Chaotic dynamics of an autophoretic particle

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Abstract

Chemically active, or autophoretic, particles that isotropically emit or absorb solute molecules are known to undergo spontaneous self-propulsion when their activity is increased beyond a critical Péclet number \((Pe)\). Here, we conduct numerical simulations of a spherical rigid autophoretic particle in unsteady rectilinear translation, which reveal that its motion progresses through four regimes, as \(Pe\) is increased: quiescent, steady, stirring, and chaos. The particle is stationary in the quiescent regime, and the solute profile is isotropic about the particle. At \(Pe = 4\) the fore-aft symmetry in the solute profile is broken, resulting in its steady self-propulsion, as has been shown in previous studies. A further increase in \(Pe\) gives rise to the stirring regime at \(Pe \approx 27\), where the fluid undergoes recirculation, as the particle remains essentially stationary in a state of dynamic arrest. As the Péclet number is increased further, the dynamics of the particle is marked by chaotic oscillations at \(Pe \approx 55\) and higher, where its velocity undergoes rapid reorientations. The mean square displacement of particles in the chaotic regime exhibits a subdiffusive behavior with an apparently universal scaling exponent at long times for all values of \(Pe\) studied. However, the time-scale for the decorrelation of the swimming velocity decreases with an increase in \(Pe\), and this time-scale also governs the transition in the mean square displacement from early-time ballistic to long-time subdiffusive motion.

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1. INTRODUCTION

Autophoretic colloids that isotropically emit or absorb solute molecules at their interface are prototypical examples of synthetic active matter. At low levels of chemical activity (quantified by a suitably small intrinsic Péclet number, $Pe$), diffusion is dominant enough to homogenize any perturbations to the solute distribution around such a particle, thereby rendering the concentration profile isotropic, and the particle stationary. Beyond a threshold Péclet number, however, small perturbations to the concentration field result in the breaking of the fore-aft symmetry of the concentration profile, and the particle may undergo self-propulsion along a rectilinear path, or, at sufficiently large $Pe$, execute meandering, helical or chaotic motion. The spontaneous self-propulsion of autophoretic particles and droplets has been predicted theoretically [1, 2], as well as being observed in experiments [3–6] and numerical simulations [1, 7]. While the steady self-propulsion of autophoretic particles is well-characterised, dynamics of autophoresis in the chaotic regime, and the transition from steady to chaotic self-propulsion, is relatively less so.

Michelin, Lauga, and Bartolo [1] established from numerical computations of rigid spherical autophoretic particles that a transition from quiescence to steady self-propulsion occurs at $Pe = 4$. They observed a maximum in the swimming speed at $Pe \approx 9$, after which the speed decreases up to $Pe = 20$, which was the largest value of $Pe$ they studied. Morozov and Michelin [7] performed simulations on autophoretic particles with a tuneable parameter $m$ that dictates the relative importance of diffusiophoretic effects to Marangoni flow, with $m = 0$ corresponding to an active droplet that moves solely under the effect of Marangoni stresses, and $m \to \infty$ corresponding to a rigid particle moving solely due to diffusioosmotic slip. A larger range of Péclet numbers is explored in their work, and the transition of a particle (with $m = 2$) from its quiescent state to rectilinear self-propulsion, and ultimately chaotic motion is predicted as $Pe$ is increased. Their calculations assume that the solute concentration and flow field around the particle remain axially symmetric about its initial direction of translation; hence, the particle undergoes unsteady, rectilinear translation. Interestingly, Morozov and Michelin [7] observe a ballistic mean square displacement (MSD) scaling in the chaotic regime: that is, they do not observe a transition to non-ballistic motion associated with the chaotic dynamics. They do, however, comment that much longer computations than they conducted might be needed to fully characterize the chaotic regime. They also note that their computational approach, which employs a truncated spectral expansion of the concentration field, converges slowly with the number of Legendre modes for large $Pe$, rendering computations expensive in this region of parameter space. Computations of autophoretic circular disks by Hu et al. [2], in which the particle is allowed to move in two dimensions, show that: (a) the transition to chaos occurs via an intermittency scenario [8]; and (b) the chaotic regime is characterized by a change in the scaling of the mean MSD of the particle as a function the lag time $\tau$, from a short-time ballistic profile ($\sim \tau^2$), to normal diffusion ($\sim \tau$) at longer times. Experiments on autophoretic droplets confined between walls in a Hele-Shaw type configuration [5] show that an increase in the Péclet number results in a transition from ballistic motion to a two-dimensional self-avoiding walk ($\sim \tau^{3/2}$) at long times, as the droplets tend to avoid the chemical trail that they emit. More broadly, it is known that chaotic maps can lead to either normal [9] or anomalous diffusion [10, 11]. Delay-differential equations, used to model phenomena such as blood cell production and the transmission of light from optical ring cavities, have also been shown to exhibit chaotic diffusion [12, 13]. Given the differing theoretical and experimental results mentioned above,
it is not evident what the MSD scaling of autophoretic particles in the chaotic regime is.

