JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Perspective

Open Questions of Chemically Powered Nano- and Micromotors

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Cite This: *J. Am. Chem. Soc.* 2023, 145, 27185−27197

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ABSTRACT: Chemically powered nano- and micromotors are microscopic devices that convert chemical energy into motion. Interest in these motors has grown over the past 20 years because they exhibit interesting collective behaviors and have found potential uses in biomedical and environmental applications. Understanding how these motors operate both individually and collectively and how environments affect their operation is of both fundamental and applied significance. However, there are still significant gaps in our knowledge. This Perspective highlights several open questions regarding the propulsion mechanisms of, interactions among, and impact of confinements on nano- and micromotors driven by self-generated chemical gradients. These questions are based on my own experience as an experimentalist. For each open question, I describe the problem and its significance, analyze the status-quo, identify the bottleneck problem, and propose potential solutions. An underlying theme for these questions is the interplay among reaction kinetics, physicochemical distributions, and fluid flows. Unraveling this interplay requires careful measurements as well as a close collaboration between experimentalists and theoreticians/numerical experts. The interdisciplinary nature of these challenges suggests that their solutions could bring new revelations and opportunities across disciplines such as colloidal sciences, material sciences, soft matter physics, robotics, and beyond.

1. INTRODUCTION

Nano- and micromotors are a unique class of colloidal particles that self-propel by consuming energy stored in their environments. Since their inception in the early 2000s,[1−5] the research field of nano- and micromotors has seen a rapid increase in both the number of publications and the academic attention. Much of the interest stems from their potential usefulness in biomedicine,[6−8] sensing,[9,10] environmental remediation[11] or microassembly and microtransport.[12,13] Moreover, nano- and micromotors serve as effective model systems for active matter and complex systems operating at nano- and microscales,[14,15] a forefront interdisciplinary topic.

Among the many ways to power a nano- and micromotor, chemical reactions are a popular source of power,[5,16−20] either by producing bubbles[21,22] or more subtly by producing a chemical gradient that leads to phoresis (i.e., transport in a gradient).[23−25] A distinct advantage of chemical propulsion is the vast choices in reactions, so that motors can be made of materials and powered by fuels of a wide variety. Moreover, the chemical gradient extends from the motor surface to its neighbors, enabling population-wide communication and collective behaviors that are inaccessible to other propulsion mechanisms (Figure 1). Because of these features, chemical propulsion has been popular since the very beginning of nano- and micromotor development.

However, despite its success and popularity over the past two decades, we still do not fully understand the fundamentals of chemically powered nano- and micromotor. Gaps in our understanding include the detailed mechanism of Pt Janus micromotors[26] or bimetallic microrods,[1] two of the most iconic examples of chemically powered nano- and micromotor. We also know little of exactly how chemical motors communicate with each other or how hydrodynamic interactions or the confining surfaces contribute to their collective behaviors. We know even less about their dynamics in confined spaces, an emerging topic that is attracting much attention.[27] There has been exciting theoretical and simulation progress on these fronts, but experiments often lag.

While these gaps in understanding impede progress, they also highlight promising avenues for research. In this Perspective, I will discuss three key areas of nano- and micromotor research where challenges and opportunities abound: propulsion mechanisms, collective behaviors, and the impact of confinements (Figure 1). Each area contains a few important, yet unsolved questions drawn from my own experiences working in this field. I will describe the problem and its significance, analyze the status-quo, explain the bottleneck issue, and suggest potential solutions. As the title of this paper suggests, we do not yet have clear answers to these questions. But by thinking about and articulating what we do not know and emphasizing on why these questions matter, I hope this Perspective can inspire new progress that solve the puzzles and move this research forward.

I note a few caveats to highlight the scope and limitations of the Perspective. First, this Perspective focuses on chemical micro- and nanomotors powered by chemical gradients, more specifically by self-electrophoresis and self-diffusiophoresis (see

Received: August 23, 2023
Revised: November 20, 2023
Accepted: November 21, 2023
Published: December 8, 2023

https://doi.org/10.1021/jacs.3c09223
J. Am. Chem. Soc. 2023, 145, 27185−27197

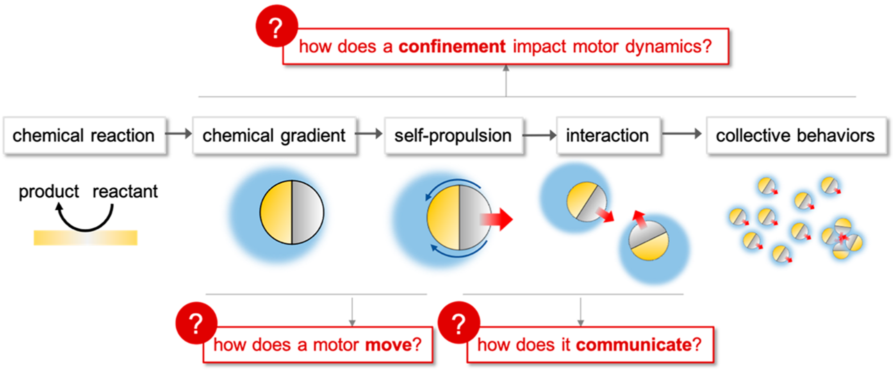

Figure 1. Three key questions about nano- and micromotors powered by chemical gradients.

sections below for definitions), rather than by released bubbles, thermophoresis,[28−31] or Marangoni flows,[32,33] which are all viable propulsion mechanisms. Second, the open questions addressed in this perspective are mostly about the fundamental principles of micromotors, rather than about their applications. Third, the questions, comments, and solutions presented here are subjective and limited by my own knowledge and ignorance. Finally, the primary goal of this article is to identify good, worthwhile scientific questions. However, by articulating these questions and identifying the bottleneck problems, this article will hopefully lead the readers (myself included) to careful experimental measurements and close collaboration between experimentalists and theoreticians and simulation experts that will ultimately solve these questions.

