Eppur si muove, and yet it moves: Patchy (phoretic) swimmers

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Abstract

Advances in colloidal synthesis allow for the design of particles with controlled patches. This article reviews routes towards colloidal locomotion, where energy is consumed and converted into motion, and its implementation with active patchy particles. A special emphasis is given to phoretic swimmers, where the self-propulsion originates from an interfacial phenomenon, raising experimental challenges and opening up opportunities for particles with controlled anisotropic surface chemistry and novel behaviors.

Keywords: Interfacial Transport, Phoresis, Patchy, Active Colloids.

1. Introduction

This review article focuses on *active* patchy colloids, here defined, as self-propelling particles a.k.a. swimmers. Self-propulsion comes at a cost: particles need to harvest free energy from their environment and convert it into mechanical work. The emergent phenomena, originating from the non-equilibrium nature of the system, are a pivotal issue of the Active Matter field [1, 2] but will not be discussed here. For example, collections of active particles can form clusters [3, 4], "living crystals" [5] or flocks [6] and confined vortices [7]. The advancement of a "thermodynamics" and unified framework for those systems

[1] Phrase attributed to Galileo Galilei, commenting on his trial and abjuration. The historic accuracy of the quotation is questionable.

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in an ongoing work [8, 9]. It notably unveiled a Motility-Induced Phase Separation (MISP), arising from the persistence of the particles, colliding heads-on and driven by the rotational diffusion of the propulsion [10, 11, 12, 13, 14, 15]. Some equilibrium concepts have been extended: active pressure [16, 17, 18, 19], or surface tension [20], but experiments remain unfortunately scarce [21, 22].

This article is not intended as an exhaustive review of the swimmers, as available in [23, 24, 25, 26, 27]. It is aimed at the colloidal scientist willing to get a better grasp on active colloids, and an insider view on this large body of work. It surveys the different experimental strategies to build self-propelled colloids and focuses on *phoretic* engines. Our presentation presents a brief description of interfacial transport through a qualitative description of electro-osmosis and broadens the conclusions to the phenomenon of diffusio-phoresis or migration in a solute gradient. We point towards recent results showing that, in practice, model-systems are more complex than originally thought. We conclude by discussing the opportunities offered by patchy phoretic particles.

2. Self-propelled Colloids

2.1. Swimming at the microscale

Autonomous microswimmers experience low Reynolds number dynamics or "dynamics in a very viscous fluid", following Stokes equation, which is time-independent [28, 29]. As stated by Purcell in his seminal paper [28], "time doesn't matter, the pattern of motion is the same, whether slow or fast, whether forward or backward in time", and propulsion from a reciprocal stroke, akin to an opening and closing hinge, is precluded[3]. Propulsion can be achieved from non-reciprocal patterns of motion, e.g. wave propagation in an oscillating artificial flagella [30, 31] or corkscrew motion of actuated magnetic structures [32, 33, 34, 35]. Such systems are macroscopically actuated and the direction of propulsion is set by an external operator. Alternatively, *autonomous* systems,

[3] In a Newtownian fluid

akin to bacteria in Nature, embed a propulsive machinery and propel along a direction set internally. The collective arrangement and the emergence of large scale coherent motion is a key question in non-equilibrium systems and makes artificial swimmers an adequate probe to explore the driving principles of dissipative systems. An effective route toward propulsion at small scale, taking advantage of the miniaturization, is to harness interfacial phenomena. Phoretic effects, by which a field gradient sets colloidal particles into motion, thus appear as a relevant vessel for micro-propulsion. Swimmers propelled by non-interfacial phenomena such as bubbles [36, 37, 38, 39, 40], acoustic waves [41] or ultrasounds [42, 43] or in complex fluids [44, 45, 46, 47, 48, 49, 50, 51] are current topics of research but will not be discussed in this review. An overview of available swimmers is presented on [Fig.1].

2.2. Individual Dynamics of Autonomous Swimmers

In the simple case of particles moving in 2D on a substrate, swimmers perform a *persistent random walk*. The direction of self-propulsion decorrelates over a typical persistence time τ_p. Particles exhibit a ballistic motion for $t \ll \tau_p$ and an effective diffusive behavior for $t \gg \tau_p$ [Fig.2A]. The expression of the 2D Mean Square Displacement (MSD) from the projection of a 3D motion is given by [52, 53] [Fig.2B]:

$$\Delta L^2(\Delta t) = 4D_0\Delta t + \frac{V^2\tau_p^2}{3}\left[\frac{2\Delta t}{\tau_p} + e^{\frac{-2\Delta t}{\tau_p}} - 1\right] \quad (1)$$

where D_0 is the diffusion coefficient of the particle at equilibrium. The dynamics is analogous to the dynamics of a Brownian particle predicted by a *Langevin model*, with the persistence time replacing the inertial time scale ($\sim$ns). Rotational and translational dynamics are often decoupled in the experiment, $\tau_p \sim \tau_R \propto R^3$, where τ_R is the equilibrium rotational time and R, the radius of the particle [53, 54, 5, 55]. The rotational diffusion can be extracted from the MSD, but the uncertainty on the determination from the non-linear fit is often broad. Direct measurement of the rotational dynamics could be alternatively implemented following recent microscopy developments, e.g. confocal

imaging [56] or differential dynamic microscopy (DDM), originally developed for translational diffusion [57], then bacterial motility [58] and recently adapted to probe rotational dynamics [59].