In this paper, using a spectral element based algorithm to simultaneously solve the unsteady advection-diffusion equation governing the concentration profile of the solute, and the quasi-steady Stokes equations governing the velocity field, we aim to chart the transition of a rigid autophoretic particle from steady self-propulsion to chaotic motion. Our computations are performed on an axisymmetric model, so the motion is restricted to unsteady rectilinear translation. A primary question we will address is the nature of the chaotic motion, i.e., does the active particle execute ballistic motion as predicted by Morozov and Michelin [7], normal diffusion as seen in Hu et al. [2], or super-diffusion as observed by Hokmabad et al. [5]? In fact, our computations indicate that none of these outcomes are attained. Instead, we find that the chaotic dynamics are characterised by long-time subdiffusion, where the MSD scales sublinearly with $\tau$. Notably, the scaling exponent is nearly identical for all values of $Pe$ studied.

In §2, we specify the governing equations for a neutrally buoyant, rigid, spherical autophoretic particle. The numerical details for the solution of the coupled system of nonlinear partial differential equations governing the transient evolution of the concentration field and the quasi-steady velocity field about the rigid particle are provided in §3 along with the details of the MSD and the velocity autocorrelation (VAC) calculations. We present and discuss the results in §4 followed by concluding remarks in §5.

2. PROBLEM FORMULATION

We consider a rigid, spherical autophoretic particle of radius $a^*$, freely suspended in an incompressible Newtonian fluid of viscosity $\eta^*$, whose flow obeys the Stokes equations. Above and henceforth, dimensional variables are marked with an asterisk as superscript. There is a constant flux $\mathcal{A}^*$ of solute at the particle surface, which is positive (negative) when the solute is being emitted (absorbed) at the interface. Far away from the particle, the uniform solute concentration is $C^*_\infty$, and the difference between the local concentration and its far-field value is denoted by $c^* = C^* - C^*_\infty$. The solute molecules, of diffusivity $D^*$, interact with the active particle via a short-ranged potential whose characteristic length is $b^*$, such that $b^* \ll a^*$. These interactions give rise to a tangential slip velocity along the particle surface [14], whose magnitude is set by the concentration gradient of the solute at the interface, and the mobility parameter, $\mathcal{M}^* = \pm k_B^* T^* b^*/\eta^*$, where $k_B^*$ is Boltzmann’s constant and $T^*$ is the absolute temperature. Attractive (repulsive) interactions between the solute and the active particle are described by a negative (positive) $\mathcal{M}^*$ [15]. The concentration profile of the solute, therefore, evolves due to diffusion and advection by fluid flow.

Following Michelin, Lauga, and Bartolo [1], length, time, fluid velocity, pressure, and concentration are scaled by $a^*, a^* D^*/|\mathcal{A}^* \mathcal{M}^*|, |\mathcal{A}^* \mathcal{M}^*|/D^*, \eta^* |\mathcal{A}^* \mathcal{M}^*|/a^* D^*$, and $a^* |\mathcal{A}^*|/D^*$, respectively. In the subsequent discussion, variables without asterisks are the dimensionless equivalent of their dimensional counterparts. A key dimensionless parameter is the intrinsic Péctlet number,

$$Pe = \frac{a^* |\mathcal{A}^* \mathcal{M}^*|}{D^2},$$

which quantifies the relative importance of the solute advection with respect to its diffusion, and is a measure of the chemical activity of the particle. It is convenient to introduce the
scaled flux and mobility parameters,

\[ A = \frac{A^*}{|A^*|}, \quad M = \frac{M^*}{|M^*|}. \]  

