appendix

The following derivation is from Ref [1] and was provided by Prof. Felix Höfling (TU Berlin). It has been included in the thesis for the benefit of the reader. Please refer to Ref [1] for further details.

3.6.1 Mean-square displacement of a self-propelled particle atop a crystalline surface

Active motion on a periodic potential can be modelled by overdamped Langevin equations as

\[ \dot{x}(t) = v(t) - \zeta^{-1} \nabla U(x_c(t)) + \sqrt{\frac{2kT}{\zeta}} \eta(t), \quad (A1) \]

Here \( x(t) \) and \( v(t) \) are particle position and velocities projected on to the plane of crystalline surface, \( \eta(t) \) is two dimensional Gaussian white noise with zero mean and unit co-variance to describe passive Brownian motion on a plane where the diffusion constant is \( D_0 = kT/\zeta \).

Diffusion in a periodic surface potential is described by the Langevin equation [Eq. (A1) and setting \( v = 0 \)]

\[ \dot{x}_c(t) = -\zeta^{-1} \nabla U(x_c(t)) + \sqrt{\frac{2kT}{\zeta}} \eta(t), \quad (A2) \]

the solution of which is well approximated by \(^2,3\)

\[ \Delta R_s^2(t) = 4(D_0 - \Delta D_c) t - 4 \Delta D_c \tau_c(e^{-t/\tau_c} - 1). \quad (A3) \]

This equation describes a crossover from free diffusion with \( D_0 = kT/\zeta \) at short times to diffusion at long times with reduced diffusion constant \( D_0 - \Delta D_c \), where \( \Delta D_c \) is the reduction of longtime diffusion constant due to crystalline surface. The crossover occurs at the time scale \( \tau_c \), after which the particle has explored a single potential minimum. The
inverse $\tau_c^{-1}$ may be interpreted as the attempt rate for escaping from the minimum. The corresponding velocity autocorrelation function is given by

$$Z_c(t) = \frac{1}{4} \frac{d^2}{d^2 t} \Delta R_c^2(t) = D_0 \delta(0) - \frac{\Delta D_c}{\tau_c} e^{-t/\tau_c}. \quad (A4)$$

Combining Eq. (A4) with the active motion [Eq. (A1)] simply adds the autocorrelation of the propulsion velocity,

$$Z(t) = Z_c(t) + \frac{1}{2} \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle, \quad (A5)$$

Assuming, the diffusive motion in the potential is independent from the propulsion velocity, i.e., $\mathbf{\eta}(t)$ and $\mathbf{v}(t)$ are independent random increments. Modelling the persistence of the propulsion directions by $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle = v^2 e^{-t/\tau_{\text{rot}}}$ (e.g., due to rotational diffusion) immediately yields the MSD after integration:

$$\Delta R_{a,c}^2(t) = 4 \int_0^t (t - s) Z(s) \, ds \quad (A6)$$

$$\Delta R_{a,c}^2 = 4 \left( D_{a,p} - \Delta D_c + \frac{v^2 \tau_{\text{rot}}}{2} \right) t - 4 \Delta D_c \tau_s (e^{-t/\tau_c} - 1) + 2 v^2 \tau_{\text{rot}}^2 (e^{-t/\tau_{\text{rot}}} - 1). \quad (A7)$$

**Additional References**