3. Basics of Interfacial Transport

In fluid dynamics, surfaces are often considered as boundary conditions for the fluid domain without taking into account the nanoscopic structure of the layer at the solid/liquid interface. In this section, we introduce physical phenomena demonstrating the impact of this nanometric layer at large scale. The thermodynamic force arising from an interfacial gradient of a field O can either drive a fluid under motion with respect to a wall by osmosis, or reciprocally move a particle by phoresis. The field O can be an electric potential Φ, the temperature T, or a solute concentration c, in the cases of respectively, electrophoresis, thermophoresis, and diffusiophoresis.

3.1. Electro-osmosis for Dummies®

In this section, we discuss the phenomenon of electro-osmosis, *i.e.* the interfacial flow resulting from the application of an electric field. More detailed derivations and discussions on electrokinetic effects can be found in [60, 61, 62, 63].

A solid surface immersed in an aqueous solution spontaneously gets charged. We consider a negative charge as in the case of silica in water ($SiOH=SiO^- + H^+$). Cations are attracted to the charged surface and anions repelled, leading to the formation of a screening double layer of ions [Fig.3A]. In the Debye-Huckel limit of weak potentials[4], the electric potential , $\Phi(z)$, decays exponentially from the wall , $\Phi(z) = \zeta e^{-z/\lambda_D}$, where $\lambda_D^{-2} = 2q^2\rho_0/\epsilon k_B T$, λ_D is the Debye length, ϵ is

[4] We assumed a Gouy-Chapman mean field approximation, which neglects the fluctuations of potential, considering only the mean value of the charge distribution, and we neglected the ions-ions and ions-solvent interactions.

the permittivity of the considered medium, k_B is the Boltzmann constant, q the charge of the cation and ρ_0 the bulk concentration of ions[5].

The total charge density is approximated by:

$$\rho = \begin{cases} = 0 & \text{if } z \geq \lambda_d \\ \neq 0 & \text{if } z < \lambda_d \end{cases}$$

An electric field $E\mathbf{e}_x$ is applied along the solid surface [Fig.3A]. The system S =[surface+Debye-Huckel layer+bulk solution] is neutral and so that the total electric force acting on S is zero[6], $\mathbf{F}_e = \int_S \rho \mathbf{E} \mathrm{d}V = \mathbf{0}$.

The total charge density follows the Poisson-Boltzmann equation, $\Delta\Phi = -\rho/\epsilon$, leading to $\zeta/\lambda_D^2 \sim -\rho/\epsilon$, where the ζ-potential is the potential drop in the Debye layer. The ions in the double layer undergo a net volume force $\mathbf{f} = \rho\mathbf{E}$ and move. The velocity within the layer determines the velocity field outside the layer $\mathbf{V}_{eo} = V_{eo}\mathbf{e}_x$. Since λ_D is nanometric, we rewrite the force as a surface stress: $\sigma_E \sim \rho\lambda_D\mathbf{E} \sim -\frac{\epsilon\zeta}{\lambda_D}\mathbf{E}$. This is the driving power of the motion [Fig.3A]. It is balanced by the viscous stress resulting from the velocity gradient in the double layer, [7] $\sigma_\eta \sim \frac{\eta}{\lambda_D}\mathbf{V}_{eo}$, leading to the electro-osmotic velocity:

$$\mathbf{V}_{eo} \sim -\frac{\epsilon\zeta}{\eta}\mathbf{E} \tag{2}$$

This result was first derived by Smoluchovski [64].

3.2. Electro-phoretic motion of a colloidal particle

We consider the effect of an electric field on a charged colloid of radius R. In the thin Debye layer limit $R \gg \lambda_D$, the curvature is negligible, and the problem is akin to the electroosmotic flow induced by the tangential electric field, as discussed in the previous section. The particle *electrophoretically* migrates in the direction opposite to the electro-osmotic flow. Solving the phoretic velocity

[5] For a centimolar aqueous solution of a monovalent salt, $\lambda_D \sim 3\,\mathrm{nm}$.

[6] Swimming bacteria are an other example of propulsion at zero net force as the drag balances the thrust, and forms, to lowest order, a force dipole.