(2)

The concentration field is governed by the unsteady advection-diffusion equation,

\[ Pe \left( \frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c \right) = \nabla^2 c, \]  

(3)

where \( t \) is time and \( \mathbf{v} \) denotes the velocity field. Eq. 3 is subject to the two boundary conditions of: (i) constant flux of the solute at the surface of the active particle

\[ \frac{\partial c}{\partial r} = -A \quad \text{at} \quad r = 1, \]  

(4)

and (ii) an attenuation condition far away from the sphere

\[ c \to 0 \quad \text{as} \quad r \to \infty. \]  

(5)

We employ a cylindrical coordinate system \((z, \rho, \phi)\) with its origin attached to the particle centre. The \( z \)-axis represents the axis of symmetry along which the particle motion is constrained. The perpendicular distance from the \( z \)-axis is measured by the \( \rho \)-coordinate, and \( \phi \) denotes the azimuthal angle of rotation about the \( z \)-axis. This frame of reference is non-inertial since the particle is accelerating during its unsteady translation. However, this choice does not affect the advection-diffusion equation or the Stokes equations, since the motion occurs at zero Reynolds number. The particle surface is denoted by \( r = 1 \) where \( r = \sqrt{\rho^2 + z^2} \). The axisymmetric flow around the particle is represented as

\[ \mathbf{v} = v_z(\rho, z) \mathbf{e}_z + v_\rho(\rho, z) \mathbf{e}_\rho, \]  

(6)

where \( \mathbf{e}_z \) and \( \mathbf{e}_\rho \) are unit vectors along the \( z \) and \( \rho \) axis, respectively. It is useful to define the polar angle \( \theta \equiv \arctan(\rho/z) \) measured anticlockwise such that \( \theta = 0 \) lies on the positive \( z \)-axis.

The velocity field, \( \mathbf{v} \), in (3) is governed by the incompressibility criterion and the Stokes equation,

\[ \nabla \cdot \mathbf{v} = 0, \quad \nabla^2 \mathbf{v} = \nabla p, \]  

(7)

where \( p \) is the dynamic pressure, and subject to the following boundary conditions

\[ \mathbf{v} \equiv M \nabla_s c = v_s (\cos \theta \mathbf{e}_\rho - \sin \theta \mathbf{e}_z) \quad \text{at} \quad r = 1, \]  

(8)

where

\[ v_s = M \left( \cos \theta \frac{\partial c}{\partial \rho} - \sin \theta \frac{\partial c}{\partial z} \right), \]  

(9)

and

\[ \mathbf{v} \to -U \mathbf{e}_z \quad \text{as} \quad r \to \infty. \]  

(10)

The far-field speed \( U \) in eq. (10) is unknown \emph{a priori}, and is determined iteratively by requiring that the total hydrodynamic force on the particle in the \( z \)-direction is zero at all
times. The presumed axisymmetry of the problem permits us to rewrite the velocity field in terms of the Stokes streamfunction $\psi$,

$$\mathbf{v} = \frac{1}{\rho} \left( e_z \frac{\partial \psi}{\partial \rho} - e_\rho \frac{\partial \psi}{\partial z} \right).$$

(11)

Taking the curl of the Stokes equations and introducing the vorticity vector $\mathbf{\omega} = \nabla \times \mathbf{v}$ eliminates the pressure from the governing equations, resulting in the following system of coupled partial differential equations,

$$\omega \rho + E^2 \psi = 0,$$

(12)

$$\nabla^2 \omega - \frac{\omega}{\rho^2} = 0,$$

(13)

where $\omega$ is the $\phi$-component of the vorticity $\mathbf{\omega}$ about the $z$-axis, with the other components ($\rho$ and $z$) of the vorticity vector vanishing due to symmetry, and the operators

$$\nabla^2 = \frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial}{\partial \rho} \right) + \frac{\partial^2}{\partial z^2},

