Synthetic model microswimmers near walls

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Conclusions and Outlook

Biological swimmers are not only omnipresent in nature but are also instrumental in numerous processes relating to the production of food and fuel, bioremediation, and human health, and are thus of great importance for both fundamental science and industrial applications. Heavily inspired by their efficient propulsion strategies, self-regulating abilities, and adaptability within complex and crowded environments, an entire field of research has emerged in recent years aiming at developing, understanding and controlling synthetic swimmers at the microscopic scale.

To gain insights into synthetic microswimmer motion as is desirable for fundamental research and applications, in this thesis we studied the motion of synthetic model microswimmers near confining boundaries. Our model swimmers have been colloidal particles equipped with a Pt coating which covers half their surface that achieve self-propulsion in aqueous H_2O_2 environments *via* catalytic reactions taking place on the Pt. These reactions create chemical gradients which give rise to fluid flows around the particles, moving them in turn in the direction away from the Pt.

In **chapter 2**, we explored the behavior of these model swimmers near planar walls. Swimmers have the tendency to propel themselves downwards and thus quickly reach the bottom wall of their container; upon encountering the wall, they typically remain self-propelling parallel to it. Through changing the material properties of the wall, we found that walls impact their speeds. Our modeling showed that this effect can stem from the interplay between the hydrodynamic boundary condition on the wall and the chemical species produced by the reaction interacting with the wall, on the basis of an osmotic coupling mechanism. We concluded that fluid flows along the wall in conjunction with the flows along the swimmer surface are important in determining microswimmer speeds. Therefore, we proposed that wall effects can at least in part explain disparate speeds in the literature under similar conditions.

In **chapter 3**, we furthermore developed a diffusion-based height analysis to extract swimmer-wall separations. With this method, we found that microswimmers move in close proximity to the wall at gap heights of less than 300 nm, in agreement with previous observations of swimmers being stopped by steps with heights of a few hundred nanometers and with wall-dependent speed findings [103, 105, 155, 156]. In addition, we found that system parameters typically affecting the height in passive Brownian systems are less important for the active system; that is, catalytic particles tend to fixed heights thus exhibiting ypsotactic behavior. Despite the relatively unaffected height, we additionally found a speed decrease with increasing salt concentration. We proposed a wall-centric picture as an alternative to self-electrophoresis that was previously reported in

the literature: ionic diffusioosmosis along the wall stemming from long-range H_2O_2 gradients on the wall creates a flow that counteracts particle motion hence causing the speed decrease. Based on all the above, we overall concluded that walls are important factors in controlling swimmer motion and should be taken into account in future modeling.

As a next step, we exploited the swimmers' affinity for surfaces and further restricted their motion along closed one-dimensional paths in **chapter 4**. By printing secondary microstructures on the planar wall, we introduced additional geometric constrains for the swimmers which tended to accumulate on said structures. We were in turn able to identify a plethora of activity-induced interactions, caused by an effective potential stemming from a competition between chemical and hydrodynamic coupling. These interactions ranged from collective swimmer speedups for swimmers co-moving along the structures to the active assembly of swimmer chains that exhibited highly dynamic behaviors, with the latter being tunable through the local path curvature. We concluded that the concept of cooperative motion, a crucial element of biological swimmer systems, is even identifiable in synthetic active systems, opening the door towards exploiting cooperation for applications inside complex environments requiring increased swimming efficiency and directionality.

Finally, we explored the effect of swimmer shape by studying the near-wall motion of symmetric and asymmetric dumbbell swimmers. Unlike their passive state motion where preferred angles with the wall can be observed as in **chapter 5**, in the presence of activity dumbbell-shaped particles moved strictly in two dimensions in the direction perpendicular to their long axis. In **chapter 6**, we found highly tunable swimming trajectories spanning from straight-like to circular depending on the degree of particle asymmetry with respect to the propulsion direction. We concluded that, apart from employing confinement for path patterning, microswimmer shape is another promising route for tuning the directionality of active motion, allowing for different navigation strategies and control in the microscale.

Outlook:

Following the work presented in this thesis, we hereby propose routes for future research on synthetic microswimmers. We and other groups have reported on the importance of wall effects on microswimmer speeds [103, 105, 155, 156]. However, due to their gravitactic as well as ypsotactic tendencies, swimmer measurements in bulk are lacking. Such measurements could prove useful in identifying missing details of the propulsion mechanism of catalytic swimmers, as they would allow for propulsion force measurements in the absence and presence of salt near and away from walls. We have already briefly explored the

possibility of employing an optical-tweezer setup to trap such particles near the wall as well as in the bulk of the fluid. Although this approach is typically viable for non-coated particles, we were not able to efficiently utilize it on our colloids equipped with metallic caps; the reason being that once the asymmetric colloid feels the trap, the radiation pressure aligns it such that it is rapidly propelled out of the trap. However, it can still be worthwhile to attempt systematic experiments to finely tune experimental parameters such as size, metal coating thickness, coating surface coverage, or the setup itself, i.e. to adjust the trap radius through defocusing of the laser beam and laser power. Another promising possibility would be to employ acoustic levitation, see Ref. [293] for a review on acoustic propulsion. Although this technique has predominantly been employed in bimetallic nano- and microrod systems, acoustic trapping has also been utilized on polystyrene-Pt spheres which otherwise self-propelled along the air-water interface [294].

