Phoretic Self-Propulsion

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Abstract
It is well-known that micro- and nanoparticles can move by phoretic effects in response to externally imposed gradients of scalar quantities such as chemical concentration or electric potential. A class of active colloids can propel themselves through aqueous media by generating local gradients of concentration and electrical potential via surface reactions. Phoretic active colloids can be controlled using external stimuli and can mimic collective behaviors exhibited by many biological swimmers. Low–Reynolds number physicochemical hydrodynamics imposes unique challenges and constraints that must be understood for the practical potential of active colloids to be realized. Here, we review the rich physics underlying the operation of phoretic active colloids, describe their interactions and collective behaviors, and discuss promising directions for future research.
1. INTRODUCTION

Self-propulsion at the micrometer scale is abundant and important in biological systems (Bray 2001, Lauga 2016, Lauga & Powers 2009). In the low–Reynolds number regime, any mechanical swimming motion must be time asymmetric, in accordance with the well-known Scallop theorem (Purcell 1977). In the natural world, this is typically achieved through the actuation of cellular appendages such as flagella, which typically move in wave-like patterns. However, microscale self-propulsion is not confined to the biological realm. Inspired by swimming microorganisms, the design of many synthetic swimmers has attempted to reproduce the motions of appendages such as cilia (Dreyfus et al. 2005, Sanchez et al. 2011) or flagella (Ghosh & Fischer 2009, Zhang et al. 2010), which are found on both eukaryotic and prokaryotic cells. This motion must be actuated by external forces, such as those exerted by magnetic fields, and thus most synthetic mechanical swimmers are not truly autonomous motors. In contrast, various devices without moving parts have been predicted or demonstrated to swim nonmechanically using energy they store internally or harvest from their local environments (Dey et al. 2016, Ebbens 2016, Wang et al. 2013a). Micro- and nanoscale self-propelling devices are being developed for a wide variety of applications, including the transport of micrometer-scale cargo many times the size of the motor (Baraban et al. 2012, Burdick et al. 2008, Popescu et al. 2011), self-assembly of nanoscale structures (Wang 2009), targeted drug delivery (Gao & Wang 2014, Gao et al. 2015), and motion-based active sensors (Kagan et al. 2009, Wu et al. 2010), as well as environmental monitoring (Soler & Sánchez 2014) and remediation (Teo et al. 2016).

One approach to developing synthetic self-propelled particles, which avoids the challenge of achieving time-asymmetric mechanical microswimming, takes advantage of short-ranged interactions between a colloidal particle and a local gradient in a scalar quantity that can generate fluid motion at the particle surface. These phoretic effects occur for particles in externally imposed gradients of solute concentration, electric potential, or temperature and can drive particle motion (Anderson 1989). The term phoresis refers to the motion of particles by phoretic effects (i.e., particle migration induced by a scalar gradient). When the particle itself is capable of generating these gradients, such as through chemical surface reactions or by emitting or absorbing heat, phoretic effects can generate self-propelled motion. This idea has led to significant research activity in recent years, motivating the current review.

This review focuses on synthetic swimmers that move due to phoretic effects. Given the volume of work on phoretic swimmers, we do not focus on synthetic microswimmers that move mechanically, nor do we consider bubble-propelled microswimmers, although those particles also show promise for practical applications (Gao et al. 2015). Here we focus on self-diffusiophoresis (propulsion due to self-generated solute concentration gradients) and self-electrophoresis (propulsion due to self-generated electric fields). Some particles move by self-thermophoresis, in which a particle moves by generating a temperature gradient around itself (Jiang et al. 2010, Yang & Ripoll 2011). Self-thermophoresis is less common than self-diffusiophoresis and self-electrophoresis and is not considered in detail in this review. We discuss the physicochemical hydrodynamics underlying phoretic propulsion mechanisms in general and highlight theoretical and experimental advances. We then discuss some of the complex and collective behaviors of these particles.

1.1. Models of Phoretic Self-Propulsion

Models of phoretic motors typically consider a solitary particle suspended in an infinite fluid that contains a dilute dissolved solute. In this case, the solute concentration is described by the species
conservation equation,
\[ \frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{j}_i = 0, \]
where \( c \) is the concentration of species \( i \) and \( \mathbf{j} \) is the flux, given (in the dilute limit) by the generalized Nernst-Planck equation including advection,
\[ \mathbf{j}_i = c_i \mathbf{u} - D_i \left( \nabla c_i + \frac{c_i}{k_B T} \nabla \psi_i \right). \]
Here \( \mathbf{u} \) is the fluid velocity, \( D \) is the diffusion coefficient of the solute, \( k_B \) is Boltzmann’s constant, \( T \) is the absolute temperature, and \( \psi \) is a generalized interaction potential that describes the overall interaction between the solute species \( i \) and its environment. If the dissolved species is ionic, the interaction potential reduces to \( \psi_i = z_i e \phi \), where \( z_i \) is the valence, \( e \) is the elemental charge, and \( \phi \) is the electrostatic potential. The three terms on the right-hand side of Equation 2 represent fluxes due to advection, diffusion, and migration due to gradients in \( \psi \), respectively.

We consider low-Reynolds number flows, and thus the fluid momentum balance is given by the Stokes equations
\[ \nabla \cdot \mathbf{u} = 0, \quad \eta \nabla^2 \mathbf{u} = \nabla p + \mathbf{f}_b, \]
where \( \mathbf{f}_b \) is a generalized body force whose form depends on the interaction mechanism between the solutes, solvent, and particle. If the solute concentration becomes very high at a given point, the density and viscosity may vary locally, although this variation is negligible under typical conditions (de Graaf et al. 2015). The particle reaches a terminal swimming velocity when the net force on the particle is zero and the Stokes fluid drag is equal and opposite to the phoretic force (Anderson 1989, Brady 2011). Equations 1–3 constitute the basic system of equations that governs both self-electrophoresis and self-diffusiophoresis.

A common strategy for mathematically analyzing phoretic swimmers is to split the fluid domain into two regions: the bulk fluid and the interfacial region around the particle with characteristic thickness \( \lambda \), which is typically taken as small compared to the particle size \( a \), \( \lambda/a \ll 1 \) (Anderson et al. 1982, Brady 2011). The phoretic effects that lead to propulsion of the particle are generally assumed to be confined to this region. This thin-layer approximation allows the phoretic effects to be represented by a slip velocity at the surface of the particle that is proportional to the local gradient of \( \psi \) (Anderson 1989, Golestanian et al. 2007). The slip velocity is generally written as the product of the local gradient (projected along the particle surface) multiplied by a phoretic mobility \( M \) that quantifies the surface’s response to the local gradient (Golestanian et al. 2007). It can then be shown from the force-free condition for phoretic motion, together with the Lorentz reciprocal theorem (Brenner 1964), that the net migration velocity of the particle is equal in magnitude and opposite in sign to the area average of the slip velocity over the particle surface (Golestanian et al. 2007, Stone & Samuel 1996).

When the assumption of a thin interaction layer is valid, the terms representing the fluid body force and migration-driven flux in the momentum and transport equations, respectively, are nonzero only in the thin region and may be omitted elsewhere (Brady 2011, Córdova-Figueroa et al. 2013, Frankel & Khair 2014, Golestanian et al. 2007, Michelin et al. 2013, Popescu et al. 2010). This assumption may not always be satisfied in reality and has been relaxed in more detailed studies of self-diffusiophoresis (Sabass & Seifert 2012a, Sharifi-Mood et al. 2013). This thin-layer approximation was used, assuming negligible advection and constant reactive surface flux, to provide a general framework for the modeling and design of self-diffusiophoretic, self-electrophoretic, and self-thermophoretic particles (Golestanian et al. 2007). This analysis is applicable to various mechanisms (autonomous diffusio-, electro-, and thermophoresis) and provides guidelines for the design of phoretic motors in terms of phoretic mobility, \( M \), and characteristic surface activity.
A. For example, for a Janus sphere, the velocity is given by $U = (1/8B)(A_+ - A_-)(M_- + M_+)$, where the subscripts denote different halves of the particle, $B$ is the diffusivity, $D$, of the solute produced or consumed by the particle (for self-diffusiophoresis), or the electrical or thermal conductivity of the solution (for self-electrophoresis or self-thermophoresis, respectively). For self-diffusiophoresis under typical conditions, the mobility $M$ scales as $k_B T \lambda^2/\eta$, whereas for self-electrophoresis it scales with the Helmholtz-Smoluchowski expression $\varepsilon \zeta / \eta$. For self-diffusiophoresis, the surface activity $A$ is equal to the scalar flux magnitude $J$ (which may depend on position), and for self-electrophoresis $A$ is equal to the current density.

1.3. Nondimensional Parameters

Three main dimensionless parameters describe the fluid mechanics, reactions, and transport in phoretic motors. The first parameter is the Reynolds number, $Re = \rho U a / \eta$, which is always much less than 1 (with the characteristic length typically set to the particle radius $a$), and thus the Stokes equations (Equation 3) may be used in all cases considered here.