2. MYSTERIES ABOUT PROPULSION MECHANISMS

2.1. Introduction to Phoretic Self-Propulsion. Chemical reactions have historically been used to drive machines in our daily lives and were also one of the earliest ways to power microscopic machines. In a pioneering study,[34] the Whitesides lab designed a millimeter-sized disk with a piece of Pt attached to its end, which catalyzed H_2O_2 into oxygen bubbles that moved the disk. Inspired by this work, the Sen and Mallouk laboratories[1] reported an even smaller synthetic microswimmer-- a bisegmented nanorod made of gold and platinum that autonomously swam in H_2O_2 solutions. Later, the same groups discovered that,[35] although similar in designs, the Pt-containing nanorods did not move by releasing bubbles as the Pt microdisks did, but rather moved in a completely different mechanism referred to as "self-electrophoresis", which means the nanorod is a short-circuited battery moving in a self-generated electric field. This electric field arises because different half reactions occur on different parts of a motor, so that ions are distributed asymmetrically within the electrical double layer around the motor. Other examples of micromotors powered by self-electrophoresis include Au−Pt microspheres,[36,37] Cu−Pt nanorods,[38] and TiO_2−Au photocatalytic microspheres.[39]

Under the dome of chemical propulsion, new players soon began to take on the stage. Among them, self-diffusiophoresis emerges as a powerful and versatile mechanism to power microscopic machines.[40,41] Diffusiophoresis is a well-established concept[42−44] that refers to the transport of a colloidal particle in a gradient of chemicals. Self-diffusiophoresis then suggests that the gradient is generated by the colloidal particle itself. Depending on the nature of the chemical species, self-diffusiophoresis can be further grouped into neutral (or nonelectrolyte) self-diffusiophoresis in a gradient of neutral molecules,[45] and ionic (or electrolyte) self-diffusiophoresis in that of ions.[46] Notable examples of ionic self-diffusiophoresis include $CaCO_3$ micromotors and pumps that release Ca^{2+}, OH^- and HCO_3^-,[47−49] AgCl motors that release H^+ and Cl^-,[40,50] motors coated with urease that convert urea into NH_4^+ and HCO_3^-,[51] Ag motors that react with H_2O_2 to release Ag^+ and OH^-[52] (or OOH^-[53]), and motors coated with enzymes that catalytically turn their substrates into ions (such as urease[54−56]).

Understanding the detailed mechanism of how chemical gradients power micromotors is of great importance. This is not only because all chemical reactions produce chemical gradients, so that phoresis is universal, but also, more importantly, because the detail of individual propulsion could propagate into how motors interact with each other and ultimately impact their collective behaviors. Although all three mechanisms—self-electrophoresis, neutral self-diffusiophoresis and ionic self-diffusiophoresis—are all well studied (see refs 15, 25, 57, 58 for more details of these mechanisms), and that the theoretical understanding of electrophoresis and diffusiophoresis have matured since the 1970s, there has been ongoing confusion and controversy about which mechanism is responsible for a particular motor type, or the chemical detail that gives rise to a particular mechanism. The following three sections illustrate these open questions on three different aspects.

2.2. How does a Pt Janus micromotor move? Using the same catalytic decomposition of H_2O_2 as occurring on a Au−Pt nanorod motor, Howse et al. first reported in 2007 the self-propulsion of polystyrene microspheres half-coated with Pt in H_2O_2.[26] This micromotor design, referred to as a Pt Janus micromotor, quickly became popular, especially among soft matter physicists because of its ease of fabrication and sample uniformity. Here, the underlying chemistry appears rather simple, as oxygen bubbles produced by the decomposition of H_2O_2 are clearly seen trailing a Pt Janus micromotor made from large microparticles[59−61] (say a microsphere with a diameter larger than 10 μm).

However, the microscopic details of the self-propulsion of smaller Pt motors that do not produce visible bubbles are much less obvious and still debatable. In the early days, it was believed to be powered by neutral self-diffusiophoresis,[60] arising from the gradient of oxygen molecules that were more abundant near the catalytic Pt end. However, the fact that these motors move more slowly in salt waters[62−64] argues against neutral self-diffusiophoresis. Later, it was proposed[62,63] that the decomposition of H_2O_2 could produce transient, charged species that moved a motor by ionic self-diffusiophoresis. Alternatively, it has been proposed[62,63] that H_2O_2 is electrochemically, rather than chemically, decomposed, with cathodic and anodic half

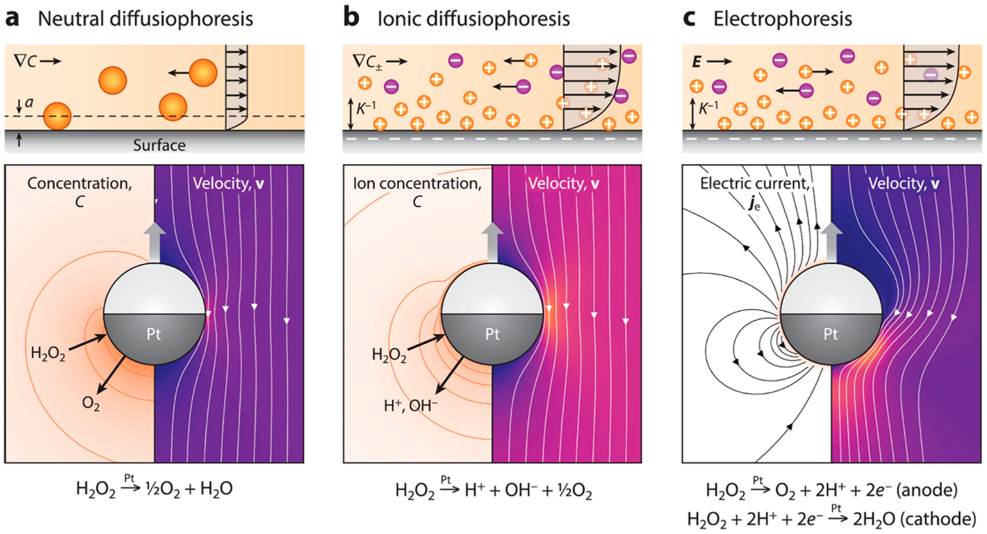

Figure 2. Three competing mechanisms explain the self-propulsion of a Pt Janus microsphere in H_2O_2. Reprinted or adapted with permission under a Creative Commons CC-BY 4.0 from ref 66. Copyright 2023 Annual Reviews.

reactions occurring on different regions on the Pt cap. This kind of bipolar electrochemistry that drives a Au−Pt nanorod motor could happen for a Pt Janus microsphere, possibly because the thickness of the Pt coating varies along the metal cap,[62,63] or because different regions of Pt coating have access to different amounts of rate-limiting species.[65] Either way, a Pt motor could be powered by self-electrophoresis in H_2O_2 in the same way as a bimetallic nanorod. These three possibilities for powering a Pt motor—neutral self-diffusiophoresis, ionic self-diffusiophoresis and self-electrophoresis—are nicely described in a recent review article (see also Figure 2).[66]

Our own studies favor self-electrophoresis for a Pt Janus micromotor in H_2O_2. For example, our recent study[67] revealed that a microsphere half-coated with Pt or catalase (an enzyme that converts H_2O_2 into water and O_2) did not necessarily self-propel despite high catalytic turnover rates. This surprising result suggests that the chemical decomposition of H_2O_2 is not sufficient to power a Pt motor and that the exact way Pt coats the surface matters significantly, which can only be rationalized by self-electrophoresis. A later study of ours[68] further supports self-electrophoresis as the dominant mechanism for a Pt motor by comparing their individual and collective dynamics against a set of rules that distinguishes self-diffusiophoresis and self-electrophoresis. More recently,[69] Unruh et al. rationalized the self-propulsion of Pt microdisks of various shapes in H_2O_2 under the framework of self-electrophoresis proposed in ref 65, and the good match between simulation and experiments provide further support to this mechanism in powering a Pt motor.