E^2 = \nabla^2 - \frac{2}{\rho} \frac{\partial}{\partial \rho}.$$

(14)

Equations (12) and (13) must be solved subject to the following boundary conditions

$$\mathbf{n} \cdot \nabla \psi = -\rho v_s \quad \text{at} \quad r = 1,$$

(15)

$$\mathbf{n} \cdot \nabla \psi \to -\rho U \sin \theta \quad \text{as} \quad r \to \infty,$$

(16)

$$\mathbf{n} \cdot \nabla \omega \to 0 \quad \text{as} \quad r \to \infty,$$

(17)

$$\psi = 0 \quad \text{at} \quad r = 1,$$

(18)

with $\mathbf{n} = \cos \theta e_z + \sin \theta e_\rho$ being the unit normal to the particle surface pointing into the fluid; and the symmetry condition

$$\psi = \omega = 0 \quad \text{along} \quad \rho = 0.$$

(19)

There exists a trivial solution to the system of equations given by eqs. (3), (12), (13), which is the isotropic concentration profile $c = 1/r$, corresponding to the quiescent state of zero phoretic velocity and no fluid motion at all times. Beyond $Pe = 4$, however, the quiescent state becomes unstable with respect to dipolar perturbations in the concentration field [1, 7], and the autophoretic particle sets into motion. Further types of perturbation (such as quadrupolar) are unstable at larger values of the Péclet number as the higher hydrodynamic modes are excited. We therefore supply an asymmetrical concentration field as the initial condition to eq. (3), as follows

$$c(r, t = 0) = \frac{1}{r} - \delta_{\text{per}} \left( \frac{\cos \theta}{r^2} \right),$$

(20)

with $|\delta_{\text{per}}| < 1$.  

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3. NUMERICAL SOLUTION METHODOLOGY

As the first step in the numerical solution process, the initial condition given in (20) is used to specify the slip boundary condition (8) for the flow problem. The self-propulsion speed \( U(t) \) at any instant of time \( t \) must satisfy the requirement that total hydrodynamic drag force on the particle in the \( z \)-direction, \( F_z \), given by

\[
F_z \equiv \pi \int_0^\pi \left[ \frac{\partial (\omega r)}{\partial r} - 2\omega \right] r \sin^2 \theta d\theta \quad (21)
\]

vanishes at \( t \). The self-propulsion speed is evaluated iteratively using a secant method, as described in Chisholm et al. [17]. Given two initial guesses \( U^{(j)} \) and \( U^{(j-1)} \) at time \( t \), where \( j \) denotes the iteration number, the hydrodynamic drag at the two values of the self-propulsion speed are evaluated. Using linear interpolation, an improved estimate for \( U \) is obtained as:

\[
U^{(j+1)} = \frac{U^{(j)} F_z^{(j-1)} - U^{(j-1)} F_z^{(j)}}{F_z^{(j-1)} - F_z^{(j)}}.
\]

The procedure is terminated when the magnitude of the difference in the computed speeds between successive iterations \( |U^{(j)} - U^{(j-1)}| \) is reduced below \( 10^{-5} \). The converged solution for the flowfield \( (\psi, \omega) \) at each time instant is then used to solve the advection-diffusion equation for the concentration field.

Numerical computations require the stipulation of a finite outer boundary, and a value of \( R_o = 100 \) is chosen as the radius of the spherical shell on which the far-field boundary conditions are specified. The computational domain is discretized into quadrilateral spectral elements of order \( N_o = 8 \) using the GMSH software package [18], and the system of equations given by (3), (12), and (13) is solved using a custom code based on the spectral element method [19]. A detailed account of the solution methodology and its validation is provided in Chisholm et al. [17] and Khair and Chisholm [20]. We only briefly recap the salient features here.