The second parameter is the Péclet number, $Pe = a U / D$, which describes the relative importance of advection to diffusion in solute transport. In most cases, the Péclet number is taken to be small. This effectively eliminates the effect of the fluid flow on the solute transport, although the solute concentration field still drives fluid motion through the body force $f_b$. The solute concentration field can be determined by solving the solute transport equations (Equations 1 and 2) and substituting it into the fluid problem. In common fuels, such as hydrogen peroxide, it is difficult to obtain a Péclet number that is unity or larger because of the high diffusivity of the solute molecules. Typically, particle diameters are limited to a few micrometers (because otherwise they would settle due to gravity) and would require the particle to swim at several hundred body lengths per second to achieve a Péclet number of order unity. Moderate–Péclet number cases can arise when the solute diffusivity is small, especially for large molecules such as proteins and surfactants used by self-propelled Marangoni droplets (Schmitt & Stark 2013, Thutupalli et al. 2011, Yoshinaga et al. 2012). When the Péclet number is not negligible, advection of the solute significantly affects the phoretic velocity and in some cases can lead to self-diffusiophoretic motion for isotropically patterned particles (Michelin et al. 2013), as discussed in Section 2.5.

The third important dimensionless parameter is the Damköhler number, which quantifies the relative importance of chemical reactions on the particle surface, which generate the reactant and product gradients around the particle that drive phoretic locomotion, and diffusive transport, which tends to smooth out scalar gradients. The Damköhler number is typically expressed as $Da = ka / D$, where $k$ is a reaction rate constant. At small to moderate values of $Da$, an increase in the reaction rate leads to a proportional increase in the swimming speed (Córdoval-Figueroa & Brady 2008, Golestanian et al. 2007). At large $Da$, the reactions are limited by mass transport of the reactant to the particle surface, so the swimming speed no longer depends on the reaction rate. When a kinetic model is not used for the reactions (e.g., if the reaction flux is simply a prescribed function), the Damköhler number takes the form of a dimensionless flux (Córdoval-Figueroa et al. 2013) but retains the same physical meaning.

2. SELF-DIFFUSIOPHORESIS

Self-diffusiophoresis occurs when a colloidal particle generates a concentration gradient of a solute and moves in response to propulsive forces generated by that gradient. Self-diffusiophoresis is analogous to diffusiophoresis, the motion of particles due to externally imposed concentration gradients, which has been studied since the 1940s (Derjaguin et al. 1947, 1961; Dukhin & Derjaguin 1974). For a spherical particle immersed in a solution of an uncharged solute with
a uniform concentration gradient $\nabla c$ far from the particle, the diffusiophoretic velocity $\mathbf{U}_{DP}$ is $\mathbf{U}_{DP} = \left( k_b T / \eta \right) K L^* \nabla c$, where $k_b$ is Boltzmann’s constant, $T$ is the absolute temperature, and $K$ and $L^*$ are length scales that depend on the physical interactions among the particle and solute molecules (Anderson 1989). Derjaguin et al. (1947) introduced the idea that solute gradients can induce fluid flows and studied a concentration-gradient-driven slip flow over a planar surface and the phoretic migration of colloids due to an electrolyte concentration gradient (Derjaguin et al. 1961). In the 1980s, diffusiophoresis was observed experimentally in both electrolyte and nonelectrolyte gradients (Staffeld & Quinn 1989a,b) and analyzed theoretically for gradients of nonelectrolytes (Anderson et al. 1982) and electrolytes (Prieve et al. 1984).

In this section, we focus on neutral-solute self-diffusiophoresis, in which self-propulsion arises from gradients of electrically neutral solute molecules or particles (Figure 1). Self-diffusiophoretic motion requires that the particle and solute experience a mutual repulsive or attractive interaction(s), which may include steric repulsion, van der Waals forces, electrostatics, or others. Asymmetry in the solute concentration generally leads to asymmetry in the interaction forces.

**Figure 1**  
(a) Schematic illustration of self-diffusiophoresis due to neutral solute gradients with one reactant (blue) and one product (yellow). The reactant and product can be modeled as colloidal particles having radii $b_R$ and $b_P$, respectively. The swimmer is a colloidal Janus sphere with inert (light gray) and catalytic (dark gray) hemispheres. In this realization of self-diffusiophoresis, the catalytic half promotes the conversion of one reactant particle into two product particles, $R \rightarrow sP$ (where $s=2$) whenever an $R$ particle comes into contact with the catalytic surface. Here, the far-field concentration of reactants is $c_{R,\infty}$ and that of products is zero. The swimmer experiences a generalized repulsive interaction with both solutes that is significant over a length scale $\lambda$, and is described mathematically by a potential function $\psi$. As a result of the interactions, a phoretic fluid flow occurs from the inert to the catalytic side of the swimmer, and the $P$ particles migrate, due to the chemical potential gradient, in the direction opposite the fluid flow. In this figure, the swimmer moves from right to left (i.e., toward lower concentration of $P$). (b) Concentration of reactant species $R$ (red) represents low concentration; blue represents the uniform far-field concentration $c_{R,\infty}$ near a self-diffusiophoretic swimmer. As in panel a, here the right half of the motor is reactive and the left half is inert. However, in this case, the motor consumes reactants only and does not release any product particles. Thus, panel b depicts a special case of panel a, specifically when $s = 0$. The swimmer experiences a repulsive interaction with the reactants and hence, in this case, would move from left to right (toward the catalytic half and lower $R$ concentration). Here, the effects of the fluid flow on the concentration distribution of $R$ are assumed negligible ($Pe = 0$). Panel b adapted with permission from Córdova-Figueroa & Brady (2008). Copyright 2008, American Physical Society.
acting on the particle. These forces, integrated together, can lead to a net propulsive force on the particle.

It was first reported in 2007 that nonconducting microspheres half-coated in platinum moved through hydrogen peroxide solutions with the platinum end directed backward (Howse et al. 2007). The particles displayed behavior consistent with the self-diffusiophoresis mechanism, with the system presumably driven by self-generated gradients of molecular oxygen (a product of the hydrogen peroxide decomposition occurring on the platinum surface). However, there is currently consensus that self-diffusiophoresis is, at the very least, not the only operative mechanism in this system, with the discovery of electrokinetic effects with these particles (Ebbens et al. 2014), and that the direction of motion can be reversed upon the addition of an ionic surfactant (Brown & Poon 2014). To our knowledge, with the possible exception of a so-called polymerization-powered motor (Pavlick et al. 2011), there has not been an experimental system in which the propulsion is unambiguously dominated by neutral solute self-diffusiophoresis. Nevertheless, the mechanism has been analyzed extensively from a theoretical standpoint, and many interesting predictions have been made.

Self-diffusiophoresis may occur in natural systems. For example, it has been suggested as an origin of actin-polymerization-driven motility (Lee & Liu 2008), a form of locomotion observed in one type of cell crawling, and in pathogens such as *Listeria monocytogenes* (Condeelis 1993, Tilney & Portnoy 1989). The vast majority of theoretical and experimental studies on self-diffusiophoresis have considered engineered colloidal swimmers.

### 2.1. Mathematical Model of Self-Diffusiophoresis

Most models of self-diffusiophoresis consider the particle and surrounding solution at the macroscopic (continuum) level, with a constitutive model for the reactions at the surface that generate the concentration gradient. These phenomena may also be described at a more fundamental level by modeling the solute molecules as discrete colloidal particles undergoing Brownian motion, with an effective diameter related to their diffusivity by the Stokes-Einstein relation (C´ordova-Figueroa & Brady 2008, C´ordova-Figueroa et al. 2013) (Brady 2011) (see the sidebar, Physical Interpretation of Self-Diffusiophoresis). The continuum-level description, which is more commonly used and described below, relies on two simplifying assumptions: (a) The solute is dilute enough that...
interactions between individual solute molecules can be neglected, and (b) the effective size of the solute molecules is much smaller than the diffusiophoretic particle. In contrast, the microscopic colloidal description is generally valid and does not rely on these assumptions (Brady 2011).

Let us consider a colloidal particle immersed in a solvent containing a neutral solute with concentration $c$. As stated above, solute transport is governed in the dilute limit by the basic conservation law (Equation 1), where the flux $j$ (Equation 2) includes transport due to gradients in both solute concentration and the interaction potential $\psi$. The interaction potential characterizes the interactions between the solute and diffusiophoretic particle and in some cases may also incorporate interactions between the solvent (typically water) with the solute and swimmer (Parsegian & Zemb 2011, Sharifi-Mood et al. 2013). The potential is defined such that $-\nabla \psi \equiv f$ is the net (position-dependent) force experienced by a solute molecule (Anderson et al. 1982). In most models, a solute molecule only experiences the force $f$ when its separation distance from the diffusiophoretic particle is less than a characteristic length $\lambda$. This force is ultimately transmitted to the fluid, resulting in a body force $f_b = -c \nabla \psi$ on a fluid element, as described by the Stokes equations (Equation 3).

Michelin & Lauga (2014) identified the conditions for the validity of the thin–interfacial layer limit for diffusiophoretic self-propulsion. Specifically, if the dimensionless quantity $(\lambda/a)^2 P_e \ll 1$, it is appropriate to model the fluid flow in the interfacial layer as a slip velocity (from the perspective of the outer solution) so that, macroscopically, the swimming particle appears to violate the no-slip condition on its surface. Additionally, if $(\lambda/a) P_e \ll 1$, then advection within the interfacial layer can be neglected, and the solute simply diffuses radially in the interfacial layer. In other words, the transport of solute along the surface is negligible, analogous to the assumption of negligible surface conduction in electrophoresis (Bikerman 1933, Lyklema & Minor 1998).