[7] We consider non-slip boundary conditions at the wall

requires the resolution of the Stokes flow with the appropriate boundary conditions (zero flow at infinity and electro-osmotic slip on the particle surface). It gives, for an homogeneous particle of arbitrary shape, with $\lambda_D \ll R$, [65]:

$$\mathbf{V}_{EP} = \frac{\epsilon\zeta}{\eta}\mathbf{E} = -\mathbf{V}_{EO}$$

3.3. Diffusio-osmosis, Diffusio-phoresis

Neutral Diffusio-osmosis

We extend our understanding of interfacial transport to the phenomenon of diffusio-osmosis: the interfacial flow induced by a concentration gradient of solute. The phenomenon was first reported by Derjaguin in 1947 [66], then by Prieve and coworkers [67, 68]. It converts the energy stored in solute gradients into mechanical energy and motion. It is a rather subtle phenomenon, relevant in the variety of natural and artificial situations with concentration gradients, e.g. evaporation, mixing, imposed gradients or asymmetric reactions... In this review, we mainly focus on the results important for the design of active patchy particles, details and examples of diffusio- transport are discussed in [60, 69, 70]. A solid substrate is immersed in a solute solution of bulk concentration c_0. The solute interacts with the substrate through a potential $U(z)$ with typical range λ, e.g. $\lambda = \lambda_D$, the Debye length, for electrostatics. At thermal equilibrium, the distribution of (non-interacting) solute particles is given by the Boltzmann distribution, $c(z) \approx c_0 e^{-\frac{U(z)}{k_B T}}$. Provided a macroscopic profile $c_0(x)$, one can rewrite $c(x,z) \approx c_0(x) e^{-\frac{U(z)}{k_B T}}$. The resulting unbalanced osmotic pressure in the interaction layer λ is the driving force of the diffusio-osmotic flow [FIG.3B]. It is balanced by the viscous stress and leads to the diffusio-osmotic flow [60, 71] :

$$V_{DO} = -(k_B T/\eta)\Gamma L \frac{dc_0}{dx}\mathbf{e_x} = \mu_{DO}\frac{dc_0}{dx}\mathbf{e_x} \tag{3}$$

where $\Gamma = \int_0^\infty dz[e^{-U(z)/k_B T} - 1]$ measures the excess of solute induced by the presence of a solid wall [8], $L = \Gamma^{-1}\int_0^\infty dz z[e^{-U(z)/k_B T} - 1]$ is the range of

[8] $\Gamma < 0$ for depletion of solute and $\Gamma > 0$ for solid-solute attraction

interaction, and μ_{DO} the diffusio-osmotic mobility. This description for neutral species is called *chemio-osmosis*.

Diffusio-osmosis of charged species

In the case of charged species, an additional *electrophoretic* contribution needs to be accounted for. In an electrolyte gradient, an electric field **E'** is generated to maintain a zero electrical current:

$$\mathbf{j}_e = -(-q)D_-\nabla c_0 - qD_+\nabla c_0 + (-q)c_0\mu_+^E\mathbf{E}' + qc_0\mu_-^E\mathbf{E}'$$

with $q > 0$ the electrical charge of the cation[9], $D_\pm$, the thermal diffusivity of the cations (respectively anions) and $\mu_\pm^E$, the electrical mobility of the cations (respectively anions). The fluctuation-dissipation theorem relates the electrical mobility and diffusivity :$\mu_\pm^E = \frac{\pm qD_\pm}{k_BT}$ [55]. At zero current, $\mathbf{E}' = \beta\frac{k_BT}{q}\nabla\log(c_0)$, where the factor $\beta = \frac{D_+ - D_-}{D_+ + D_-}$ is ion specific. The charged surface sets an electro-osmotic flow in the self-induced electric field **E'**:

$$\mathbf{V}_E' = -\frac{\epsilon\zeta}{\eta}\mathbf{E}' = -\beta\frac{\epsilon\zeta k_BT}{\eta q}\nabla\log(c_0)$$

The diffusio-osmotic velocity for charged species becomes:

$$\mathbf{V}_{DO} = -D_{DO}\nabla\log c_0$$

with

$$D_{DO} = -\beta\frac{\epsilon\zeta}{\eta}\frac{k_BT}{q} + \frac{\epsilon}{2\pi\eta}(\frac{k_BT}{q})^2\log(1-\zeta^2)$$

where the first term is the self-induced electrophoretic contribution and the second term is the complete expression for chemio-osmosis [60]. In practice, the chemio-osmotic contribution is often negligible [10]. As in electrophoresis, a

[9] For the sake of simplicity, we assume that anions and cations have the same absolute charge.

[10] Comparing LiCl and KCl electrolytes, in controlled microfluidic gradients, the diffusio-phoretic mobility of latex or silica particles in KCl concentration gradients, $\beta_{KCl} \sim 0$, was reported only $\sim 10\%$ of the diffusio-phoretic mobility in LiCl gradients, for which β is larger [72, 73, 74].

colloid migrates diffusiophoretically in an solute gradient, with $\mathbf{V}_{DP} = -\mathbf{V}_{DO}$. Important features of phoresis for the design of active colloids summarize:

- The flow relies on interaction of a solute species with the solid substrate, e.g. electrostatics for the electrophoresis.
- The interaction range is nanometric. The osmotic velocity appears, macroscopically, as an apparent slip velocity.
- The velocity is independent of geometry of homogenous particles of size R, provided $R \gg \lambda$. Phoresis is robust to downsizing.