The shape functions are defined as tensor products of 1D Lagrange polynomials of order \( N_o \), supported at \( N_o + 1 \) Gauss-Lobatto quadrature points over the standard region \([-1, 1]^2\). The time-derivative in eq. (3) is discretized using the backward Euler algorithm, as follows

\[
\frac{\partial c}{\partial t} \approx \frac{c^{(i+1)} - c^{(i)}}{\Delta t}, \quad (22)
\]

where \( c^{(i)} \) denotes the value of the concentration at the discrete time \( t^{(i)} \), and \( \Delta t \equiv t^{(i+1)} - t^{(i)} \) is the width of the discrete timestep. The concentration variable is taken to be the arithmetic mean of its values at the current and previous timestep, that is,

\[
c \equiv \frac{c^{(i+1)} + c^{(i)}}{2}. \quad (23)
\]

Equations (22) and (23) together represent the implicit Crank-Nicolson scheme [21] that is second-order accurate in the timestep width, \( \Delta t \), and also unconditionally stable [22]. A value of \( \Delta t = 1.0 \) is used for simulations with \( Pe < 20 \), while a timestep width of 0.1 is used at higher values of the Péclet number.

The spatial integral over each element is computed using the Gauss-Lobatto quadrature rule, resulting in a system of algebraic equations which is solved iteratively using a Newton-Raphson scheme. The discretised version of eq. (3), being linear (when the velocity field

\[
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\]
is prescribed), converges in one step, while the iterative procedure for the solution of the nonlinear system [eqs. (12) and (13)] is terminated when the $L^2$-norm of the difference between the solutions in successive steps, computed over all discretisation points, drops below $10^{-6}$.

Previous investigations [1, 2] on autophoresis have established that for particles with oppositely signed $A$ and $M$, perturbations to the concentration field vanish in the long-time limit, where the particle remains stationary. We therefore concern ourselves with the nontrivial case of similarly signed $A$ and $M$ values, which result in the self-propulsion of the active particle, and we pick $A = M = 1$ without loss of generality.

At $Pe \leq 10$ the solver is supplied an initial condition of the form given by eq. (20), with the choice of $\delta_{\text{per}} = 0$. It is observed that different values of $\delta_{\text{per}}$ in this regime result in the same long-time prediction for the steady phoretic velocity. At $Pe > 10$ the concentration profile computed at a previous (lower) value of the Péclet number is used as the initial condition for the subsequent simulation at the next higher $Pe$.

The axisymmetry of the flow field restricts motion of the particle along the $z$ axis. From the computed time-series of the swimming speed, the particle position at a discrete time $i + 1$ is evaluated as

$$z(i + 1) = z(i) + U(i) \Delta t; \ z(0) = 0.$$  \hfill (24)

In the time interval $[0, t_{\text{sim}}]$, a total of $N \equiv t_{\text{sim}}/\Delta t$ data points are recorded. The MSD and VAC, $C_v$, at the $n^{\text{th}}$ time interval are evaluated as follows

$$\text{MSD}(n) = \frac{1}{N - n} \sum_{i=0}^{N-n} [z(i + n) - z(i)]^2,$$  \hfill (25)

$$C_v(n) = \frac{1}{N - n} \sum_{i=0}^{N-n} [\mathbf{e}_u(i + n) \cdot \mathbf{e}_u(i)].$$  \hfill (26)

where $\mathbf{e}_u(i) \equiv U(i)/|U(i)|$ is the unit direction vector of the self-propulsion speed at discrete time $i$, and can take the value of +1 or −1. Equations (25) and (26) represent calculations of the time average over a single trajectory. The lag-time is defined as $\tau \equiv n \Delta t$ and used in reporting the MSD and VAC results. For $Pe \geq 50$, the total simulation time is at least $t_{\text{sim}} = 5 \times 10^4$, while that for $Pe = 75$ and $Pe = 80$ are $t_{\text{sim}} = 1 \times 10^4$ and $t_{\text{sim}} = 2 \times 10^4$, respectively. Data points corresponding to at least the first $1 \times 10^4$ timesteps in these runs are discarded prior to the calculation of the MSD and VAC, to remove the effects of transients.