Although these studies lend strong support to the self-electrophoresis mechanism, at least two direct pieces of evidence are needed to truly solve the puzzle of how a Pt motor moves. Both relate to the separation of cathodic and anodic half reactions in self-electrophoresis. One evidence would be the experimental confirmation that electrons flow from the equator to the poles in the Pt cap of a Janus microsphere and/or that protons flow in the same direction in the surrounding liquid, as predicted by self-electrophoresis. This remains technically challenging for now, but perhaps similar measurements could be performed on a flat Pt film as preliminary evidence. The second piece of evidence would be the fundamental understanding and conclusive experimental proof of why different regions of a Pt cap behave as the cathode or anode. This question pertains to understanding not only Pt motors but bimetallic motors as well, as we elaborate below.

2.3. What makes the Pt end anodic and the Au end cathodic for a Au−Pt bimetallic motor moving in H_2O_2, but not the other way around?

The most accepted propulsion mechanism of a bimetallic motor in H_2O_2 is as follows.[35] The two metal ends (e.g., Au and Pt in a Au−Pt nanorod motor) have different capacities in catalyzing H_2O_2. When paired together, they assume the role of anode (Pt) and cathode (Au), and they catalyze the oxidation and reduction half reaction of H_2O_2, respectively. This electrochemical process generates an excess of protons near the anode end, and a shortage near the cathode end, which leads to an asymmetric distribution of space changes and thus an electric field that moves the charged nanorod. This is the self-electrophoresis mechanism we described earlier, and its core component is *bipolar electrochemistry*; i.e., the decomposition of H_2O_2 is split into two half reactions occurring on each end of a rod. This was strongly supported by the results of Yang et al. in 2006,[35] which confirmed through careful experiments that Pt served as the anode and Au the cathode (Figure 3a).

However, this seminal work by Yang et al. only confirmed that when placed in contact with each other in H_2O_2, the oxidative half reaction preferred to occur on one metal over the other (manifested by their mixed potentials), without explaining why from a microscopic and fundamental level. Answering this fundamental question goes beyond fulfilling my own curiosity, and could lead to better designs of catalytic nanomotors of high speeds, as in the curious case of extremely fast nanomotors made of Au−Ag alloys.[70] However, if the answer is as simple as the difference in catalytic capability, then one might draw the naïve conclusion that more catalytically active metals tend to serve as anodes, as in the case of Pt vs Au. Following this argument, Pt, being orders of magnitude more catalytically active in decomposing H_2O_2 than Ru, Rh or Au,[71] should always be the anode and the leading end in H_2O_2 when paired with Ru/Rh/Au in a bimetallic nanorod. Yet, the result from Yang et al.[35] is quite the opposite: the Rh end leads a Rh−Pt nanomotor. The other possibility is the electronegativity of these metals, yet their values[72] do not match the observed preferences. Unfortunately,