4. Active Patchy Particles

4.1. Self-propelled Nanorods

A natural avenue for self-propelled particles is the design of particles with fore-aft asymmetry and using phoretic phenomena. A pioneering realization is the making of gold-platinum bimetallic nanorods immersed in a solution of hydrogen peroxide H_2O_2 [75, 76, 77, 78]. The nanorods are typically 2μm in length and 200nm in diameter [Fig.1D] and propel with a velocity $V \sim 15\mu$m/s. They exhibit a persistent random walk, though more subtle dynamics due to the curvature of the nanorods have been reported [79]. The system constitutes a short-circuited battery, with a platinum anode and a gold cathode. The addition of an insulating section between the electrodes suppresses the propulsion. The electrochemical decomposition of H_2O_2 results in a gradient in proton concentration, associated to a self-induced electric field pointing from Pt to Au. It sets into motion the positive double layer surrounding the negatively charged nanorod, exhibiting a self-electrophoretic propulsion with the platinum heading [Fig.1E]. Details on reaction-induced charge auto-electrophoresis can be found in [80, 81]. The non-equilibrium electric field is not screened by the static double layer and results in long-range interactions between pairs of nanorods [82] or tripartite Au-Pt-Au rods which assemble into stable rotors [83]. It also accounts for the surprising increase of the propulsion velocity of nanorods in confining

channels [84].

Numerous modifications have been performed on the original gold-platinum design. For example, the addition of magnetic segments allow to steer them externally [76, 85, 86]. Different combinations of metals (Pt, Pd, Ni, Au, Ru, and Rh) modify the difference of mixed potential between the electrodes and result in changes in speed and direction of propulsion [87]. The addition of Carbon NanoTubes (CNT) within the platinum segment enhances the electron-transfer and leads to speeds up $\sim 100\mu$m/s. Similarly, the addition of hydrazine to the solution enhances the decomposition of hydrogen peroxide and lead to speed $\sim 200\mu m/s$ [88]. *A contrario*, the addition of salt reduces the speed of the nanorods (unless it is silver salt, which deposits on the gold segment and increases the mixed potential difference between the electrodes) [89]. The phenomenon can be qualitatively understood since the driving stress (the motion of the double layer due to the auto-induced electric field) scales as the Debye length λ_D, $\sigma_D \propto \lambda_D$, and the viscous dissipation as the shear rate $\sigma_\eta \propto \frac{V}{\lambda_D}$ leading to a propulsion velocity $V \propto \lambda_D^2 \propto 1/\rho_0$, decaying with the salt concentration ρ_0.

4.2. Autophoretic swimmers

An alternate design is the Janus colloid, where only one side of the particle is active [90, 91]. Such particles are typically synthesized by sputtering of a material (Au, Pt, C...) on a monolayer of homogeneous spheres [Fig. 1F,G].

4.2.1. Diffusio-phoretic swimmers

Platinum-dielectric Janus, a model system?

Diffusio-phoretic swimmmers exhibit catalytic patches on dielectric particles [90, 91]. They self-propel, in the auto-induced concentration gradient, with velocity $V_p \propto \frac{\alpha\mu}{D}$, which depends on (i) α, the reaction rate of the reaction on the catalytic site, (ii) μ, the diffusio-phoretic mobility of the particle in the concentration gradient of the considered specie [See Eq. 3] and (iii) D, the diffusion coefficient of the chemical in the medium [90, 91]. The prefactor depends on the geometry of the patches on the particle. (i) and (ii) are surface properties of

the particle, while (iii) depends on the medium. In this simple phoretic picture, the propulsion velocity is independent of the particle size. However, the concentration gradient is set by the particle itself, which can lead to size dependence of the velocity. The velocity of Pt-PS janus particles exhibits size-dependence, $V_p \propto 1/R$, for radii in the range [250nm $-$ 5μm]. This can be simply understood in the diffusion limited regime, where the concentration of fuel at the active patch is 0 and the bulk concentration C_0, on the inert side, leading to $V_p = \mu \nabla C \propto \mu \frac{C_0}{R}$ [92]. The relationship between the geometry and the speed for self-phoretic Janus particles was recently discussed in [93].

Diffusio-phoretic swimmers were first obtained by sputtering a nanometric platinum cap on polystyrene spheres [Fig.1F] and immersed in hydrogen peroxide (typically $0.1 - 10\%$) [52]. Platinum is a catalyst for the decomposition of hydrogen peroxide, $2H_2O_2 = 2H_2O + O_2$ and the particle creates a concentration gradient. The velocity follows a Michaelin-Menten behavior with the concentration of fuel, suggesting a two-step process where hydrogen peroxide first forms a complex on platinum before breaking down in water and oxygen [52]. The particles propel at speeds up to $\sim 10 - 15\mu$m/s.