4. RESULTS AND DISCUSSION

We analyze the dynamics of the autophoretic particle as a function of the Péclet number. Michelin, Lauga, and Bartolo [1] have shown that the particle remains stationary until $Pe = 4$. This range, $0 \leq Pe \leq 4$, may be termed as the quiescent regime. As the Péclet number is increased beyond 4, the fore-aft symmetry in the concentration profile is broken, and the particle executes steady rectilinear self-propulsion. In fig. [1] the steady self-propulsion speed $U$ from our computations is plotted as a function of $Pe$, and it is seen that $U$ attains a maximum at $Pe \approx 9$, and decreases smoothly up to a value of $Pe \approx 26$. This range, $4 < Pe \leq 26$, is classified as the steady self-propulsion regime. Furthermore, the good agreement of our results with data from Michelin, Lauga, and Bartolo [1] establishes the
FIG. 1. (Colour online) Steady self-propulsion speed of an autophoretic particle at various Péclet numbers across the quiescent, steady, and stirring regimes. The unfilled diamonds (○) represent results obtained by Michelin, Lauga, and Bartolo [1], and the unfilled circles are from the present work.

FIG. 2. (Colour online) Steady-state concentration profile and streamlines of the flow around the autophoretic particle at $Pe = 20$ [(a),(b)] and (b) $Pe = 30$ [(c),(d)]. The flow and concentration fields are symmetric about the horizontal axis; therefore only half the particle is shown. The colour bar indicates the value of the solute concentration $c$.

validity of the numerical procedure used in the present work.

At $Pe \approx 27$, however, there is another qualitative change in the motion of the active particle, as it experiences a drop of almost three orders of magnitude in its self-propulsion speed, becoming practically stationary and entering what we refer to as a stirring regime. The seemingly abrupt transition in particle motion may be understood by considering the relative growth rates of the various angular modes near the Péclet number at which the transition is observed. In fig. 1 of Michelin, Lauga, and Bartolo [1], analytical solutions to
FIG. 3. (Colour online) Time evolution of the self-propulsion speed at (a) $Pe = 10$, (b) $Pe = 40$, (c) $Pe = 52$, (d) $Pe = 53$, (e) $Pe = 55$, (f) $Pe = 60$.

the growth rates of the various unstable modes are plotted as a function of the Péclet number. Near $Pe \approx 30$, the growth rates of the higher order modes are seen to outweigh the dipolar self-propulsion mode, and this could be a reason for the qualitative change in the dynamics of the particle from the swimming to the stirring regime. The transition may also be examined by a comparison of the concentration profile of the solute cloud, and the streamlines of the flow profile, at two different values of $Pe$, as illustrated in fig. 2. The solute distribution around the autophoretic particle is fore-aft asymmetric at $Pe = 20$, but is nearly fore-aft symmetric at $Pe = 30$ with a maximum concentration at the front and rear stagnation points. Furthermore, the streamlines in fig. 2(d) indicate a recirculation of the fluid around the autophoretic particle, where fluid is brought in along the polar axis and expelled at the equator. This flow pattern is consistent with the dominance of a quadrupolar disturbance to concentration profile. This region of parameter space $27 \leq Pe \leq 50$ is therefore analogous to the symmetric extensile pumping regime identified by Morozov and Michelin [7], wherein the activity of the particle results in the stirring of the fluid around it, without resulting in its translation.

In figure 3, the instantaneous self-propulsion speed of the autophoretic particle is plotted
as a function of time for various values of $Pe$. The swimming speed in the steady regime, as seen from fig. 3 (a), settles to a constant value of $O(10^{-1})$ following an initial transient, while that in the stirring regime (shown in fig. 3 (b)) is orders of magnitude lower. Beyond $Pe = 51$, an onset of oscillations in the swimming speed is observed. While these oscillations are transient and vanish at longer times for $Pe = 52$, they become more persistent at $Pe = 53$, as seen from figures 3 (c) and (d), respectively. With a further increase in $Pe$, the particle begins to move back and forth along the $z$-axis, the time scale for the reversal in self-propulsion direction decreases and the magnitude of the instantaneous self-propulsion speed increases, as seen from figures 3 (e) and (f). The region $Pe \geq 55$ may be termed as the chaotic regime, characterized by short bursts of self-propulsion in arbitrary directions (along the $\pm z$-axis) and sharp changes in both the magnitude and direction of the self-propulsion.
The dynamics in the chaotic regime is explored further by considering a representative case of Pe = 75. The time series of instantaneous self-propulsion speed at Pe = 75 is shown in figure 4 (a). Following an initial transient that lasts till t ∼ 3000, the velocity settles into a characteristic pattern, with intermittent bursts of chaos that interrupt nearly regular oscillations of slowly varying amplitude [23]. The instantaneous position of the particle along the z-axis, evaluated using eq. (24), is plotted in fig 4 (b) as a function of time. After a transient period, the particle is seen to oscillate about a mean position of z = −1. The time-averaged concentration profile and streamlines of flow around the autophoretic particle, evaluated in the window t ∈ (3000, 8000), are plotted in figs. 4 (c) and (d), respectively. The concentration map is largely fore-aft symmetric, and this is consistent with the limited (net) mobility of the particle seen in (b). The pattern of the streamlines is qualitatively similar to that observed in the stirring regime (cf. fig. 2 (d)). A similar behaviour is observed at Pe = 80, following an initial transient period that lasts till t ≈ 1500. The intermittent bursts of chaos are more frequent, however, as observed in figure 5 (a). Due to the more frequent injections of this ‘turbulent’ motion, the particle travels a larger distance than at Pe = 75, as seen from figure 5 (b). While the velocity and displacement time series of the autophoretic particle in the chaotic regime vary markedly depending upon the Péclet number, an analysis of the particle’s mean square displacement and velocity autocorrelation reveals certain unifying features, as discussed below.