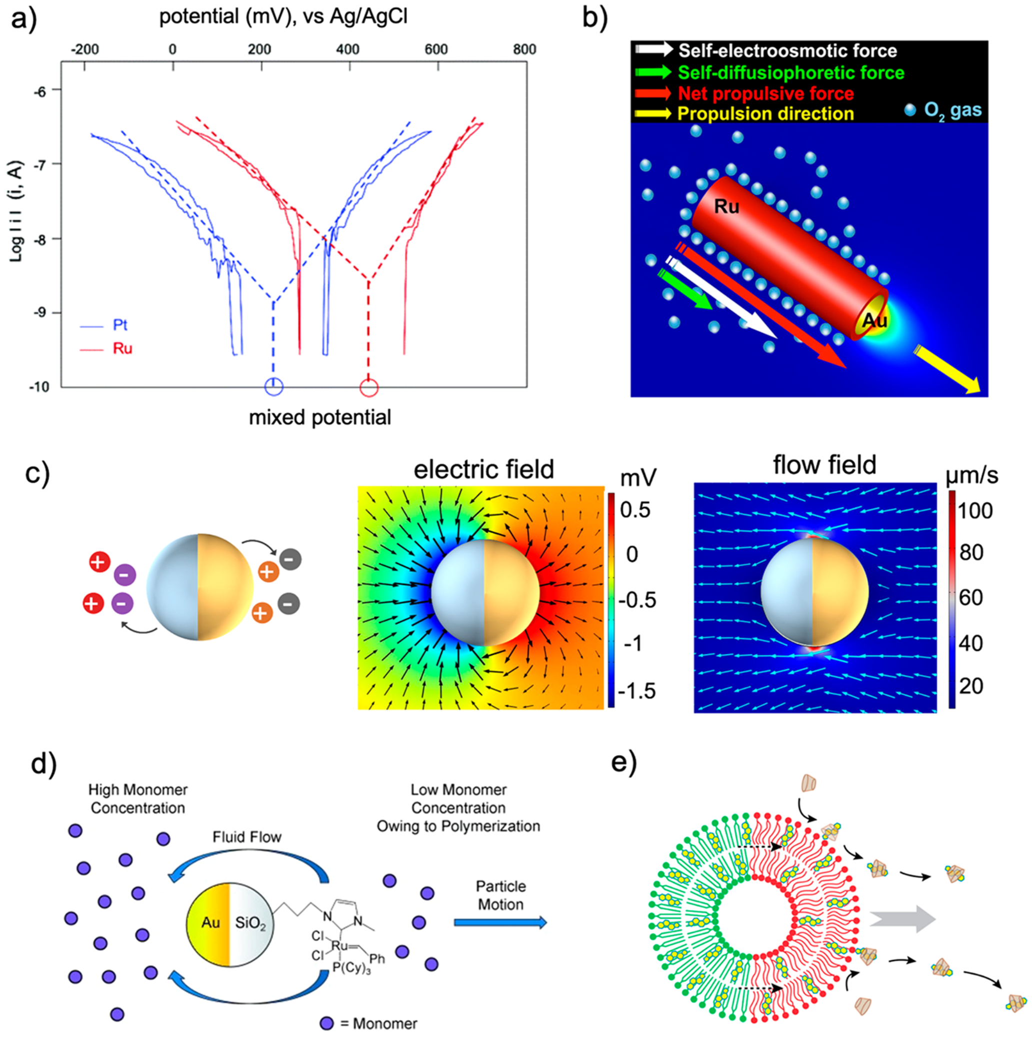

Figure 3. Questions on the propulsion mechanisms of chemical micromotors. a) Tafel plots of Pt and Ru metals in H_2O_2. Mixed potentials are the potentials at which the cathodic and anodic currents are equal, and metals of a more positive mixed potential prefer to serve as the cathode in a bimetallic nanomotor in H_2O_2. Figure adapted from ref 35. Copyright 2006 American Chemical Society. b) The combination of self-diffusiophoresis and self-electrophoresis in the propulsion of a Au−Rh core−shell nanomotor in H_2O_2. Figure adapted from ref 73. Copyright 2016 American Chemical Society. c) A diffusiophoretic motor that releases two pairs of ions from both hemispheres are similar to a self-electrophoretic motor. left: cartoon schematic. middle and right: numerical simulations of the electric field (middle) and the flow field (right) around such a motor. Figure adapted from ref 68. Copyright 2022 Wiley. d) A Au-SiO_2 microsphere that asymmetrically catalyzes a polymerization reaction is suspected to move via neutral self-diffusiophoresis. Figure adapted from ref 74. Copyright 2011 Wiley. e) A Janus liposome microsphere where cholesterols are extracted asymmetrically is suspected to move via neutral self-diffusiophoresis. Figure adapted from ref 75. Copyright 2022 American Chemical Society.

I am not aware of any ongoing or past investigation to provide an answer, which could be related to the electronic structures of various metals that ultimately affect the kinetics of H_2O_2 half reactions on the surface of catalytic metals.

2.4. Distinguishing between Self-Electrophoresis and Self-Diffusiophoresis. The close examination of a bimetallic nanorod moving in H_2O_2 not only reveals the holes in our understanding of self-electrophoresis but also hints at a deep connection between self-electrophoresis and self-diffusiophoresis that are commonly perceived as separate mechanisms.

For example, a 2016 study[73] that I participated in showed that the speed of a core−shell bimetallic nanorod in H_2O_2 increased with its length (Figure 3b). This result disagreed with earlier studies of bisegmented nanorods that moved more slowly as they became longer, as predicted by self-electrophoresis. To explain the discrepancy, we proposed that the nanorod was powered by both *both* self-electrophoresis and self-diffusiophoresis. The former comes from the bipolar *electrochemical* decomposition of H_2O_2, and the latter comes from its *chemical* decomposition. An earlier study[76] even put a number to these two competing processes: only 0.1% of all H_2O_2 went through electrochemical decomposition that contributed to self-electrophoresis for a Au−Pt nanorod motor, while the remaining 99.9% was chemically decomposed and could contribute to self-diffusiophoresis. Such coexistence of both mechanisms could be common, but it remains a challenge to tell if we have both and the contribution of each.

Even when one mechanism dominates, it is still not straightforward to tell which because both self-electrophoresis and ionic self-diffusiophoresis arise from ionic gradients and both suffer from high ionic strength. Motors powered by either mechanism thus move in seemingly indistinguishable ways. To experimentally distinguish them typically starts from the identification of the chemical reactions powering the motor, then that of the chemical species (and their diffusivity) generating the gradient, and finally a phenomenological model supported by simulations. This whole process is challenging to say the least and prone to errors, so that the exact way a chemical reaction powers a motor sometimes remains a black box.

We have recently solved the problem of experimentally distinguishing self-electrophoresis and ionic self-diffusiophoresis by proposing a set of two phenomenological rules.[68] These rules are based on the fact that ionic self-diffusiophoresis leads to a net production of ions, but self-electrophoresis does not (see ref 68 for details). As a result, motors powered by ionic self-diffusiophoresis will raise their local ionic strength and move more slowly in a dense population, because the magnitude of this mechanism, like any other type of colloidal electrokinetic phenomena, scales inversely with the ionic strength.[77] Therefore, self-diffusiophoretic motors also form a growing cluster over time. A self-electrophoretic motor, on the contrary, hardly changes its speed in a dense population and forms dynamic clusters that constantly break and reform.

Although successful in the proposed rules, our study in ref 68 also suggests the peculiar cases where self-electrophoresis and ionic self-diffusiophoresis are fundamentally indistinguishable. Imagine a micromotor that produces one pair of cation/anion on one side of its Janus body and a different pair of ions on the other (Figure 3c). This motor is essentially composed of two diffusiophoretic caps. But, with the right choice of ions on either cap, this diffusiophoretic motor can produce electric field and flow streamlines very similar to those of a self-electrophoretic motor. This special motor design then leads to the question: is it self-diffusiophoretic or self-electrophoretic, and is such labeling important for us to understand its behaviors?

2.5. Is neutral self-diffusiophoresis a viable mechanism? My last comment on the phoretic propulsion of chemical nanomotors is on neutral self-diffusiophoresis, i.e., propulsion in a self-generated gradient of neutral molecules. Its underlying principle is well-established,[42,45] so I am not questioning its viability, but rather whether it is powerful enough to move a nano- or microscopic object beyond Brownian motion, or if there is indeed an experimental example of it.