A highly interesting research avenue, of which we have only scratched the surface in our current work, is that of microswimmers inside patterned environments [106]. So far, these studies have been limited to either spherical particles or microrods. Combining our works on spherical swimmers along microprinted structures with that on symmetric and asymmetric dumbbell swimmers could yield novel insights into microswimmer interaction with boundaries; for example, we may be able to understand what is the combined effect of particle curvature and wall curvature on active motion by studying the behavior of symmetric and asymmetric dumbbells inside microprinted environments that employ structures with intricate shapes as for example in Figure 7.1A. Such effect could play a crucial role in fully unraveling the impact of confinement on microswimmer motion and, in turn, in further harnessing active particles inside, e.g., lab-on-a-chip devices, as well as aid in a deeper understanding of how biological swimmers are able to navigate complex environments.

Patterned environments may also enable researchers to go beyond single particle studies and towards unraveling collective behaviors in dense active systems, a vast research topic that remains experimentally largely unexplored especially for nonspherical synthetic swimmers. That is, environments may be patterned in controlled ways to direct the accumulation of particles with arbitrary shapes. Finally on the topic of patterning, equipping planar walls with secondary structures and once again exploiting their surface affinity may open new possibilities for exploring the three-dimensional motion of synthetic microswimmers. Apart from optical and acoustic trapping as discussed above, employing such structures can be an alternate route for guiding active particles in three dimensions, i.e. away from planar walls and towards bulk motion. In preliminary experiments using microprinted domes, see Figure 7.1B-C, we saw that spheri-

cal swimmers can follow the curvature of the dome and actively diffuse on its top. Although our bright field experiment in two dimensions would not allow for accurate particle tracking of the three-dimensional motion, fluorescent particles and microstructures could be employed instead to facilitate particle tracking, see Figure 7.1D. Overall, we believe that 3D microprinting for patterning both swimmer shapes [88] and their environments will create new opportunities for efficient swimmer utilization in future applications.

Lastly, we have so far highlighted the benefit of exploiting shape as a way to fabricate synthetic swimmers that more closely resemble their biological counterparts. Yet, the key aspect of structural flexibility and, even more so, spatiotemporal shape regulation through, e.g., segmented flexibility as is the case in biological systems, remains entirely unexplored in synthetic systems. That is, studies have focused either on rigid particles or semi-flexible particle assemblies [45, 295–297]. Recent work has shown that fully flexible structures can readily be prepared through particle functionalization with surface mobile DNA linkers, leading spherical particles functionalized with complementary linkers to assemble into structures that resemble colloidal polymers and molecules [298–300].