In figure 6, the MSD of the particle is plotted as a function of the lag time for a range of Péclet numbers. At Pe = 5, corresponding to steady self-propulsion, the MSD grows as ∼ τ^2, since the particle moves rectilinearly at a constant speed. Péclet numbers in the range 27 ≤ Pe < 50 are not examined since the particle is in a state of dynamic arrest, with only the fluid around it undergoing symmetric pumping, or stirring. In the chaotic
FIG. 6. (Colour online) Mean square displacement of an active particle at various Péclet numbers.

FIG. 7. (Colour online) Velocity autocorrelation of an active particle (a) at $Pe = 80$, and (b) over a range of Péclet numbers.

regime, the MSD initially grows ballistically before transitioning to subdiffusive motion ($\sim \tau^{0.8}$). The timescale for the crossover in scaling is pushed to smaller values as $Pe$ is increased. The subdiffusive exponent of 0.8 is observed over a range of Péclet numbers between $55 \leq Pe \leq 80$, and thereby appears to be a universal signature of chaotic dynamics in the axisymmetric motion of autophoretic particles.

Anomalous diffusion (that is, MSD $\sim \tau^\alpha$ with $\alpha \neq 1$) is observed in several contexts, including: the dynamics of colloidal tracers in entangled actin filament networks [24]; the motion of RNA tracers and DNA loci in living cells [25, 26], and that of bacteriophages in...
mucus layers [27]; and the self-diffusion of sticky polymers in associated networks [28]. The two most commonly attributed reasons for this phenomenon are fractional Brownian motion or continuous time random walk [29–31]. While a particle subject to fractional Brownian motion evolves its position in time due to a Gaussian noise with a long-range correlation, that undergoing a continuous time random walk process takes steps of random length, with the waiting time between jumps also sampled from a probability distribution. Neither of these two stochastic models, however, directly describe the subdiffusive motion in our computations of an autophoretic particle, which is deterministic and free from external noise. Geisel and Thomae [10] have shown that discrete maps of the form $x_{t+1} = x_t + h x_t^{\mu}$, where $h > 0$, and $\mu > 1$, result in chaotic dynamics, and can exhibit subdiffusive behavior upon tuning the $\mu$ parameter. This occurrence of subdiffusion in the chaotic dynamics of a deterministic system is in line with our computations.