First, the magnitude of neutral diffusiophoresis is difficult to calculate. Here I quote an earlier comment from ref 57 that I believe still holds true today:

> *"(in neutral diffusiophoresis) the molecules interact with the particle through forces beyond electrostatics, such as van der Waals forces, excluded volume effects, etc. The particle speed is governed in this case by Equation 6:*
>
> $$U = \frac{k_B T}{\eta} K L \nabla C \tag{6}$$
>
> *where K and L together...determine the nature (attraction/repulsion) and strength of the solute−particle interaction. ...neither the sign nor the magnitude of K or L are easy to predict or measure. Most studies on colloidal motors driven by non-ionic self-diffusiophoresis are theoretical, and we are not aware of any experimental measurement of the solute−particle interactions. ...In fact, to the best of our knowledge, there is no experimental report of colloidal motors driven undeniably and solely by non-ionic self-diffusio- phoresis, as it is often challenging to rule out the possible existence of charged intermediates or the contributions from electrokinetics."*

Several published studies are arguably in favor of neutral self-diffusiophoresis but lack definitive proof. For example, one article by Pavlick et al. in 2011[74] reported a 70% enhancement in the diffusion of a SiO_2−Au Janus microsphere in norbornene (Figure 3d), which polymerizes on the SiO_2 cap functionalized with a Grubbs catalyst. As a result, the monomer concentration is higher on the Au side and lower on the SiO_2 side, setting up a gradient of neutral molecules that move the motor. More recently, an article by Cui et al.[75] reported the enhanced diffusion of micrometer-sized liposomes in β-cyclodextrin (Figure 3e), which extracts cholesterol from the lipid membrane. Here, the microstructure of the liposome is specially designed so that cholesterols are extracted preferentially at one side of the liposome, establishing a gradient of cholesterols within the membrane as well as gradients of empty and filled β-cyclodextrin molecules around a liposome. Some enzyme-powered nanomotors (with diameters of hundreds of nms) are also suspected to move via neutral self-diffusiophoresis, especially the ones coated with catalase (converting H_2O_2 into H_2O and O_2)[51,78−81] and glucose oxidase (converting glucose into gluconic acid and H_2O_2)[51,79,81] that do not seem to produce ions in their respective fuels. In some cases, such as ref 78, an enzymatic motor was *not* significantly slowed down in phosphate-buffered saline of a high ionic strength, consistent with neutral self-diffusiophoresis.

Although neutral self-diffusiophoresis is possible for the above cases, there is still room for questioning. For one, the enhanced diffusion of the micrometer-sized motors from refs 74 and 75 is ∼50−70%, and 20% in the case of catalase-functionalized micromotors,[82] suggested by mean squared displacement. Such enhancement is small, and mean squared displacement measurements are known to be error-prone, unless a large amount of data is available and drift is corrected.[83−85] Second, there are more reports of nanomotors than micromotors powered by catalase or glucose-oxidase—two enzymes that do not intuitively produce ions—which could suggest that neutral self-diffusiophoresis is more effective for nanomotors than micromotors. This speculation also aligns with our own observation that catalase-functionalized microspheres cannot effectively self-propel.[67] Moreover, there is always the possibility (as small as it might seem) of charged intermediates that, in one way or another, could be released in these experiments and cause ionic self-diffusiophoresis. In addition to all these experimental uncertainties, there is also little clue as to how the neutral molecules interact with the particle surface, the microscopic detail that is critical for justifying neutral self-diffusiophoresis in the above cases (i.e., the issue of K and L as described above).

To confirm the presence of neutral self-diffusiophoresis calls for at least two pieces of knowledge. First, because neutral self-diffusiophoresis is insensitive to the ionic strength, adding salt could be a simple yet powerful way to determine whether ions are involved in the motor's propulsion. The idea behind this test is that the magnitude of electrophoresis and ionic diffusiophoresis scales inversely with solution conductivity,[62,68,77] yet neutral diffusiophoresis is not strongly dependent on it. But do note that changing the ionic strength changes other properties of the system, such as the surface charges of the motor and the bottom substrate, which could affect the motor's mobility or its height from the substrate.[86] Adding salt could also reduce the catalytic activity of metals[87] or enzymes,[88] which could slow the motor down even for those powered by neutral diffusiophoresis. With these complications, neutral self-diffusiophoresis cannot be simply ruled out if a motor slows down in salt water, unless the reduction in speed from these additional factors is carefully accounted for.

The second piece of critical knowledge is how the neutral molecule interacts with the particle's surface, at least whether it is attractive or repulsive. Unfortunately, we have not seen any experimental attempt in measuring such interactions among common molecule/particle pairs in micromotor studies (e.g., H_2O_2 and O_2 interacting with PS, SiO_2 or Pt).

The pursuit for a micromotor powered unambiguously by neutral self-diffusiophoresis is tantalizing, primarily because of the possibility of effective propulsion in high salt medium such as blood, contaminated water, or seawater. However, I suspect that it is very weak for microscopic motors. For example, ref 62 estimated the speed of SiO_2−Pt motors in H_2O_2 powered by neutral self-diffusiophoresis arising from van der Waals interactions, concluding that it is ∼80 times smaller than experimental measurements. Our own study[67] also suggests that the speed of neutral self-diffusiophoresis (at least for a microscopic motor) is much weaker than the propulsion by self-electrophoresis or ionic self-diffusiophoresis. Interestingly, the magnitude of neutral diffusiophoresis can be potentially greatly enhanced for hydrophobic motors, or motors moving near hydrophobic surfaces, which has been theoretically predicated by ref 89. In addition, as I mentioned earlier, neutral self-diffusiophoresis could be more effective for nanoscopic motors than microscopic motors, although I do not have enough experimental evidence or theoretical proof to back this hypothesis.

3. INTERACTIONS BETWEEN CHEMICALLY POWERED MICROMOTORS

3.1. Interaction Pathways. Micromotors rarely move alone. In the lab or our bodies, a micromotor is often surrounded by either its peers or foreigners in the environment, such as cells, microorganisms, debris, etc. The inevitable interaction of a micromotor with its neighbors[90,91] could give rise to a rich variety of collective behaviors including schooling, swarming, dynamic clustering, and even predator−prey interactions (see refs 92−96 and references therein). Understanding how these interactions arise is therefore important for fundamental and applied reasons.

Below I describe open questions about the interactions between chemically powered micromotors that interact physically or chemically (Figure 4). A more expanded discussion is given in the following two subsections, but to give an overview, physical interactions are mediated by direct forces, which include phoretic, osmotic, and hydrodynamic interactions that generally apply to motile or immotile colloidal particles alike. Chemical interactions are, on the contrary, mediated by chemical signals. Here, "chemical signals" refer to the release of specific chemicals or a change in their spatiotemporal profiles that do not produce forces directly (through phoresis or osmosis) but rather cause a dramatic change in the orientation, speed, or direction of nearby motors. Examples include chemotaxis of motors up or down a chemical gradient,[97−101] or a small amount of Ag^+ released from one motor that accelerates a nearby motor.[102,103]

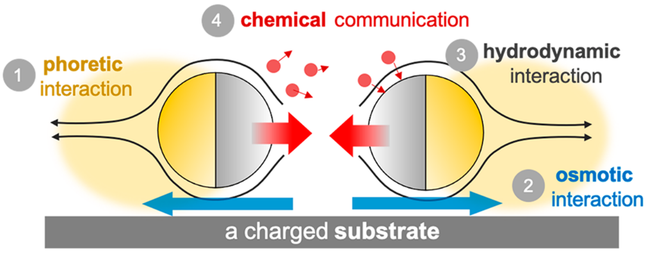

Figure 4. Interaction pathways between two chemical micromotors. See the main text for descriptions.