This system was initially considered a model system for the study of active colloids. The particles are conveniently synthesized: platinum can be sputtered on a wide range of commercially available dielectric, e.g. polystyrene or silica colloids. The yield is often limited by the intrinsic 2D nature of the process. Novel approaches have since been proposed to scale up the synthesis [94]. The chemical decomposition of hydrogen peroxide, $2H_2O_2 = 2H_2O + O_2$, only involves neutral species, which presumably simplifies the dependence of the self-propulsion on surface chemistry, such as the ζ potential of the colloid or the pH of the solution. Along this line, neutral diffusio-phoresis was shown to provide an explanation for the observed reorientation of propelling Pt/dielectric Janus, with their hemisphere perpendicular to the substrate surface [95, 96].

However, subsequent results hint that charged species are involved and that neutral diffusio-phoresis alone can not account for. The swimming velocity is

strongly reduced by the presence of salt (and ionic impurities) and the direction of swimming is reversed in correlation with a change or ζ potential of the particle [97, 98]). Similarly the addition of cationic surfactant CTAB allows the direction of self-propulsion to be changed. The strong effects of pH-neutral salts would suggest ionic self-diffusiophoresis as an alternative mechanism of propulsion of the Pt-dielectric Janus particles but would require unrealistic potential for the colloids, $\zeta \sim 30$V, to account for observed velocities[11] [96]. However, a mechanism of self-electrophoresis, akin to the self-propulsion of the nanorods, is compatible with the experimental data. The phenomenon is argued to emerge from different spatial areas involving oxidations and reductions on the cap and akin to the short-circuited battery [96] or the thickness-dependent reaction rate of the decomposition, larger at the pole than at the equator, leading to a flux of protons [99]. Further work is required to better understand this seemingly simple system, since even the direction of propulsion was reported to depend on the thickness of the platinum cap [96]!

Light-activated Diffusiophoretic Swimmers

Light-activated swimmers provide a convenient class of systems, where the propulsion is switched on and off externally. Light can be modulated spatially and temporally or with different wavelengths [100], offering routes towards complexity without experimental *complications*, and providing a fast switch to return to equilibrium, thanks to the fast diffusion of molecular species ($<$ 1ms for 1μm).

Catalytic swimmers, where the platinum is replaced by a photocatalytic material activated by light, were subsequently proposed. Hematite, (Fe_2O_3) [101], partially embedded in a dielectric material and immersed in hydrogen peroxide (pH=6.5) self-propels in 3D under blue illumination. So does titania (TiO_2, anatase phase), under illumination by UVA (390nm) [100]. We infer that semi-

[11] Indeed, diffusiophoretic velocities measured in microfluidics experiments were also significantly lower $V \sim 1 - 2\mu$m/s [72, 73, 74]

conductors, illuminated above their bandgap, generate electron-holes pairs, and act as photocatalyst for the decomposition of H_2O_2. Alternatively, Janus titania particles exposed to UV, use water splitting to propel in an bio-compatible fuel [37].

An elegant example of light-activated propelled particles is provided by Janus silica-gold particles immersed in a critical binary mixture of water and -2,6-lutidine. Under illumination, the gold cap heats up above the critical temperature and induces the demixing of the binary mixture. The particle subsequently propels in the established gradient and exhibits a persistent random walk with the velocity set by the local light intensity [54]. Interestingly, the direction of propulsion is reversed by hydrophobically-functionalizing the gold cap, stressing the role of controlled patches to harness propulsion.

4.2.2. Thermophoretic Swimmers

Thermophoretic swimmers generate a thermal gradient resulting in thermophoretic propulsion [102]. For example, the gold cap of Janus gold-dielectric spheres heats up under under irradiation (40mW, 1064nm), setting a temperature gradient of $\sim$ 2K, leading to velocities of 10μm/s [103]. Similarly, thermophoretic propulsion was reported for silica particles partially covered with a magnetic material and exposed to an AC field. The hysteretic response of the magnetic material heats up of the cap, leading to self-propulsion in water [104].

5. Other types of Swimmers

Patchy swimmers

Silica spheres coated with metals and covered with a thin SiO_2 protective layer (so that their surface properties are uniform) are immersed in deionized water and sedimented near a bottom substrate. Subject to an A.C. electric field perpendicular to the bottom substrate, the particles self-propel, isotropically, along the plane. The propulsion is due to the different polarizability of the two hemispheres exhibiting an asymmetric Induced Charge ElectroPhoresis (ICEP)

leading to the propulsion of the particle with the dielectric heading [105, 106]. The propulsion of metallodielectric particles by ICEP was previously reported in [107] but the nifty use of an electric field perpendicular to the substrate plane made possible to obtain Janus swimmers with isotropic propulsion, though intrinsically planar. The system exhibits different collective behaviors tuning the interaction between particles thanks to the control of the amplitude and frequency of the A.C. electric field [108].