### 2.2. Reaction Models and Interaction Potentials

To swim by self-diffusiophoresis, a particle must continuously inject or consume solute molecules at its surface to sustain the concentration gradient. Solute injection or consumption is represented mathematically by a boundary condition expressing the continuity of solute flux at the reactive surface, $\mathbf{n} \cdot j = J(r_{\text{surf}})$, where the flux vector $j$ is defined in Equation 2, $r_{\text{surf}}$ is a point on the particle surface, and $J$ is the local surface reaction rate (having units of solute flux), which generally depends on the location $r_{\text{surf}}$.

Phoretic swimmers interact with both solute and solvent molecules through a variety of different mechanisms (Table 1). The three most commonly studied intermolecular interactions are (a) a steric excluded-volume potential (Córdova-Figueroa & Brady 2008, Frankel & Khair 2014, Michelin et al. 2013, Popescu et al. 2010, Sharifi-Mood et al. 2013), (b) an exponential interaction (Sabass & Seifert 2012a, Sharifi-Mood et al. 2013), and (c) a long-range van der Waals attraction (Sabass & Seifert 2012a, Sharifi-Mood et al. 2013).

The hard- or soft-sphere excluded volume potential is commonly used to model steric interactions between the phoretic particle and solute molecules, as well as interactions of solute molecules with each other. The potential is set to a nonzero value (finite or infinite) for particle-solute or solute-solute separation distances less than a certain critical distance and vanishes for separation distances larger than the critical value. Physically, this manifests as a repulsion that becomes very strong as two molecules (or particles) come into contact with one another. The length scale $\lambda$ characterizing these interactions is typically on the order of the effective size of a solute molecule (on the order of angstroms). Due primarily to its simplicity and the ubiquity of steric interactions, the excluded-volume potential is the most commonly used interaction mechanism in theoretical models of self-diffusiophoresis.
### Table 1  The most commonly used particle-solute interaction potentials and their physical origin

<table>
<thead>
<tr>
<th>Interaction mechanism</th>
<th>Physical origin</th>
<th>Mathematical model</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>van der Waals</td>
<td>London dispersion forces</td>
<td>$\psi(r) \sim \frac{A}{r^6}$</td>
<td>Sabass &amp; Seifert 2012a, Sharifi-Mood et al. 2013</td>
</tr>
<tr>
<td></td>
<td>Dipole-dipole forces</td>
<td>$\psi(r) = \begin{cases} b &amp; r &lt; a + \lambda \ 0 &amp; r &gt; a + \lambda \end{cases}$ (soft or hard repulsion)</td>
<td>Anderson 1989, Brady 2011, Sharifi-Mood et al. 2013</td>
</tr>
<tr>
<td></td>
<td>Hydrogen bonding</td>
<td>$\psi(r) \sim \exp[-(r - 1)/\lambda]$ (exponential repulsion)</td>
<td>Leikin et al. 1993, Parsegian &amp; Zemb 2011, Quemada &amp; Berli 2002, Sharifi-Mood et al. 2013</td>
</tr>
<tr>
<td>Steric</td>
<td>Finite size of solute molecules</td>
<td>$\psi(r) = ze\phi(r)$</td>
<td>Brown &amp; Poon 2014, Ebbens et al. 2014</td>
</tr>
<tr>
<td>Hydration</td>
<td>Finite size of solute and solvent molecules</td>
<td>$\psi(r) \sim \exp[-(r - 1)/\lambda]$</td>
<td>Leikin et al. 1993, Parsegian &amp; Zemb 2011, Quemada &amp; Berli 2002, Sharifi-Mood et al. 2013</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>Electrical charge of solutes and particle surfaces</td>
<td>$\psi(r) = ze\phi(r)$</td>
<td>Brown &amp; Poon 2014, Ebbens et al. 2014</td>
</tr>
</tbody>
</table>

For hard-sphere repulsion, the parameter $b$ is set to infinity. For soft repulsion, $b$ is set to a finite value. The van der Waals potential can generally be attractive or repulsive but is typically assumed attractive to model long-range attractive forces arising from induced and permanent dipoles (Sabass & Seifert 2012a,b, Sharifi-Mood et al. 2013). Hydration forces due to the finite of solvent molecules can be captured most efficiently by an exponential repulsion. This exponential repulsion is also sometimes used as a model for steric repulsion between the solute and swimmer.

The exponential potential, for which the length scale $\lambda$ is typically taken to be on the order of 1 nm, is known to characterize repulsive hydration forces (forces between individual water molecules) between surfaces immersed in an aqueous phase (Leikin et al. 1993, Parsegian & Zemb 2011, Quemada & Berli 2002). The exponential potential also may be used (with $\lambda$ ranging from 1 to 10 nm) to describe repulsive interactions between polymer brushes attached to surfaces (Israelachvili 2011). These may be the forces at work in the swimmer reported by Pavlick et al. (2011), who attributed the motion to an asymmetric polymerization of a monomer on the particle’s surface, leading to a polymer concentration gradient and self-diffusiophoretic swimming.

The van der Waals forces are a group of intermolecular forces (London dispersion forces, dipole-dipole forces, and hydrogen bonding), which can arise between solute molecules and between the solute and phoretic particle. In models of self-diffusiophoresis, van der Waals forces are included less frequently than steric and exponential interactions, but they have been shown to result in higher-order corrections to the swimming speed of diffusiophoretic motors (Sabass & Seifert 2012a, Sharifi-Mood et al. 2013).

We are not aware of any studies that attempt to measure the interaction potential for a given solute-particle composition, nor are we aware of any detailed discussions of how these potentials can be validated using experiments. A more fundamental physical study of the interaction mechanisms that are prevalent in given experimental situations would be valuable.

#### 2.3. Effect of Reaction Rate

Models of the surface reactions that give rise to self-diffusiophoresis can be broadly grouped into two categories, namely constant flux models and reaction kinetic models. Although some studies consider both cases (Michelin & Lauga 2014), most simple models of self-diffusiophoresis assume a constant flux, i.e., that the reaction-driven flux is simply given as a constant that does not depend on any system parameters (e.g., the reactant concentration).
In general, when the reaction-driven flux is small compared to the characteristic diffusive flux, the swimming speed increases linearly with the reaction rate (this is true for both flux-based and kinetic models). In this regime, the reaction does not proceed fast enough to significantly alter the solute distribution (equivalent to the assumption of small Damköhler number). For the case of self-diffusiophoresis with constant surface flux, at low flux rates the swimming speed is found to be $U = JkBT/8\eta D$ (Córdova-Figueroa et al. 2013). As is typical in phoretic problems, the speed in this regime is independent of the particle size (this is also the case, e.g., for electrophoresis at low applied electric fields). In the limit in which reaction-driven flux is very fast compared to diffusion (large Damköhler number), the steady-state speed for the constant-flux case is $U = \sqrt{JakBT/3\eta}$. In this regime, the speed depends on the square root of both the reaction rate $J$ and particle size $a$ (Córdova-Figueroa et al. 2013). This suggests that significant swimming speeds may be achieved for large particles and fast reactions. However, this prediction has yet to be observed experimentally and contradicts the most well-documented experimental trend, that the speed of platinum-polystyrene Janus swimmers depends inversely on particle size, both for platinum-polystyrene Janus particles (Ebbens et al. 2012) and for self-electrophoretic platinum-gold Janus spheres (Wheat et al. 2010). One must also keep in mind that this expression allows the reaction rate (and thus the swimming speed) to be arbitrarily large. Of course, in real systems, the reaction rate is often limited by the availability of reactant, the dissolution rate of the surface [e.g., if the surface is being corroded (Gao et al. 2012, 2015)], or the availability of reaction sites.

Unlike constant-flux models, kinetic models of surface reactions typically assume that the reaction rate is linearly dependent on the concentration of a dissolved reactant. The simplest variant of a first-order reaction is the one-step conversion of one reactant molecule $R$ into $s$ product molecules $P$, $R \rightarrow sP$ (Córdova-Figueroa & Brady 2008), at a rate proportional to the concentration of $R$ at the surface: $J = kR$. In this case, the functional dependence of particle speed is best expressed by the Damköhler number. For particles which consume solute only ($s = 0$), there is a linear relationship between speed and $Da$, but this relationship is only observed at low to moderate values of $Da$ (Córdova-Figueroa & Brady 2008). This is analogous to the linear relationship between speed and reaction-driven flux observed in constant-flux models, described in the preceding paragraph. At large values of $Da$ (generally for $Da > 10$), diffusion generally is too slow to replenish the supply of reactants or remove products from the particle surface, which generally tends to reduce phoretic effects (Córdova-Figueroa & Brady 2008, Michelin & Lauga 2014).