Although a chemical gradient can cause both physical interactions (via phoresis and osmosis) and chemical interactions (via chemical signals), the latter affects motors only, but not passive tracers. An analogy would be that a moving naval ship can create waves to knock over nearby unmanned boats ("direct interaction") and can also fire water cannons to scare away nearby manned boats ("indirect interaction"). Water mediates the interaction in both cases but in very different ways.

3.2. Physical Interactions: Phoretic, Osmotic and Hydrodynamic Interactions. As nicely described in a recent review article,[104] chemical micromotors typically interact with each other via phoretic interactions, osmotic interactions and hydrodynamic interactions. Both the phoretic and osmotic interactions originate from the production of a local chemical gradient around a chemical micromotor. For a Au−Pt bimetallic rod, this is gradients of protons, O_2 and H_2O_2. For AgCl motors, it is H^+ and Cl^-, etc. In addition to causing a motor to move, as we discussed in a preceding section, such a chemical gradient also transports its neighbors via diffusiophoresis and electrophoresis. These are referred to as a phoretic interaction. In addition, the same chemical gradient also couples with a substrate and causes diffusio-osmosis and electro-osmosis (if the substrate is charged, which it typically is), so that neighboring colloidal particles are advected by osmotic flows. Such action is referred to as an osmotic interaction.

A moving micromotor also generates a flow field that advects nearby particles (in a way different from the osmotic interaction described above), and this is termed a hydrodynamic interaction. In this case, a micromotor is also a moving pump.[105,106] Note that, in addition to the flows generated by the motion itself, a micromotor can significantly change the density of its surrounding liquid as a result of an endo- or exothermic reaction or from the accumulation or consumption of heavy/light molecules. Such buoyancy-induced convective flows have been well documented for catalytic[107−109] and electrical micropumps[110] (that are fixed in space), but often wrongly neglected for moving micromotors.

All three types of physical interactions—phoretic, osmotic, and hydrodynamic—could coexist between two micromotors or between a micromotor and a nearby tracer, and identifying their relative contributions is both critical and challenging. Unlike the case with swimming microorganisms for which hydrodynamics typically dominate their physical interactions, there has been intense debate on which physical interaction dominates for chemical micromotors.[111−113] It is perhaps safe to say that all three interactions are important and which dominates depends critically on the type of motors, the environment (e.g., substrate, medium) it is located in, and the population density.

To clarify this vague statement requires careful experimental measurements and powerful simulations. On the experiment side, although numerous studies have demonstrated the attraction and repulsion of tracers to micromotors,[90,91] or the pairwise interaction between two or more micromotors,[114,115] measurements of the interaction potential around a moving/fixed micromotor are few.[116−120] These potentials can help distinguish between phoretic and hydrodynamic interactions, noting that the former is isotropic in space, while the latter is

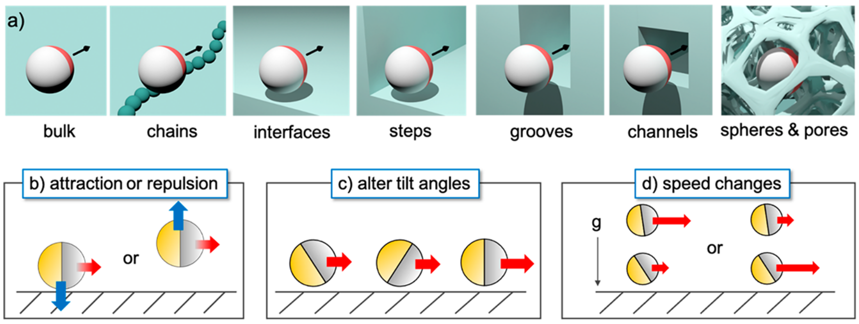

Figure 5. Micromotors in confinements. a) Different types of confinements. Figure adapted from ref 27. Copyright 2019 American Chemical Society. b-d) Three types of impact of confinement on the dynamics of micromotors.

anisotropic at a far field. For example, two previous studies[117,119] have measured the attraction of tracers toward micromotors, and confirmed that the attractive force was isotropic in space and scaled with 1/r,[2] which the authors argued to be consistent with phoretic interactions. But in neither case is the motor actively moving nor is the substrate considered. Such measurement is better performed in the absence of a substrate to minimize osmotic interactions and simplify discussions, and acoustic levitation could prove useful in this regard[121] (or to perform the experiments in microgravity[122]). Alternatively, one can also change the substrate material to probe if osmotic flows are important while keeping in mind that the sedimentation height of the particle may change as the substrate material is changed.

Numerical simulation could help distinguish the contributions of the three interaction mechanisms, with the power to selectively turn each on or off.[123,124] However, a model complete with all three interaction mechanisms as well as near field details can be challenging or computationally costly, especially when it is applied to a dense and large population. More subtly yet crucially, simulations are sensitive to user input, so that accurate simulations require accurate knowledge of the physico-chemical profile of a micromotor and its surroundings. These details include the surface charges of motors/tracers/substrate, the exact chemical species being produced or consumed and their diffusivity, and the reaction kinetics, among others. These parameters are not only challenging to acquire experimentally with confidence but could also vary over space and time. Alternatively, these details could be approximated by an effective interparticle interaction potential, which requires experimental measurements that, as described above, are rare. The use of an effective potential also risks losing near field details that are critical for understanding the interactions of chemical micromotors. Nor does it take into account the overlapping of chemical concentration fields among many motors.

3.3. How do micromotors communicate chemically?

Beyond generating a chemical gradient that causes phoresis and osmosis, a unique feature of a chemical micromotor is its ability to chemically communicate with others.[125−127] This can be done by micromotors releasing chemicals that "modify" nearby particles, thus affecting their mobility. For example, a 2017 study[102] reported that Ag-containing micromotors releases Ag^+ in H_2O_2 as it moves, which diffuses and deposits on nearby Pt Janus micromotors. As a result, the Pt motor accelerates, possibly because of a rough surface and the formation of Ag/Pt sites of enhanced catalytic capability as compared to a Pt motor before Ag deposition. However, the exact details of how Ag is deposited and how it affects Pt remain unknown. On the other hand, we have reported that nonoscillatory bimetallic nanorod motors seemingly "learned" to oscillate when placed next to oscillatory, Ag-containing micromotors.[103] Again, it was suspected that Ag was released from oscillatory motors and deposited onto nonoscillatory motors, but details of how this happened remain to be elucidated.