Catalytic locomotion of Au/Ru core-shell nanowires was recently reported in the presence of hydrogen peroxide. Unlike conventional bimetallic nanowires, experimental observations pointed toward a propulsion from combined self-diffusiophoresis and electroomosis in the oxygen gradient [109].

Isotropic Swimmers

In this section, we briefly review examples of isotropic particles, which nonetheless propel. The propulsion, a priori counter-intuitive, relies on a spontaneous symmetry-breaking mechanism.

The first example is provided by insulating spheres immersed in a conducting fluid. When an electric field $\mathbf{E}$ is applied above a critical amplitude, the particles start rotating at constant speed around a random direction transverse to $\mathbf{E}$, this is the Quincke effect [110, 111]. Sitting near the bottom substrate, the particles start rolling at velocity $\sim$ mm/s [6].

Spontaneous autophoretic motion of isotropic particles has also been proposed theoretically. In a nutshell, a stagnant particle consuming fuel generates an isotropic concentration cloud. A random fluctuation moves the particle to one side, steepening the gradient on this side, possibly providing a route for spontaneous symmetry breaking. It was shown that this nonlinear interplay between surface osmotic flows (velocity U) and solute advection (diffusion D) can produce spontaneous and self-sustained motion of isotropic particles of radii R. It needs to distort the chemical cloud to amplify the fluctuation, *i.e.* $Pe = \frac{UR}{D} > 3$ [112]. This condition is difficult to realize experimentally with colloidal particles $Pe \sim \frac{30\mu\text{m/s}\times 3\mu\text{m}}{10^3\mu\text{m}^2/\text{s}} \sim 0.1$ but can be achieved with larger droplets [113] and sug-

gests an interesting pathway to motility. The vicinity of an impermeable wall can, alternatively, break the symmetry and induce propulsion of active isotropic colloids [114] or guide self-propelled Janus particles [115, 95].

6. Remarks and Perspectives

Around diffusiophoresis, perspective and open questions

This section stresses important features and questions raised by diffusiophoretic mechanisms, with possible impact and ramifications in natural and artificial situations. Interesting phenomena emerge when the interaction length of diffusiophoresis (or Debye length if the interaction is electrostatic), compares with the typical size of the system: the conductivity in a pore is larger than bulk conductivity when the Debye length becomes larger than the pore radius [116]. Similarly, the diffusiophoretic mobility becomes size dependence when the radius of a colloid compares with the interaction range [117].

Harnessing the subtlety of diffusiophoresis allows to sort particles by size in dead-end channels using solute gradients or super-imposition of salt gradients, at fixed total ionic strength [117, 118] or design long-range, surface-specific interactions in suspensions [119] or exclusion zone near certain walls [120].

The diffusiophoretic velocity is proportional to the gradient of the logarithm of ions, $\mathbf{V}_{DP} = D_{DP}\nabla \log c_0$. This can lead to the focusing of colloidal suspensions colloids [117, 72, 121] and raises the question of the sensitivity of diffusiophoretic migration for vanishingly small ionic concentrations, in particular in the ultra dilute-limit, where the inter-ions distance compares with the colloid radius.

The potential relevance of diffusiophoresis (and phoretic transport) within the context of complex fluids is an open question: it has been predicted that diffusiophoresis of a rigid sphere in a Carreau fluid differs significantly from the Newtonian case [122] and reported that colloidal particles oscillate at the constriction of a microchannel under electrophoresis in a viscoelastic fluid [123].

Finally, diffusiophoresis could play a role during oil extraction as salty water is often injected into reservoir to increase oil recovery [124]. The possibility to replace salty water in this process by dissolved and dissociating gas, such as carbon dioxide, has not been explored. Diffusiophoresis offers numerous opportunities *owing to* its subtlety and provides uncharted (non-equilibrium) territories to explore, from oil-extraction to the origin of life [125].

Comments on Active Patchy Swimmers

In this last section, we discuss the challenges and opportunities offered by phoretic patchy particles. First, it can be difficult to properly describe the propulsion mechanism of the active particles. They often sit near a surface, a possible source of osmotic flow, which can contribute to the propulsion. Similarly, tracer particles are often phoretically active, which needs to be accounted to extract the hydrodynamic flow field [126]. Phenomena altering the surface of the particles can affect phoresis: surfactants, adsorbing polymers, and surface chemistry in general. Experiments need to be performed with cleaned solutions and chambers and in buffer solutions in order to control the surface chemistry. Roughness (comparable to the interaction length) or hydrodynamic slip can also have important and non trivial effects on the phoretic effect [127, 128, 71]. In spite of the conceptual simplicity, interfacial phenomena often intertwine different phenomena, e.g. (thermophoresis + diffusiophoresis), or superimpose in a non-linear fashion, as recently pointed out [118]. Hydrogen peroxide as a fuel is a practical concern for biological applications[12], which motivated the development of self-propelled particles in bio-compatible fuels and ultrasounds or bubble propelled swimmers [25, 26]. The dependability of phoretic swimmers on low ionic strength is an intrinsic weakness of the mechanims and limits their relevance in the bio-engineering context.