### 2.4. Controlling Parameters of Self-Diffusiophoresis

Several studies have considered the effect of varying catalyst/inert surface coverage on self-diffusiophoretic motion and have concluded that the particle speed is maximized when it is half coated with catalyst (de Graaf et al. 2015, Popescu et al. 2010, Sharifi-Mood et al. 2013). Provided that the reaction is occurring over more than half of the particle surface, the speed is inversely proportional to surface coverage (Michelin & Lauga 2014). The limiting case of full coverage only gives rise to motion under certain conditions, i.e., through a unique symmetry-breaking convective instability (Michelin et al. 2013).

For exponential, steric, and van der Waals interactions, the swimming speed is predicted to increase with the colloid radius with the interaction parameters held constant (Sharifi-Mood et al. 2013). However, it has been generally observed experimentally that speed decreases as the particle size increases for many common systems (Ebbens et al. 2012, Wheat et al. 2010).

Although most self-diffusiophoretic swimmers have been assumed spherical, self-diffusiophoresis has been studied theoretically and experimentally for other particle shapes. If nonspherical...
particles have a surface activity that is constant along the particle surface, the concentration of reactants and products can be asymmetric. This nonuniformity, when coupled with particle-solute interactions, results in diffusiophoretic self-propulsion of the particle (Shklyaev et al. 2014). In other words, nonspherical particles can undergo self-diffusiophoresis even if catalytic activity is uniform over the surface.

Deviations from a spherical swimmer shape generally lead to a decrease in swimming speed, although Popescu and coworkers (2010) argued that oblate disk-shaped Janus particles (having one catalytically active and one inert face) can move faster than spheres because the distance between the reactive and nonreactive halves of the particle becomes vanishingly small, increasing the concentration gradient and thus the swimming speed. Shklyaev et al. (2014) predicted that the particle shape that results in the fastest self-propulsion velocity is thin and highly curved, similar to a sail, and thus refer to this motion as chemical sailing. However, these predictions have not been verified experimentally.

### 2.5. Role of Advection

Advection alters the solute concentration distribution around a swimming particle and thus modifies the slip velocity distribution and the resulting swimming speed. The original models of self-diffusiophoresis ignored the advective transport of solute (Golestanian et al. 2005, 2007), and many surprising results are predicted to occur when advective effects are included (Figure 2). The role of advective transport was studied for externally driven diffusiophoresis (Khair 2013) and has been a central focus of several self-diffusiophoresis studies (Córdova-Figueroa & Brady 2008, Jülicher & Prost 2009, Michelin et al. 2013, Michelin & Lauga 2014, Yariv & Michelin 2015). The overall effect of advection on the self-diffusiophoretic swimming speed depends on the Péclet number.

**Figure 2**

Effects of advection on neutral solute self-diffusiophoresis. (a) Concentration of the reactant (with red representing low concentration and blue representing the far-field concentration) near a self-diffusiophoretic Janus particle at $D_\alpha = 100$ (i.e., here reaction-driven transport is much faster than diffusive transport, and the solute distribution is dominated by reactions) for four different Pe values. The right half of the motor is catalytically active (consumes reactants, does not release any products), and the particle experiences steric repulsion with the solute, resulting in swimming from left to right. At finite Pe, advection generates a wake behind the motor in which the reactant concentration is reduced (compared to the Pe = 0 case), effectively reducing the concentration gradient and limiting the self-diffusiophoretic velocity. (b) Concentration of the reactant (with black representing high and yellow representing low) at Pe = 2. The right half of the motor is catalytically active (consumes reactants), and the particle and solute experience an attractive interaction, resulting in particle motion to the left, the opposite of the situation in panel a. (c) Dependence of the swimming velocity, $U$, on Pe for Janus particles with repulsive (dashed gray line) and attractive interactions (solid gray line). For repulsive interactions, the speed is constant at small Pe, and then decreases monotonically, starting at Pe ~ $O(1)$, because advection acts to reduce the concentration gradient. For attractive interactions, advection slightly increases the propulsion speed, which reaches a maximum at Pe ~ 2, and then causes the speed to decrease as Pe exceeds 10. The maximum occurs because solute advection, at moderate Pe, increases the concentration gradient and thus enhances the swimming speed. (d) Dependence of the swimming speed on dimensionless time for the self-diffusiophoresis of spherical particles with isotropic surface activity. If Pe > 4, where $Pe = JM_u/\alpha D$ (Pe = 6 for results shown here), a random perturbation to the particle’s position (e.g., due to Brownian fluctuations), coupled with convective transport of solute, can break the spherical symmetry of the solute distribution around the particle. If the particle emits solute and is repelled by it, or consumes solute and is attracted to it, the perturbation is magnified and the particle reaches a nonzero steady-state swimming speed. This mechanism in which advection enhances the overall concentration gradient is similar to that seen in panel c near Pe = 2 for attractive solute-particle interactions (discussed in detail in Michelin & Lauga 2014). Panel $a$ reproduced with permission from Córdova-Figueroa & Brady (2008). Copyright 2008 American Physical Society. Panels $b$ and $c$ adapted with permission from Michelin & Lauga (2014). Copyright 2014 Cambridge University Press. Panel $d$ reproduced with permission from Michelin et al. (2013). Copyright 2013 AIP Publishing LLC.
value. At large Péclet numbers, advective effects cause a net decrease in the swimming speed, and the magnitude of the velocity scales as \( \text{Pe}^{-1/2} \) for both attractive and repulsive interactions (Yariv & Michelin 2015). At moderate Péclet values, advection can either increase or decrease the swimming speed, depending on the nature of the particle/solute interactions (see Figure 2c) (Michelin & Lauga 2014). Under certain conditions, advective transport can enable a spherical particle to propel itself by self-diffusiophoresis even if it emits or absorbs solute isotropically (Michelin et al. 2013) (Figure 2d). This occurs by a spontaneous symmetry-breaking mechanism in which the flow field and solute field around the particle are perturbed (e.g., by a Brownian fluctuation), generating a local concentration gradient that is amplified and sustained by the symmetric reactions and spontaneous self-diffusiophoretic velocity.

**Supplemental Table 1** summarizes the major studies of self-diffusiophoresis, including the interaction mechanism considered, swimmer geometry, closed-form expression for the swimming speed in terms of system parameters (where available), details of the driving reaction, and the type of study undertaken (follow the [Supplemental Material link](http://www.annualreviews.org) from the Annual Reviews home page at [http://www.annualreviews.org](http://www.annualreviews.org)).
3. SELF-ELECTROPHORESIS

Self-electrophoresis was first proposed to occur in biological systems by Nobel laureate Peter Mitchell (1956), who theorized that a microorganism could propel itself through aqueous media by exchanging ions with the surrounding solution. He proposed that positive ions could emanate from one end of an organism’s body, move closely along its body due to its negatively charged surface, and then be consumed at the other end. Mitchell suggested that a gradient in electric potential would develop that continually drives the movement of the ions along the surface. The charged fluid elements near the surface of the organism experience this electric field as a body force and move in response to it, causing propulsion of the organism (Mitchell 1972). A detailed history of self-electrophoresis is provided by Moran & Posner (2011). We are not aware of a biological swimmer that has been confirmed to swim by self-electrophoresis (Pitta & Berg 1995, Waterbury et al. 1985); however, technological advances have enabled the fabrication of artificial electrophoretic swimmers with similar sizes and velocities to naturally occurring locomotive microorganisms. The most studied electrophoretic swimmers are bimetallic particles that use hydrogen peroxide as a fuel, which were discovered in the early 2000s (Paxton et al. 2004). These swimmers have most often been cylindrical rods with a platinum and a gold segment in hydrogen peroxide, although other metal combinations (Wang et al. 2006) and geometries (e.g., spheres or sphere combinations; see Wheat et al. 2010) are also capable of generating self-electrophoretic propulsion. Additionally, swimmers fabricated from other materials and with different fuels exhibit self-electrophoresis. These include nanobatteries that move in Br₂ or I₂ solutions (Liu & Sen 2011), carbon fiber motors that move in glucose (Mano & Heller 2005), and zinc/platinum micromotors that move in Br₂, p-benzoquinone, and methanol (Yoshizumi et al. 2013). Paxton et al. (2005) originally proposed several mechanisms for bimetallic motor propulsion, including self-electrophoresis, which was later described in detail by Moran et al. (2010) and Moran & Posner (2011).

Self-electrophoretic locomotion requires a self-generated electric field and a charged swimmer surface. Surfaces in contact with electrolyte solution typically acquire an electrical charge and attract screening layers of counterions (ions having the oppositely signed charge of the surface) and repel coions (ions with the same signed charge as the surface). The balance between electrostatic forces, which tend to attract counterions to the surface, and diffusion, which tends to spread the counterions out, results in a diffuse screening layer of counterions near the surface. The diffuse screening layer and charged surface together constitute what is known as the electrical double layer (EDL). The characteristic thickness of the EDL is known as the Debye length, \( \lambda_D \).