A micromotor could also change its local pH and affect nearby motors. For example, such a change of pH was visualized by pH-sensitive fluorescent dyes in a recent study of ours,[128] where Ag micromotors in H_2O_2 and under UV light generated chemical waves of OH^- that activated nearby Ag micromotors, leading to motion waves. Similarly, it is possible that the acceleration of Pt motors described above[102] is not due to the deposition of Ag^+ on Pt, but rather to a local increase of pH from the oxidation of Ag by H_2O_2. In these cases, a change in local pH could affect the reaction kinetics of a micromotor or the surface charges of the micromotor and the underlying substrate. More subtly, a change in pH has also been reported to trigger the structural changes on a micromotor,[129] alter the chemical reaction pathway, or even induce phototaxis.[130] The response of micromotors to a change in local/global pH change is an interesting and important topic that remains less explored and poorly understood.

The fact that the details of the chemical communication among micromotors remain largely unknown can be attributed to two factors. First, it is often challenging to precisely determine the exact chemical species and their fluxes produced and consumed by a chemical motor. There has been inspiring progress in the measurement of local pH by fluorescent probe molecules,[128,131−133] but appropriate probes for key chemicals such as O_2, H_2O_2 and others remain to be explored. One challenge for these probes is to map the concentration at a spatial resolution of μm and temporal resolution of ~0.1 s. I suspect though that the biology community has a great pool of knowledge on suitable fluorescent probes.

The second challenge that limits our understanding of chemical communications is the molecular response of micromotors to a chemical signal. This response can be multifold and extremely sensitive, and in most cases invisible to naked eyes (except for the rare cases that the coating of a micromotor visibly dissolves[52,53] or thickens, or structures growing out of the motor surface[134]). A range of material characterization techniques, including electron microscopies, X-ray diffraction, Raman/infrared/UV−vis spectroscopy, and X-ray photoelectron spectroscopy, are often required to carefully decipher these changes. Piecing together the collected data, however, is not an easy task, not to mention the skills in using these instruments. There is also the possibility that the receiving micromotor emits a second chemical signal that affects other motors, similar to a signal relay system[128] or an enzyme cascade,[135] which adds to the layer of complexity.

4. MICROMOTORS IN CONFINEMENTS

In a lab experiment, a micromotor (of any propulsion mechanism) typically moves above a solid, charged substrate (most commonly, a piece of hydrophilic glass). The presence of this physical boundary has three important consequences: it attracts or repels a micromotor, it tilts the motor, and it alters the motor's speed (Figure 5b-d). These consequences might not be obvious unless compared with experiments without boundaries. However, such experiments where motors swim in unconfined bulk liquid are rare,[136] and their 3D dynamics with high spatial and temporal resolutions are challenging to probe.

Difficult as it might be, let us now discuss each of these three consequences by a boundary on a chemical micromotor. First, there is much experimental evidence that suggests an effective attraction between a solid boundary with a chemical micromotor, so that it follows the contour of a solid post[137−139] or a wall.[140,141] In extreme cases, such an attraction is so strong, that a micromotor moves on the "ceiling" of an experimental chamber.[142] On the contrary, it has also been observed that some micromotors spontaneously move away from the substrate, as seen for photocatalytic and bottom-heavy SiO_2−TiO_2[143] or polymer-AgCl[40] micromotors upon light irradiation, also known as negative gravitaxis. Similarly, some reports describe antigravitactic motion of Pt Janus micromotors in H_2O_2 because they are also bottom-heavy.[136] It appears that the above observations, whether attraction or repulsion, can be understood in a framework that considers the torques generated by chemical gradients, hydrodynamic flows, and gravity. A combination of these torques then determines the orientation of a Janus micromotor relative to the boundary and thus whether it stays or leaves. However, it remains to be experimentally confirmed if a torque-less mechanism could cause a chemically isotropic colloid to be attracted or repelled by a nearby boundary, in the same spirit as the hovering state predicted by ref 144.

In addition to being attracted or repelled, a chemical micromotor also moves on a substrate with a tilted body so that the axis of the motion (pointing along its body from the back to the front) does not align perfectly parallel with the substrate. Such tilting was reported for spherical Janus micromotors,[145] and (less commonly) for nanorod motors.[146,147] Following the arguments described in the preceding paragraph, such tilting is commonly explained by the torque balance among gravity, chemical gradients and fluid flows. Recently, we have discovered[148] that motor speeds are significantly affected by its orientation: by arbitrarily flipping a Janus micromotor so that its body axis is forced to be parallel to the substrate, its speed increased significantly. Naively, this dependence can be understood by the intuitive picture that a motor tilting either upward or downward has part of its propulsive force that is not contributing to its motion along the substrate. However, this simple picture neglects the redistribution of chemical gradients and flows when the motor reorients. Exactly how the tilt of a motor affects its speed or whether it is the other way around remains to be clarified.

Beyond affecting the tilting angle, the presence of a confinement can change the speed of a chemical micromotor by a few other mechanisms. The most straightforward mechanism is the no-slip or partially slip boundary condition of a boundary that imparts a high Stokes drag and thus slows down a nearby micromotor. On top of this effect, the boundary could carry electrical charges of the same sign as the motor (typically both negative in water). As a result, the boundary generates electroosmotic flows that advect the motor against its propulsion in the presence of the electric field generated by the motor. Earlier studies have suggested that this electroosmotic flow could slow the motor by 25−50%.[149,150] Interestingly, the same electroosmotic flow can facilitate a motor if it is strongly confined in a narrow channel.[151] In additional to electroosmosis, the presence of a boundary concentrates the chemicals and squeezes the electric field, typically leading to faster motors. Here, the rich literature over the past decades of regular electrophoresis in a viscous medium,[152] nanopores[153,154] or near solid boundaries[155,156] could provide inspirations for understanding chemical micromotors in similar environments.

Finally, a less considered contribution to motor speeds is the elevated ionic strength within the electrical double layer of a nearby boundary. Because many chemical motors are known to slow down significantly in salt solutions,[77] they in principle would slow down near a highly charged boundary. This contribution is significant only in the close vicinity of a boundary, typically within 100 nm, but could become important if the motor is for one reason or another very close to a charged boundary or in a very dense population of highly charged tracers or pillars. This effect could explain the observation that motor moves more slowly on a very clean, hydrophilic glass slide (carrying high surface charges[157]) or in a dense suspension of polymer tracers (our own result, not published).