In fig 7 (a), the velocity autocorrelation for an autophoretic particle with $Pe = 80$ is plotted as a function of time. Rapid changes in the direction of self-propulsion result in a decorrelation of the signal, which crosses zero at $\tau \approx 15$. This is followed by the appearance of negative dips and oscillations in the VAC: these features have also been observed experimentally by Suda et al. [6] and Hokmabad et al. [5], as discussed below in detail. The variation in the VAC with $Pe$ is illustrated in fig 7 (b), where the data for $Pe \geq 55$ have been shown only till the first instance of their crossing zero, for clarity. A decrease in the Péclet number from $Pe = 80$ results in less rapid changes in the particle motion, which is reflected in the longer time required for the velocity to decorrelate. Finally, at $Pe = 5$, the VAC is constant in time, indicating a complete correlation in the velocity, due to the persistent unidirectional translation of the particle. The timescale for the loss in correlation with a variation in $Pe$ corresponds approximately to the time at which a crossover in the MSD scaling in figure 6 is observed. Such a decrease in the correlation time with an increase in $Pe$ has also been reported by Chen et al. [32], who performed 3D simulations of a phoretic particle using the immersed boundary method. That study, however, does not report a zero crossing in the VAC for the range of lag times investigated.

We note a qualitative similarity between the trends in figures 6 and 7 and the experimental findings on active droplets suspended in an aqueous surfactant solution within a Hele-Shaw cell [5]. In their experiments, the droplets undergo self-propulsion due to a Marangoni stress imbalance at the interface, driven by a reaction between the droplet contents and the surfactant, resulting in the generation of oil-filled micelles. The active droplets undergo a transition from ballistic motion to anomalous diffusion with an increase in the Péclet number, which is also accompanied by a faster decay in the velocity autocorrelation. The droplets are found to avoid the chemical trail that they generate, and undergo a two-dimensional self avoiding walk, with $\text{MSD} \sim \tau^{3/2}$. In our model, the particle is restricted to motion along a line, where the only route for trail avoidance is a reversal in the direction of self-propulsion. The long-time MSD, therefore, grows less rapidly than the experimental system where the particle may move in two dimensions to avoid the self-generated chemical gradient.

5. CONCLUSIONS

Using a spectral element method to solve for the velocity and concentration fields around a rigid, spherical autophoretic particle in axisymmetric translation, we have demonstrated that the transition to chaotic dynamics proceeds through quiescent, steady, and stirring
regimes, as the chemical activity \((Pe)\) of the particle is increased. The motion of the particle in the chaotic regime is analyzed using the mean square displacement and the velocity autocorrelation, and the dynamics is observed to be subdiffusive in the long-time limit (that is, \(\text{MSD} \sim \tau^\alpha\), with \(\alpha < 1\)) and not ballistic. Our findings thereby answer a question posed by Morozov and Michelin \[7\] on whether axisymmetric computations of autophoretic particles could give rise to non-ballistic long-time dynamics. In fact, the value of \(\alpha\) is found to be universal in the chaotic regime \((55 \leq Pe \leq 80)\), with higher values of the Péclet number resulting in a faster decay of the velocity autocorrelation.

It would be natural to extend our analysis to particles with a finite value of the \(m\) parameter, that is, where both diffusiophoresis and Marangoni flow contribute to self-propulsion. Here, one could examine if the scaling exponent of the MSD is dependent upon the value of \(m\). This in relation to the findings by Morozov and Michelin \[7\], which suggest that some amount of diffusiophoresis is needed in order to induce the transition to chaos, thereby implying that only steady translation is observed for purely Marangoni propulsion, \(m = 0\).

The simulations in the present work are restricted to the axisymmetric case, where the particle can move along a single dimension. Active droplets swimming in 1D have been studied experimentally \[33\], albeit in the presence of a confining geometry. Picella and Michelin \[34\] have recently investigated the motion of autophoretic particles under confinement in a tube using fully 3D simulations, and observe rectilinear steady self-propulsion up to \(Pe < 15\). Should a transition to chaotic dynamics occur at larger \(Pe\), it may be that the effect of the confinement in rendering the propulsion effectively one-dimensional leads to subdiffusion as predicted here. Experiments of Hokmabad \textit{et al.} \[5\] on active droplets in a Hele-Shaw geometry reveal that the droplets undergo a self avoiding walk (\(\alpha = 1.5\)) at sufficiently large \(Pe\), while simulations of 2D active circular disks by Hu \textit{et al.} \[2\] predict normal diffusion (\(\alpha = 1.0\)). The present results suggest that the values of these scaling exponents could be universal within the regime of chaotic self-propulsion. Of course, it would be interesting to determine the scaling exponent for an autophoretic particle free to move in three dimensions, although such computations would be numerically expensive.

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