In bimetallic motors, ion exchange between the particle and solution is generally caused by electrochemical reactions on the particle surface (Figure 3a). The most common fuel used by self-electrophoretic motors is hydrogen peroxide, and in this case, peroxide oxidation occurs on the platinum (anode) end and peroxide reduction occurs on the gold (cathode) end (Paxton et al. 2005, Wang et al. 2006). The oxidation reaction produces protons, while the reduction reaction consumes them. The electrochemical reactions occurring on the nanomotor surface establish a proton concentration gradient. The relative abundance of protons near platinum and relative deficiency of protons near gold establish an asymmetric charge distribution and electrical dipole around the particle. An endogenous electric field is generated by the dipole that couples with the free charge in the particle’s EDL that generates an electrical body force in the fluid and electroosmotic slip around the particle. This phenomenon is similar to electrophoresis but with an internally generated electric field and a charge distribution modified by the reaction ion flux. The protons generated at the anode migrate to the cathode due to diffusion, electromigration,
Figure 3

(a) Self-electrophoresis of platinum-gold nanorods. Self-electrophoretic rods are typically 200–400 nm in diameter and up to 2 µm long. They function as short-circuited electrochemical cells, with the forward metal acting as the anode and the aft metal as the cathode. Hydrogen peroxide is oxidized on the platinum (anode) surface in a reaction that releases protons into the fluid surrounding the anode and electrons into the metal interior. Driven by the difference in electron affinity between the two metals, the electrons conduct through the rod to the gold (cathode) end. The protons and electrons are consumed in the reduction of peroxide on the gold end, which yields water. The reactions lead to an asymmetric charge density distribution in the diffuse layer surrounding the rod, which generates a corresponding electric field that is continually sustained by the reactions. The electric field exerts a body force on the (positive) net charge in the electrical double layer, resulting in fluid motion from the platinum to the gold end and motion of the (negatively charged) particle with the platinum end forward. (b) Magnified view of the electrical double layer near the rod surface, showing the Stern layer and the diffuse Gouy-Chapman layer. The potential drop from the rod surface to the outer Helmholtz plane (OHP), Δφ, drives the electrochemical reactions, and the potential at the slip plane (approximately the outer Helmholtz plane), ζ, represents the effective voltage across the diffuse layer and influences the electrophoretic mobility. (c–e) Simulated (c) proton concentration (colored contours) and electrical potential (contour lines), (d) charge density (colored contours) and electric field streamlines, and (e) velocity magnitude (colored contours) and flow streamlines (lines). In panel c, the electrical potential is the most negative nearest the rod surface (approaching ζ) and approaches zero as the distance from the rod increases. The velocity field in panel e is depicted in the reference frame of the swimmer. The motion of the fluid from right to left indicates that, in the reference frame of the bulk fluid, the motion of the rod is from left to right, with the anode directed forward, as is universally seen in experiments. Panels a and c–e adapted with permission from Moran et al. (2010). Copyright 2010 American Physical Society.

and, to a lesser extent, electroconvection (Moran et al. 2010). Within the rod, electrons liberated in the oxidation reaction conduct from platinum to gold to complete the electrical circuit. In other words, the nanomotor functions as a short-circuited electrochemical cell that generates a surface flux of protons at the anode (platinum end) and consumes protons at the cathode (gold end). The ions drag fluid in the same direction, leading to relative motion between the particle and fluid
such that the motor moves with the platinum end directed forward. Bimetallic swimmers may also be fabricated with other metals, and those swimmers always move with the more anodic metal directed forward (Wang et al. 2006).

Self-electrophoretic swimmers move with a velocity consistent with the Helmholtz-Smoluchowski equation, \( \mathbf{U} = \varepsilon \xi \mathbf{E}_0 / \eta \), where \( \varepsilon \) is the solution permittivity, \( \xi \) is the zeta potential of the particle (a measure of its surface charge), and \( \mathbf{E}_0 \) is a characteristic magnitude of the endogenous electric field that scales with the reaction surface flux, \( \mathbf{E}_0 \propto J \) (Moran & Posner 2014). This simplified scaling analysis, and many similar ones, shows that self-electrophoretic motors swim with a velocity that scales linearly with the particle’s charge, \( \xi \), and its self-generated electric field, \( \mathbf{E} \), that depends on the reaction surface flux \( J \). Supplemental Table 2 summarizes the major studies of self-electrophoresis, including a simple mathematical relation for the swimming speed, surface potential, reaction model, dependence on fuel concentration, and swimmer geometry.

### 3.1. Mathematical Model of Self-Electrophoresis

Self-electrophoresis can be mathematically described by the Poisson-Nernst-Planck-Stokes equations, which have been used widely to describe electrokinetic systems, including Henry’s (1931) original solution for electrophoresis. Anderson (1989) and Lammert et al. (1996) were the first to analyze the mechanics of cellular self-electrophoretic locomotion. Their early models included some simplifying assumptions but became the foundation for more sophisticated and accurate theories.

The transport of ions is governed by the basic species conservation law (Equation 1) in which the flux \( \mathbf{j} \) includes transport due to electromigration, where \( \mathbf{\phi} = z_i e \mathbf{\phi} \) (for a symmetric \( z \times z \) electrolyte) in Equation 2, and results in the Nernst-Planck equation. Any local imbalance in the ion concentrations will lead to a net charge in the fluid, with the volumetric charge density given by \( \rho_e = \varepsilon \sum z_i c_i \). With the assumption of spatially uniform solution permittivity \( \varepsilon_r \), the charge density is related to the electric potential via Poisson’s equation, \( \rho_e = -\varepsilon_r \varepsilon_0 \nabla^2 \phi \). An electric field \( \mathbf{E} = -\nabla \phi \) will exert an electrical body force on the fluid in Equation 3 given by \( \mathbf{f}_e = \rho_e \nabla \phi \). The electrical body forces are typically only significant in the EDL close to the surface of the particle where there is charge density. The distinguishing feature of a self-electrophoretic swimmer is the flux of current across its surface, which is responsible for the self-generated dipolar electric field. The interactions between this endogenous electric field and the charged surface of the particle lead to self-electrophoretic propulsion.

There are two general approaches for deriving boundary conditions for the species transport and electrical problems at the particle surface. The simple approach is to write a flux-based boundary condition that prescribes a piecewise constant ion flux on the colloid surface (Kline et al. 2006, Moran et al. 2010, Nourhani et al. 2015b). For flux-based models, the electrical potential boundary condition at the motor surface is typically a Dirichlet condition expressing a constant potential across the surface of the motor, \( \phi = \Phi \), where \( \Phi \) is a constant (usually negative) electrical potential and is often set equal to the zeta potential, \( \xi \). This uncoupled set of boundary conditions neglects interplay between the reactions and the particle surface charge, which is governed by electro-chemistry theory. Nevertheless, flux-based models can yield reasonable results when the reaction kinetics are unknown or too complicated. These models have produced trends that agree well with experiments, but generally require fitting to experiments for favorable quantitative comparison (Kline et al. 2006, Moran et al. 2010).
Another boundary condition approach reflects the coupling between the electrical and transport problems. This model employs kinetic expressions that describe the dependence of the local ion flux as a function of the reactant and ion concentrations, as well as the electrical potential distribution in the EDL surrounding the swimmer. This description unifies the physics of the EDL, from the electrokinetics literature, and reaction kinetics, from the electrochemistry literature. Since the original contributions of Frumkin (1933), the role of electrokinetic phenomena in electrochemistry has largely been ignored, and vice versa, with the exception of Frumkin-corrected Butler-Volmer models for fuel cells and battery applications (Bazant et al. 2004, Biesheuvel et al. 2009).

The sophistication of the kinetic boundary conditions varies in the literature, but here we give a detailed description of the coupled reaction kinetics and electrical potential boundary conditions and then briefly describe simplifying cases. Let us consider a simple electrochemical reaction, \( \text{RO} + me^- \rightarrow \text{R} \), involving the \( m \)-electron oxidation of a reduced species \( \text{R} \) (having concentration \( c_R \) at the electrode surface) to form an oxidized species \( \text{O} \) (having concentration \( c_O \) at the electrode surface). In general, this reaction can proceed in either direction, and the forward and backward reactions are given by a fundamental relation in electrochemistry known as the Butler-Volmer equation. Specifically, this equation gives the rate of an electrochemical reaction at an electrode as a function of the electrode potential and reactant and product concentrations. For the above reaction, the Butler-Volmer equation for the surface flux \( J \) of charged species may be written

\[
J = k_{\text{fro}} \exp \left( \frac{(1 - \alpha) m F \Delta \phi_s}{RT} \right) - k_{\text{ret}} \exp \left( -\frac{\alpha m F \Delta \phi_s}{RT} \right),
\]

where \( k_{\text{fro}} \) and \( k_{\text{ret}} \) are the rate constants for the forward (oxidation of \( \text{R} \) to yield \( \text{O} \)) and backward (reduction of \( \text{O} \) to yield \( \text{R} \)) reaction components, \( \alpha \) is a dimensionless parameter between 0 and 1 that quantifies the asymmetry of the energy barrier for the reaction (\( \alpha \) is usually set to 0.5, corresponding to a symmetric energy barrier), and \( \Delta \phi_s \) is the voltage drop across the so-called Stern layer (Moran & Posner 2011, Sabass & Seifert 2012b, Stern 1924), which is a layer of ions and neutral species immobilized on the electrode surface.