Beyond these effects on individual dynamics, the presence of boundaries also affects how a motor interacts with its neighbors. This could manifest in the introduction of osmotic interactions as I mentioned earlier, as well as unique near-field interactions as a result of fluid continuity.[158] More subtly, a boundary could also alter the decay rate of both phoretic and hydrodynamic interactions.

The above discussion is exclusively about solid−liquid interfaces, but other interfaces could affect motor speeds in unique ways. For example, it has been reported that chemical motors move faster near an air−water interface because their orientations are locked by pinning at the interface.[159] Motors moving on a water-hexane interface, on the other hand, showed a bimodal distribution of speeds.[160] But experiments of chemical motors on liquid−liquid[160−166] or liquid−air interfaces[159] are less explored than those on a solid−liquid interface.

One key challenge for unraveling the myriad of effects a boundary/interface has on a chemical micromotor is a lack of proper tool/method to controllably and *in situ* tune the relative position and orientation of a motor to a boundary/interface while minimizing the changes in other aspects. In this front, we have used acoustic levitation to compare the dynamics of individual micromotors or their collective behaviors, and determined the contribution of substrate electroosmosis on motor speeds[149] and on the collective beating of motor clusters.[167] We have also used electromagnetic fields to determine the dependence of motor speeds on tilting angles.[148] However, the success is limited, and experiments challenging, because the introduction of these external fields inevitably produces additional forces and effects that need to be carefully considered/corrected. Similarly, any modification of the boundary or interface, as an attempt to controllably study its effect on motors, could have broad and complex repercussions. For example, changing the surface charge of a bottom substrate could help clarify the role of electro-osmosis on motors, but it could concurrently change the height of the motor, the local pH or ionic strength, or even the reaction rate on the motor surface. These caveats are not trivial and seriously limit our experimental understanding of how confinements affect chemical micromotors.

Even if we acquire the proper tool and method to identify the effect of confinements, the underlying physico-chemical nature of such an effect requires measurements of the distribution of ions, electric field, and flows near a micromotor in confinement, with a spatial resolution of μm and temporal resolution of ~0.1 s. These measurements are technically challenging, and simultaneous measurements of all distributions are even more so. Notably, tracers and fluorescent molecular probes are commonly used to map the flow and chemical distributions, respectively, but they could introduce additional forces and changes to the system that complicate the situation.

5. SUMMARY AND OUTLOOK

To summarize, this Perspective has detailed the questions, challenges, and curiosities that I have personally encountered on micromotors powered by chemical gradients. At an individual level, the propulsion of chemical micromotors is sometimes a “black box”, despite extensive theoretical advancements in electrophoresis or diffusiophoresis. In particular, I have discussed the controversy and recent progress in the propulsion mechanism of Pt Janus micromotors, the connection between self-electrophoresis and ionic self-diffusiophoresis, and the doubtful cases of micromotors powered by neutral self-diffusiophoresis. A second group of mysteries involves interactions among chemical micromotors. Here, I have discussed how chemical motors communicate with each other through chemical cues and via phoretic, electrostatic, and hydrodynamic interactions. These physical and chemical interactions can be further altered in the presence of a boundary, the third and last group of mysteries. The presence of a boundary also attracts or repels a chemical motor, alters its tilt angle, and changes the motor speed through a variety of possible mechanisms.

Although this Perspective has mostly discussed motors made of inorganic materials (catalytic metals in particular), these discussions are equally applicable to organic or even hybrid motors that are driven by chemical gradients. For example, enzymatic motors are typically powered by self-diffusiophoresis and therefore suffer from the same limitations and face the same open questions as any other kinds of motors powered by this mechanism. Moreover, enzymatic motors also move near boundaries and interact with each other through physical or chemical interactions, so that the same open questions will be found for enzymatic motors and inorganic motors alike.

Some important and controversial topics are not discussed in this Perspective because of limited space and my limited knowledge of the subjects. Examples include the understanding and controlling of the emergence and evolution of collective patterns and motion,[92,128] whether molecules and enzymes that undergo chemical reactions are active matter,[168−172] the mechanism of chemotaxis of chemical micromotors,[173,174] and how to make chemical micromotors truly useful in real world applications such as biomedicine and environment remediation.[8,11]

Many of the above challenges arise from the lack of appropriate tools and methods to manipulate micromotors and measure nearby physicochemical distributions. These measurements must be precise, controllable, and in situ without introducing additional complications or compromising motor performance. Faced with these challenges, it is intuitive to turn to theory and numerical simulations, but even in these cases, experiments are still critically needed to provide key parameters and insights (e.g., zeta potential, reaction flux, locations, chemical species, etc.) and to confirm theoretical or simulation predictions. Such an interdisciplinary topic therefore requires close collaboration between theorists and experimentalists. In particular, experimentalists must take the lead in identifying the problem, the goal, and the key details of an experiment to help theorists build minimal but realistic models.

In his lecture given in 1900,[175] Lord Kelvin famously proposed two “dark clouds” over classical physics, which later lead to the development of the theory of special relatively and quantum mechanics.[176] The open questions discussed here may be less consequential, but their solutions could bring about new revelations about how chemistry powers motion in the microscopic world, a profound question in biology and nanotechnology.

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Notes

The author declares no competing financial interest.

ACKNOWLEDGMENTS

W.W. gratefully acknowledges the financial support over the years by the National Natural Science Foundation of China (T2322006, 11402069, 11774075), the Guangdong Natural Science Foundation (2017B030306005), the Shenzhen Science and Technology Program (RCYX20210609103122038, JCYJ20190806144807401, JCYJ20210324121408022, KQCX20140521144102503, JCYJ20170307150031119), and funding from HIT. W.W. is also indebted to the helpful discussions with Benno Liebchen, William Uspal and Mihail Popescu on the interactions among chemical motors, Kyle Bishop and Allan Brooks on the propulsion mechanism of Pt motors, and Jeffrey Moran on neutral self-diffusiophoresis. W.W. thanks William Uspal, Mohd Yasir Khan and Ruitong Zhu for proof reading. This article is dedicated to the 20th year of the discovery of catalytic nanomotors,[1] and the young pioneers—Wally, Tim, Yiying, Mike, Yang and many others—who, with ingenuity and perseverance, solved the early mysteries of how chemistry powers small machines.

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