We explored the possibility of combining the aforementioned technique with Pt-coated particles to create self-propelling fully reconfigurable particle assemblies in H_2O_2. We prepared colloidal-joint particles with complementary motile DNA linkers following the DNA functionalization protocol using cholesterol anchors [298]. In addition, we prepared motor particles with Pt and surface-bound DNA to propel the structures using the following new strategy: as a first step, we functionalized Pt-coated particles with the protein NeutrAvidin by following the coating protocol of Ref. [136], see also the confocal image of Figure 7.1E. We applied said protocol to TPM-COOH particles that we had already half-coated with $\approx 4\,\text{nm}$ Pt: we activated the -COOH groups on the uncoated TPM surface to form esters and then we simultaneously coated them with fluorescently-labelled Neutravidin as well as we covalently-attached a polymer layer for stability. The green patches in Figure 7.1E correspond to the NeutrAvidin used in the experiment, indicating that half the particles' surface was coated after functionalization. We also verified that the NeutrAvidin had indeed correctly coated their TPM and not their Pt sides, as they moved towards their fluorescent and away from their non-fluorescent side in H_2O_2. Subsequently, we attached surface-bound DNA on the Neutravidin following the procedure described in Ref. [298] for functionalizing colloidal particles with bound linkers. The result is shown in Figure 7.1F, where the red patch denotes the fluorescently-labelled DNA. The DNA that we used was double stranded, prepared by hybridizing the strands named as D and E in Ref. [298], and had a biotin anchor. We chose this DNA for visualization purposes as it contrasted with the dye of the NeutrAvidin, as well as because it was
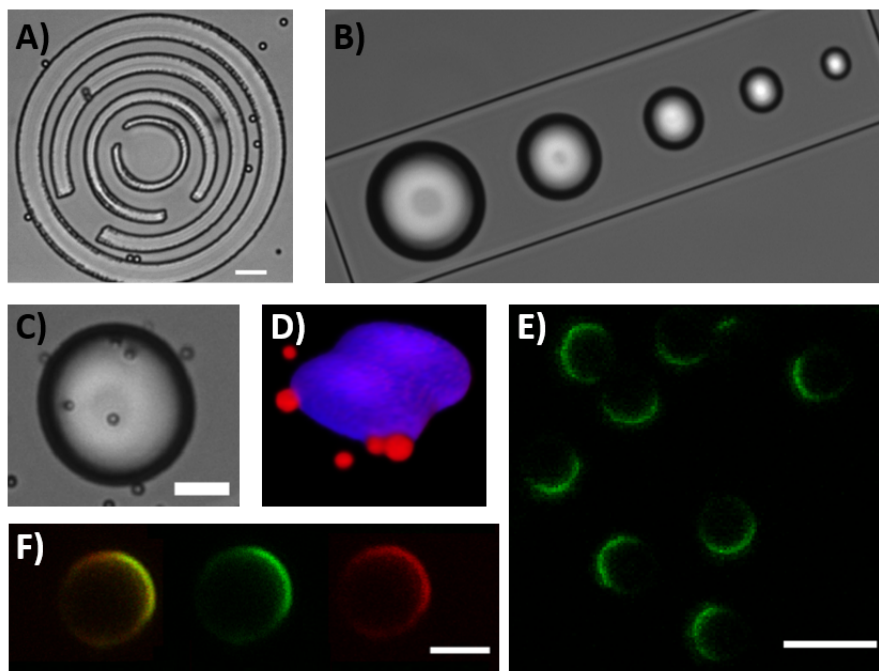
Figure 7.1: **Experiments towards microswimmers in complex environments and flexible microswimmers.** **A)** Nonspherical swimmer behavior could be studied inside intricate geometries, such as mazes, which can be readily obtained through 3D-microprinting, to potentially provide novel insights into the effect of confinement. Scale bar is 10 µm. **B)** Microprinted domes as a way to study three-dimensional motion of synthetic swimmers. **C)** Bright field microscopy image showing that active particles can follow the curvature of the dome and swim on its top. Scale bar is 10 µm. **D)** Fluorescent particles (red) and microstructures (blue) can be employed to facilitate particle tracking in three-dimensional experiments. The confocal image was reconstructed from a z-stack using commercial software. A-D) These experiments were performed in collaboration with Melissa Rinaldin. **E)** Pt half-coated particles after functionalization with fluorescent NeutrAvidin (green patches) following Ref. [136]. Scale bar is 5 µm. **F)** Particle functionalized with fluorescent NeutrAvidin and DNA bound to the NeutrAvidin imaged with green and red channels simultaneously (left), the green channel showing the NeutrAvidin (middle), and the red channel showing the fluorescently-labelled DNA (right). Scale bar is 2 µm. Such functionalized Pt-coated particles can subsequently be used for self-assembly purposes, for example as parts in flexibly linked colloidal structures.

complementary to the mobile DNA linkers used for the flexible structures.

Although motor particles were successfully prepared and could in principle be integrated into the flexible structures, we noted that salt — important for the stability of the flexible structures — diminished their velocity. As a consequence, the resulting structures would not self-propel. We concluded that combining these components was not feasible (as they were). However, we propose here that self-propelled flexible structures could be obtained in future research if either system component is modified.

The *first* possibility would be to use an assembly strategy that yields stable colloidal polymers without salt, while at the same time preserving the flexibility of the assembled structure. To this end, we propose that the self-assembly method with surface-mobile biotin linkers of Ref. [301] can be employed. The desired flexible colloidal polymer structures can then be obtained by exploiting the high specificity of biotin-NeutrAvidin bonds. This approach could subsequently also employ the half NeutrAvidin-coated and half Pt-coated particles of Figure 7.1E: after incorporation to one end of the flexible colloidal polymer, the catalytic particle could act as the structure's active motor element and push the polymer forward in H_2O_2 provided also that H_2O_2 does not affect the structural integrity and quality of the bilayer on the flexible structure.

The *second* possibility would be to use a propulsion mechanism that does not rely on the catalytic decomposition of H_2O_2 and hence is unaffected by salt. For example, thermophoretic swimmers, i.e. Au-coated particles propelled in water due to asymmetric heating, and/or acoustically propelled swimmers, maintain their propulsion even in high ionic strength solutions. Swimmers such as these could thereby serve as the active elements that propel the flexible colloidal structures assembled through surface-mobile DNA linkers. We note that the latter, i.e. eliminating H_2O_2 as a fuel, would be best in terms of biocompatibility for future applications: e.g., acoustic propulsion is not only unaffected by salt, but is also nontoxic and biocompatible, and hence more appropriate for biomedical microrobots [293].