This complexity, on the other hand, offers opportunities for a high level of

[12]FDA recommends its use for sterilization at concentration $> 2\%$

control and novel functionalities. The importance of surface chemistry allows to *tailor* the phoretic response of colloids thanks to chemically controlled patches [129, 130, 131]. Particles with non-uniform surface properties or shapes [132, 133, 134] can be used to design spinners or reconfigurable structures. Semi-dilute suspensions could potentially be used as active depletants to direct self-assembly. This would however require non-interacting particles, in contradiction with the long-range disturbance of the concentration field surrounding phoretic swimmers and predicted to induce dynamic clusters [135] and wave patterns [136]. Additionally, unless nanometric swimmers are used, the small number of active particles is likely to lead to intermittent attraction, as previously observed in bacterial suspensions [137], and qualitatively different from an equilibrium counterpart of depletion with "hot depletants". The opportunities offered are broad and largely untapped, providing a formidable playground where colloidal scientists, engineers and physicists can meet.

7. Conclusion

In this paper, we showed how phoretic transport is harnessed to design active patchy particles. The sensitivity of interfacial transport to surface properties (ζ potential, roughness, pH...) poses experimental challenges but also opens up opportunities for the colloidal scientist, which successfully control them. Numerous strategies have already been proposed to design propelled particles in a variety of fuel, or actuation mechanism. Activity beyond translational propulsion using patches has been, in large, unexplored. Their use to direct colloidal self-assembly, such as machines to weave and bread on the microscale as recently proposed by Goodrich & Brenner [138], is an uncharted territory.

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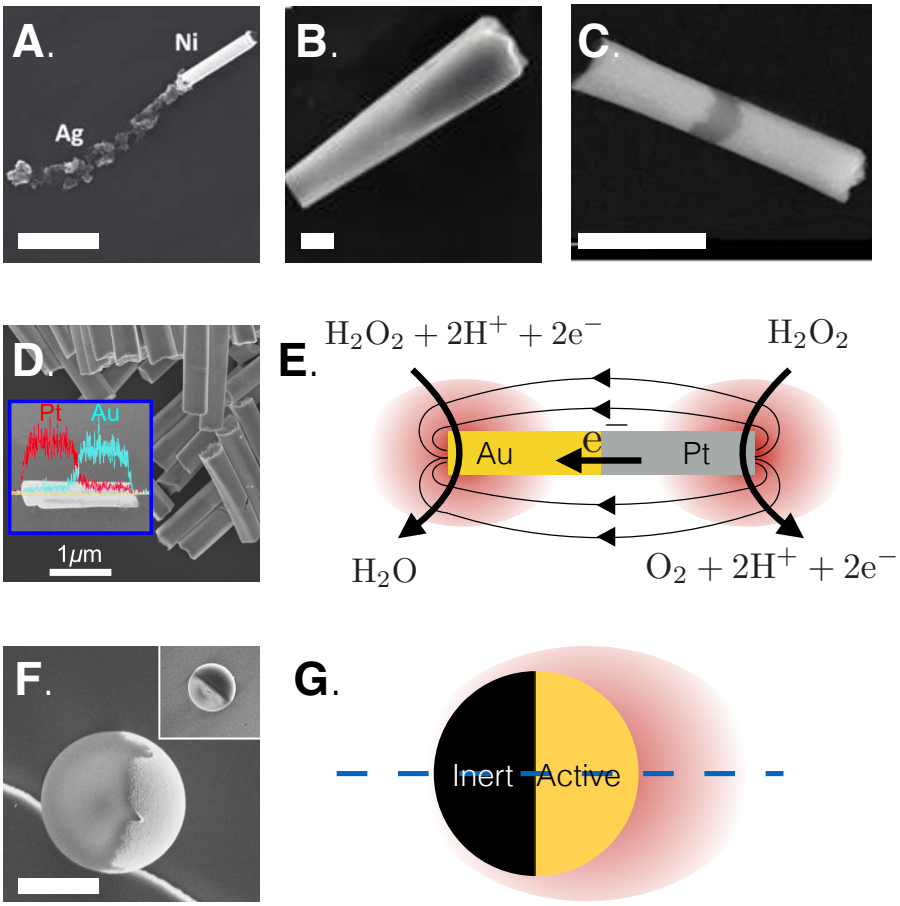

Figure 1: Overview of colloidal swimmers. (A) Self-propelled nanowire actuated by a magnetic field (reprint from [31]). (B) Bubble propelled microtube (reprint from [139]). (C) Ultrasonically propelled metal microrods micromotors (reprint from [140]). (D) Self-propelled Pt/Au nanorods (reprint from [79]). (E) Mechanism of propulsion of Pt/Au nanorods in hydrogen peroxide. The scheme shows the electrochemical reactions, the approximate charge density (red cloud) and electric fields line. The rod self-propels to the right on the scheme (reprint from [80]). (F) Scanning electron Microscopy image of a Platinum-dielectric Janus swimmer. Top corner, optical microscopy image, the light part is the Pt cap (reprint from [95]) . (G) Janus particle, one side is active, the other is inert. The particle sets up a gradient (red cloud) leading to phoretic propulsion along the poles (blue line). The direction of the propulsion depends on the details of the microscopic mechanism. Scale bars are 1μm.