Following the electrochemistry literature, Equation 4 includes the so-called Frumkin correction, which entails evaluating the concentrations of species \( \text{O} \) and \( \text{R} \) at the electrode surface (as opposed to the bulk solution). The Frumkin correction modifies the original Butler-Volmer equation to include the effect of the electrical potential drop across the Stern layer \( \Delta \phi_s \) on the electrochemical reaction rate (Figure 3b). Outside the Stern layer is a diffuse layer of ions, often referred to as the Gouy-Chapman layer, in the solution adjacent to the rod. The Stern and Gouy-Chapman layers constitute the EDL. The Stern layer is treated as a linear capacitor in series with the diffuse layer (Bard & Faulkner 2001, Bazant et al. 2005, Hunter 1981, Stern 1924), which leads to the (dimensional) mixed, Robin-type, boundary condition for the electrical potential, \( \xi - \Phi = \lambda_S (\hat{n} \cdot \nabla \phi)_{\text{OHP}} = \Delta \phi_s \), where \( \Phi \) is the electrical potential of the metal interior with respect to the bulk solution, \( \lambda_S \) is the effective thickness of the Stern layer (on the order of angstroms), and the subscript OHP indicates that the quantity is evaluated at the outer edge of the Stern layer, often termed the outer Helmholtz plane (OHP). This effectively assumes a linear potential drop across the Stern layer, with the slope determined by the normal electric field evaluated at the OHP. The zeta potential \( \xi \) is defined here as the potential at the OHP versus the bulk solution. It is the electrical potential boundary condition for Poisson’s equation and effectively sets the electrophoretic mobility of the particle. These quantities are visualized in Figure 3b.

In the coupled kinetic model, the electrical potential of the swimmer \( \Phi \) is unknown, and the problem is closed by determining the value of \( \Phi \) (which influences the reaction rates indirectly through the Butler-Volmer equation) that results in zero net current across the entire particle.
surface (Moran & Posner 2011, 2014; Sabass & Seifert 2012b). We refer readers interested in the
detailed derivation of the preceding electrochemical model to Bazant et al. (2005) and Chu (2005).

This highly coupled, nonlinear system of equations is difficult to solve analytically and is
usually solved either numerically or using suitable approximate analytical methods. In general, the
reaction flux, the Stern layer voltage $\Delta \phi_S$, and the effective surface potential $\zeta$ vary along the rod.
However, at low ion concentrations, $\Delta \phi_S$ is generally small, and thus a uniform electrical boundary
condition holds, $\Phi = \zeta$, and the exponential term in the Butler-Volmer equation for surface flux
can also be neglected, resulting in a flux boundary condition of the form $J = k c$ (Moran & Posner
2011). Some efforts have been made to capture the electrochemical kinetics analytically (Sabass
& Seifert 2012b, Yariv 2011); however, these models include simplifying assumptions to reduce
the complexity associated with the high-fidelity Frumkin-Butler-Volmer (FBV) models, including
assuming a spherical particle, imposing an artificial but mathematically convenient trigonometric
variation in rate constants across the particle surface, assuming that the same reaction occurs in
different directions on the two metal sides, and assuming a thin EDL.

3.2. Dependence on Controlling Parameters

The velocity of self-electrophoretic particles depends on several controlling parameters, including
the fuel concentration, reaction rate constants (and thus the reactants and catalyst composition),
motor size, and background ion concentration. Several researchers have found a resemblance
between the self-electrophoretic velocity and the Helmholtz-Smoluchowski equation that provides
the explicit dependence of the swimming speed on controlling parameters, as summarized in
Supplemental Table 1, showing that there is general agreement on the dependence of the
swimming speed on several key parameters (Golestanian et al. 2007, Lammert et al. 1996, Moran

Figure 4a shows the dependence of the swimming velocity on fuel concentration for several
models. The experimentally observed dependence of speed on fuel concentration is initially linear,
with some groups showing an asymptote at higher concentrations (Laoharoenruk et al. 2008,
Wheat et al. 2010). Most studies do not report the velocity behavior at higher concentrations
because of the formation of reactant gas bubbles and the large variability it typically imposes
on the experiments. Bubbles form in experiments because the gases produced by the reactions
(e.g., $O_2$ at the anode of gold-platinum/peroxide motors), which at low concentrations are soluble
in the background electrolyte, saturate at higher concentrations and lead to bubble nucleation.
Most of the self-electrophoretic scaling analyses and constant-flux models suggest that the motor’s
swimming velocity scales linearly with the flux, $J$. Several models predict the dependence of the
swimming speed on fuel concentration, but none agree precisely with experimental measurements.
Numerical models that include the electrochemical kinetics have predicted a weakly quadratic
dependence (Moran & Posner 2011) or one of the form $c / (c + 1)$ (Sabass & Seifert 2012b). In many
kinetic models, the motor electrical potential depends linearly on the fuel concentration through
the FBV equations. This dependence of both the potential and current flux on fuel concentration
accounts for the quadratic dependence on fuel concentration. This may be a physically accurate
dependence, although it neglects the effect of differential adsorption of ions or impurities in
the solution on the surface charge (Dougherty et al. 2008, Moran & Posner 2011). Arguably,
the effective zeta potential of metal rods on which electrochemical reactions are occurring will
depend on both their native charge due to differential adsorption and the kinetics of the reaction. A
kinetic model that accurately predicts the swimming speed with fuel concentration is still needed,
and the issues of the appropriate kinetic equation, the dependence of the reaction rate on the
Figure 4
Dependence of self-electrophoretic motor swimming speed as a function of controlling parameters. (a) Swimming speed as a function of fuel concentration. Experiments are roughly linear at low to moderate concentrations. Simple scaling analysis and simple simulations assuming uniform flux (Moran et al. 2010) suggest a linear relationship, whereas more sophisticated simulations (Moran & Posner 2011) and asymptotic analyses (Sabass & Seifert 2012b) predict quadratic and $c/(1 - c)$ dependence, respectively. (b) Swimming speed for bimetallic rods versus solution conductivity in 3.7% H$_2$O$_2$ for experiments, theory, and simulations. The agreement between analytical theory and simulations from Moran & Posner (2014) is excellent at high conductivity; the divergence of the two data sets with decreasing conductivity is attributed to the assumption of the analytical theory of infinitely thin electrical double layers (Golestanian et al. 2007), an assumption that becomes increasingly less accurate as the conductivity is decreased and the electrical double layer becomes thicker. Panel b adapted with permission from Moran & Posner (2014). Copyright 2014 AIP Publishing LLC.

The motor velocity is strongly coupled to the background ion concentration because the propulsion originates from electroosmotic fluid slip around the particle surface. Ions in solution alter the charge distribution surrounding the motor, which then modifies the self-generated electric field, electrical potential distribution, reaction rate, and motor electrical potential. The primary reason for the reduction in speed is that the reaction-induced self-generated electric field scales with the surface flux or current density $i$ (which is proportional to the flux) according to Ohm’s law, $E = i/\sigma$ (Paxton et al. 2006, Golestanian et al. 2007). Additional factors contributing to motor slowing is the reduction of the reaction rate and rod potential magnitude (Moran & Posner 2014, Sabass & Seifert 2012b). The reaction rate is effectively reduced in salty solutions reactant and product concentrations, and the role of the native surface potential all require deeper investigation.
because the salt counterions shield the charged motor surface, reducing the effective proton concentration, which is a reactant at the gold cathode. The rod potential also decreases with increasing ion concentration due to the requirement of current conservation, which impacts the particle surface charge through the zeta potential, $\zeta$.

One exception to the inverse relationship between speed and salt concentration is seen when bimetallic swimmers are in the presence of silver-containing salts, which lead to an increase in the swimming speed over pure peroxide (Kagan et al. 2009). This increase in speed is thought to originate from the underpotential deposition of the ions onto the gold surface, which is thought to accelerate the catalytic decomposition of hydrogen peroxide. Additionally, bimetallic particles consisting of a platinum half and a silver-gold alloy half also move more quickly (Demirok et al. 2008); however, the exact details underlying the silver-induced enhancement remain unclear.

There is a broad, and somewhat unexplored, parameter space of motor size and geometry to investigate (e.g., rods, spheres, cones), as well as the relative fraction of metals (i.e., most motors have equal parts of two catalysts) (Nourhani et al. 2015a). The reported dependence on motor size is conflicting given that fabricating motors of different sizes is complex and that most models treat the motors as if they are neutrally buoyant in an infinite medium. Scaling analyses and models that describe the swimming speed of motors as a function of length suggest that the motor speed should increase either linearly (Moran et al. 2010) or as $\ln(b)/b$ (Golestanian et al. 2007) with motor size $b$. In contrast, experimental work has shown that the motor velocity decreases with size (Dhar et al. 2006, Wheat et al. 2010). One reason for this discrepancy is that motors are not neutrally buoyant and settle, due to gravity, down to the bottom of the experimental chamber, thus experiencing a hydrodynamic, and perhaps electrokinetic, interaction with a surface (Chiang & Velegol 2014, Wheat et al. 2010).

### 4. COMPLEX AND COLLECTIVE BEHAVIOR

Considerable attention has been paid to demonstrating various advanced user-controlled functions of self-phoretic particles. Externally applied magnetic (Burdick et al. 2008, Kline et al. 2006), temperature (Balasubramanian et al. 2009), chemical concentration (Calvo-Marzal et al. 2009, Kagan et al. 2009), and sound wave pressure (Wang et al. 2012) fields have been employed for external control over phoretic swimmers. In contrast, here we specifically focus on independent complex phenomena, lacking external control, that arise from the interaction of motors with each other and with stationary flows, physical interfaces, or fields (e.g., gravity, concentration).