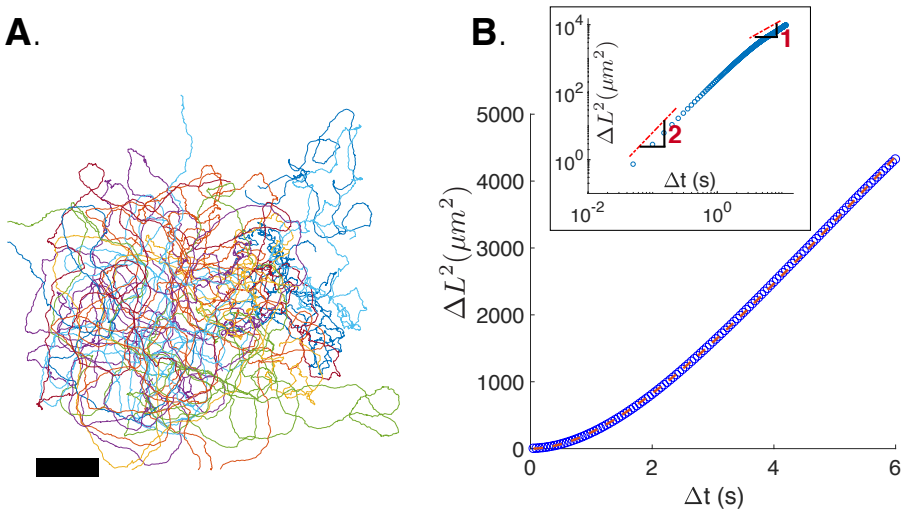

Figure 2: Individual dynamics of a swimmer. (A) Trajectories of photoactivated swimmers. The particle exhibits a persistent random walk. Scale bar is 20μm. (B) Mean Square displacement ΔL^2 obtained from the ensemble average of 24 individual trajectories (blue symbols) fit by [Eq.1] (red dashed line), giving $V_p = 17\mu$m/s and $\tau_p = 3.5$s. The equilibrium diffusion coefficient $D_0 = 0.030\mu\text{m}^2/\text{s}$ is measured independently, and averaged over 249 particles. (B-inset). Log-log plot of the MSD $\Delta L(\Delta t)$ showing the ballistic regime (slope 2) at short times, and diffusive regime (slope 1) for $t \gg \tau_r$.

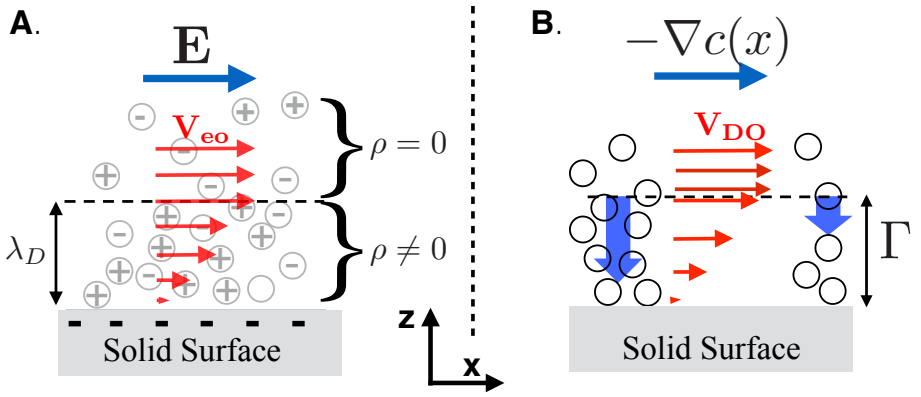

Figure 3: Interfacial Transport (A) Electro-osmosis. A solid surface immersed in an aqueous electrolyte is negatively charged.Cations are attracted to the surface, anions are repelled. They form a screening double layer of thickness λ_D (see main text). An electric field $\mathbf{E}$ exerts a force on the non neutral double layer and sets the layer in motion. The outside layer is neutral and experiences no net force. The driving force is balanced by viscous dissipation leading to a constant flow velocity $\mathbf{V}_{eo}$ outside the Debye layer. (B) Diffusio-osmosis, flow under a concentration gradient $\nabla c(x)$. The solute is attracted to the substrate, the concentration gradient $\nabla c(x)$ induces an unbalanced osmotic pressure (blue arrows) within the interaction layer Γ (notations defined in the main text), which drives the fluid in motion. This driving force is balanced by viscous dissipation and leads to a constant flow velocity $\mathbf{V}_{DO}$.

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