As they move, self-propelled particles undergo translational and rotational Brownian motions (Figure 5a). A motor’s rotational Brownian diffusivity leads to a randomization of the direction of propulsion, resulting in amplification of the mean square displacement, quantified by the effective diffusivity, $D_{\text{eff}} = D + (1/4) U^2 \tau_{\text{rot}}$ (Howse et al. 2007), where $\tau_{\text{rot}}$ is the rotational diffusion timescale. The effective diffusivity can be several orders of magnitude larger than the particle’s Brownian diffusivity $D$ (Figure 5b). Although most reports suggest that motors swim relatively straight with random perturbations due to Brownian fluctuations (Howse et al. 2007), motors have also demonstrated the ability to swim in relatively tight circular patterns (as shown in the inset of Figure 5c), with diameters of 50–100 $\mu$m due to a persistent linear and angular velocity (Ebbens et al. 2010, Kümmel et al. 2013, Marine et al. 2013, Takagi et al. 2013). Circle swimming has been demonstrated for spheres, sphere doublets, rods, and L-shaped particles. In all cases, some symmetry breaking of the hydrodynamic or phoretic forces is required. The circular motion of spheres is attributed to an asymmetric Stokes drag profile of the sphere surface due to geometric
irregularities that result from the fabrication process (Marine et al. 2013). For rods, the circular pattern is attributed to the slight curvature of the rod, which is a by-product of the fabrication process and causes the rods to follow slightly curved trajectories and stochastically switch the direction of their orbits as they flip, due to random Brownian fluctuations along their long axis (Takagi et al. 2013).

Circle-swimming motors exhibit markedly different short-time and long-time effective diffusivities that scale with the translational and rotational velocities, which vary with fuel concentration (Marine et al. 2013) (Figure 5c). The short-time diffusivities are consistent with swimmers that are randomly reoriented by rotational Brownian motion and are two to three orders of magnitude larger than the diffusivity of a Brownian sphere of the same size. The long-time diffusivities, conversely, are five times lower than the short-time diffusivities because the motors tend to swim in a circle and return to their origin, effectively lowering their mean displacement. The decrease of diffusivity with time suggests that motors will have a high collision probability in confined spaces and over short times but will not disperse over relatively long distances and times. The circle-swimming motors can exhibit a peak in long-time effective diffusivity as a function of fuel concentration (Marine et al. 2013) so that they can be separated or concentrated using gradients in fuel concentration.

Phoretic motors exhibit hydrodynamic, electrostatic, and phoretic interactions with surfaces. Motors have been shown to be directed toward and swim along the physical interface of submicrometer-scale ledges (Das et al. 2015, Simmchen et al. 2016, Spagnolie & Lauga 2012) and in temporary circular orbits around spheres (Takagi et al. 2014) (Figure 5d,b). There is convincing evidence that the primary driving forces for the experimental observations are purely hydrodynamic and depend on the geometry of the motor and the active sites (Das et al. 2015, Spagnolie & Lauga 2012, Takagi et al. 2014). Some models claim that phoretic mechanisms and modifications of the local concentration field due to wall proximity can modify the motor’s orientation and velocity due to wall-induced diffusiophoresis (Ibrahim & Liverpool 2015, Simmchen et al. 2016). For metal/insulator Janus swimmers, the wall’s modification of the swimmer trajectory may depend on the reaction and interaction potential (whether the particle moves toward or away from regions of high solute concentration), but these theories have yet to be adequately verified by experiments (Ibrahim & Liverpool 2015).

Self-electrophoretic motors can also form assemblies between motors and with charged nonactive colloids due to electrostatic and electrical dipole interactions (Wang et al. 2013b) (Figures 5e–g). Interactions between platinum-gold rods can be attractive or repulsive depending on the relative alignment of the rods because of the charge density and electric dipoles formed by the electrochemical reaction (Figure 5e). The coupling of endogenous electric fields of self-electrophoretic swimmers with proximal charged planar surfaces has also been shown to reduce swimming velocity and generate local electroosmotic pumping (Chiang & Velegol 2014).

The analogy between biological swimmers and self-propelled phoretic particles has naturally evolved into the design and analysis of synthetic swimmers that exhibit various taxis, kinesis, and pattern-formation behaviors. In biology, taxis refers to the ability of an organism to sense an external stimulus, often in the form of light or the presence of a nutrient, and to respond to the stimulus to its own benefit. Crucially, taxis is distinguished from other stimuli responses by the requirement of sensing and persistent alignment or temporal response to a scalar field or gradient. Biological swimmers exhibit a wide variety of taxis behaviors by migrating up or down gradients or fields of chemical concentration (chemotaxis), fluid velocity (rheotaxis), gravity (gravitaxis), temperature (thermotaxis), and light (phototaxis). For example, Escherichia coli bacteria migrate toward nutrient-rich regions through chemotaxis (Berg & Brown 1972), and sperm orient
Rheotaxis: movement of an organism in response to a fluid flow; a common example is the ability of organisms to exhibit positive rheotaxis in which they turn to face an oncoming current themselves upstream by rheotaxis (Bretherton & Rothschild 1961, Kantsler et al. 2014). A less well-known phenomenon is kinesis, which is distinct from taxis in that the swimmer’s response is not directional (Dunn 1981, Wheat 2011, Wilkinson 1998, Zigmond & Hirsch 1973). Biological examples of chemokinesis include human sperm (Ralt et al. 1994) and neural cells (Richards et al. 2004). We highlight the nuanced differences between the suffixes -taxis and -kinesis because these terms, and the experiments used to characterize them, are often inadvertently misused when describing the response of both living and synthetic swimmers. The biomimetic response of artificial swimmers to scalar fields and gradients is particularly compelling because it offers a potential pathway to demonstrate autonomous higher-order functions observed in biological systems and critical behaviors in the formation of large-scale collective patterns.

Phoretic particles have exhibited positive rheotaxis with the ability to migrate against a pressure-driven flow (Palacci et al. 2013). Their upstream migration originates from a viscous flow-induced
torque, which overcomes rotational diffusion to persistently align the particles with the flow. Gravitaxis, the net migration of a swimmer due to persistent alignment with a gravitational field, has been demonstrated for L-shaped particles (ten Hagen et al. 2014) and spherical Janus particles (Campbell & Ebbens 2013) (Figure 6a). In each case, a coupling of the asymmetric phoretic and gravitational forces results in a torque of the motor to provide persevering alignment with the gravitational field.

Several reports claim that phoretic swimmers exhibit chemotactic responses in which they accumulate in fuel-rich regions of a confined two-dimensional domain (Baraban et al. 2013, Chen et al. 2016, Hong et al. 2007). However, chemotaxis requires sensing of the local concentration with time or concentration gradient and a corresponding temporal response (e.g., run and tumble) or alignment that results in persistent migration in chemical gradients. There is no rigorously justified mechanism for realigning the motors along chemical gradients because Brownian motion randomly disorients the motor’s trajectory. Some experiments and models show that a fraction of motors marginally align their swimming direction up the fuel gradient, but no plausible physical description is provided for the alignment of motors with the gradients (Baraban et al. 2013, Chen et al. 2016). Contrived experiments of chemotaxis are notoriously challenging to perform and interpret (Dunn 1981, Wheat 2011, Wilkinson 1998, Zigmond & Hirsch 1973), especially for self-phoretic motors given the difficulty in generating static concentration gradients, the presence of interfaces and interfacial forces, confounding effects of diffusiophoresis, the large natural variability of motor shape and size, small sample numbers, and unrepeatable experiments. It is well established that self-phoretic swimmers reorient themselves randomly due to Brownian motion and that their linear and angular velocities are proportional to the local concentration of fuel and inhibiting solutes (e.g., salt). For these reasons, motors should exhibit a random walk through the solvent with an effective diffusivity proportional to the linear and angular velocities, which generally vary with the local concentrations of fuel. A gradient of fuel or inhibiting solutes such as salt should result in a gradient in effective diffusivity and local accumulation of motors in low effective–diffusivity regions called chemokinesis.

**Figure 5**
Complex behaviors of self-phoretic swimmers in free solution and when interacting with one or more colloidal particles and with solid interfaces. (a) Motion traces of phoretic Janus particles with increasing fuel concentration showing that the particles exhibit an enhanced random walk. (b) The mean square displacement of the motors shown in panel a as a function of time (the slope is effective diffusivity) showing superdiffusive behavior (Howse et al. 2007). The effective diffusivity increases with fuel concentration. (c) Mean square displacement of circle-swimming Janus motors showing nonmonotonic dependence of mean square displacement on time. The inset shows pathlines of motors swimming in tight circles. The effective diffusivity (slope of mean square displacement) is much larger at early times (open symbols) than at long times (closed symbols) (Marine et al. 2013). (d) Self-electrophoretic bimetallic rod transiently orbiting a larger inert particle, due to hydrodynamic interactions, and then being released (Takagi et al. 2014). (e) Simulated charge density distribution (red is positive, and blue is negative) showing induced dipoles of bimetallic self-electrophoretic motors around paired rods. Rods attract when staggered (left), repel when aligned (middle), and attract when inverted (right). Bimetallic self-electrophoretic motors interacting with (f) a positively charged sphere that migrates and adheres to the gold end due to electrostatic attraction to the negative end of the induced dipole, and (g) negatively charged spheres that migrate and adhere to the platinum end, attracted there by the positive end of the dipole. (h) Phoretic swimmer that approaches a ledge, turns, and swims along the edge due to local distortion of the self-generated concentration field. Color represents reaction products with high (red) to low (blue) concentration. Panels a and b adapted with permission from Howse et al. (2007). Copyright 2007 American Physical Society. Panel c reproduced with permission from Marine et al. (2013). Copyright 2013 American Physical Society. Panel d reproduced with permission from Takagi et al. (2014). Copyright 2014 Royal Society of Chemistry. Panels e–g reproduced with permission from Wang et al. (2013b). Copyright 2013 National Academy of Sciences. Panel b reproduced with permission from Simmchen et al. (2016). Copyright 2016 Nature Publishing Group.

**Chemotaxis**: persistent, directional movement of an organism in response to a chemical stimulus that typically requires the ability to sense the local concentration gradient or variation in time

**Chemokinesis**: net accumulation of swimmers in a chemical gradient due to the dependence of its linear velocity or turning frequency on the local concentration
Figure 6
Examples of self-phoretic motors exhibiting taxis, kinesis, and collective behaviors. (a) An L-shaped phoretic swimmer exhibiting gravitaxis. Experimental trajectories of motors (all originate at red circle) swimming against a gravity field with increasing propulsive force (ΔF). (b) Self-diffusiophoretic surfers generating crystal lattices (colored in blue, green, red, and yellow) due to a combination of phoretic forces, both self-generated and between a cluster and an individual swimmer. (c–e) Demonstration of self-electrophoretic platinum-gold rods exhibiting chemokinesis. (c) Experimental swimming traces showing that platinum-gold rods swim freely in a two-dimensional plane with steady, opposing, one-dimensional linear gradients of fuel (from left to right) and ionic strength (from right to left). Motors swim faster and exhibit greater effective diffusivities in regions with high fuel and low ion concentration (left) compared to motors in the low-fuel, high-ion-concentration regions (right). (d) Measured effective diffusivities of phoretic motors as a function of space, showing that a significant gradient in effective diffusivity (from 100× to 1× Brownian diffusivity) develops across the system. (e) The distribution of motors initially and after 12 min for the experiments, Brownian dynamics, and Fokker-Planck continuum model. The insets show that the motors accumulate after 12 min in regions of low diffusivity (low fuel and high salt). Panel a adapted with permission from ten Hagen et al. (2014). Copyright 2014 Macmillan Publishers Limited. Panel b adapted with permission from Palacci et al. (2013). Copyright 2013 American Association for the Advancement of Science. Panels c–e adapted with permission from Wheat (2011).
There have been at least two demonstrations of chemokinesis of phoretic motors. Wheat (2011) demonstrated that self-electrophoretic platinum-gold motors swam faster and showed greater effective diffusivities in regions with high fuel and low ion concentration compared to motors in the low-fuel, high-ion-concentration regions. Over several minutes, the motors exhibited chemokinesis by accumulating in the regions of low effective diffusivity (low fuel and high ionic strength) (Figures 6c–e). Saintillan and coworkers (Ezhilan et al. 2015) used a source of silver ions to show that self-electrophoretic motors exhibit chemokinesis. The motors increased in velocity when in proximity to the silver ions, and as a result, the swimmers in silver-rich regions exhibited an increased effective diffusivity and wider dispersion compared to passive particles. The particles were overall depleted from the high-silver-concentration regions where the motors swim faster, consistent with a chemokinetic response.

It may be possible to engineer phoretic swimmers that exhibit true chemotactic behavior by including components that can sense and align themselves relative to an external concentration gradient. These motors would likely require multiple phoretically active elements that are geometrically separated, allowing the motor to orient itself with respect to the gradient (Attard 2012, Wheat 2011). The interactions among phoretic swimmers are challenging to study theoretically or experimentally. Models need to be able to resolve the physicochemical hydrodynamics of a large number of individual motors in complex scalar gradients, with the added challenge that the neighboring swimmers and interfaces can modify their local environment, requiring time-dependent simulations that resolve a large number of particle-particle interactions. A substantial challenge in experiments is interpreting the observed behavior and distinguishing it from the other inexorable, confounding physical phenomena that are present (e.g., capillary forces, classical electrolyte-driven diffusiophoresis, steric or van der Waals interactions) due to the imposed spatial gradients. A key question in using models to faithfully recreate experimentally observed phenomena is how to correctly integrate the physicochemical hydrodynamic interactions among swimming particles, at interfaces, in scalar gradients.

In light of studies that have been conducted on the hydrodynamic phenomena occurring very near swimmer surfaces, it will be crucial to the development of this field to make use of computational simulation methods that incorporate both hydrodynamics and thermal fluctuations, both of which are essential in describing the dynamics of swimmer suspensions. Biological swimmers are often classified as pushers or pullers, depending on the velocity field they create in their vicinity. Active colloids typically show the hydrodynamic signature of a neutral swimmer although, in some novel cases, such as the spontaneous autophoretic motion of isotropic particles, the particle is a pusher in the far field (Michelin et al. 2013).

An example modeling technique that may prove useful in future studies is multiparticle collision dynamics (Görze & Gompper 2010), which has already been used to show that hydrodynamic near fields acting between swimmers, as well as between swimmers and bounding walls, crucially determine their collective motion (Zöttl & Stark 2014). A similar technique, known as Stokesian dynamics (Brady & Bossis 1988), has been used to study the collective dynamics of suspensions of pushers, pullers, and neutral swimmers, showing that their complex hydrodynamic interactions result in instabilities and particle ordering (Evans et al. 2011). Methods such as these, and others (Molina et al. 2013) that consider both the host fluid and swimming particles, offer a promising avenue to account for other important interactions, such as electrostatics. We expect that these computational tools will be indispensable in the coming years for interpreting previous experimental observations, as well as for predicting new ones.
SUMMARY POINTS

1. Active colloids can self-propel by creating localized fluid motion, which results from a surface reaction-generated local gradient in a scalar quantity such as concentration for self-diffusiophoresis, or electric potential for self-electrophoresis. These active colloids are known as phoretic swimmers.

2. An asymmetry in the surface reactions, geometry, or concentration fields generated through either asymmetric surface activity or advection-driven instability is required to generate a phoretic slip velocity.

3. When advective or reaction-driven fluxes dominate over diffusion, the swimming speed of phoretic particles is generally reduced.

4. In general, both self-electrophoretic and self-diffusiophoretic mechanisms are strongly inhibited by the presence of electrolytes.

5. Self-phoretic motors display complex interactions with each other and with interfaces, as well as exhibit biomimetic collective behaviors in response to scalar fields and gradients.

FUTURE ISSUES

1. What is the role of electrokinetic phenomena in neutral-solute self-diffusiophoresis, especially in the presence of electrolytes and in reactions having ionic reactants or products?

2. Why is the motion of platinum/polystyrene Janus particles sensitive to the electrolyte concentration, in disagreement with the self-diffusiophoresis mechanism, and what is the role (if any) of self-electrophoresis in this system (Brown & Poon 2014, Ebbens et al. 2014)?

3. Why do self-electrophoretic swimmers experience enhanced motion in silver-containing salts (Kagan et al. 2009), in contrast to their significantly reduced speeds observed in other electrolytes (Moran & Posner 2014, Paxton et al. 2006)?

4. What is the appropriate kinetic expression for the electrochemical reactions on the surface of a self-electrophoretic motor? How do the reaction kinetics depend on the floating electrode potential of the particle interior, and the zeta potential, which may be influenced by native surface charge? How does this affect the relationship between swimming speed and fuel concentration?

5. What are the criteria for a transition in the propulsion mechanism from self-diffusiophoresis to bubble propulsion for platinum-polystyrene Janus particles (Wang & Wu 2014)?

6. Is it experimentally feasible for self-diffusiophoretic swimmers to achieve the finite Péclet numbers required for advective effects identified in Section 2.5 to be important?

7. Are there any real-world examples of self-diffusiophoretic motors whose behavior is dictated primarily by attractive or repulsive van der Waals forces, as has been theoretically predicted (Sabass & Seifert 2012a, Sharifi-Mood et al. 2013)?
8. How can we rigorously verify the rich variety of theoretical predictions of self-diffusiophoretic motors? Is it possible to devise and implement a system in which self-diffusiophoresis is clearly uncoupled from other modes of self-propulsion (e.g., self-electrophoresis)?

9. We encourage unambiguous experimental design and demonstration of self-phoretic colloids that can realize artificial chemotaxis through persistent alignment or temporal response (e.g., E. coli’s run and tumble) relative to an external concentration gradient.

10. We recommend the continued development of Stokesian dynamics to model the physicochemical hydrodynamic and electrostatic interactions of self-phoretic swimmers with each other, in proximity to surfaces, and in complex environments.

DISCLOSURE STATEMENT

The authors are not aware of any biases that might be perceived as affecting the objectivity of this review.

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