Pairing, waltzing and scattering of chemotactic active colloids

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Abstract

We study theoretically an active colloid whose polar axis of self-propulsion rotates to point parallel (antiparallel) to an imposed chemical gradient. We show that the coupling of this ‘chemotactic’ (‘antichemotactic’) response to phoretic translational motion yields remarkable two-particle dynamics reflecting the non-central and non-reciprocal character of the interaction. A pair of mutually chemotactic colloids trap each other in a final state of fixed separation resulting in a self-propelled active dimer. A second type of bound state is observed when the polar axes undergo periodic cycles leading to phase-locked circular motion around a common centre. A pair of swimmers with mismatched phoretic mobilities execute a dance in which they twirl around one another while moving jointly in a wide circle. For sufficiently small initial separation, the speed of self-propulsion controls the transition from bound to scattering states. Mutually anti-chemotactic swimmers always scatter apart. For the special case in which one of the two colloids has uniform surface activity we succeed in exactly classifying the fixed points underlying the bound states, and identify the bifurcations leading to transitions from one type of bound state to another. The varied dynamical behaviours are accessible by tuning the swimmer design and are summarised in state diagrams.

1. Introduction

Gradients in the concentration of a solute along the surface of a particle in a fluid produce pressure differences, and thus a slip flow, parallel to the surface. If not anchored, the particle moves through the fluid in the direction opposite to the slip velocity. This phenomenon, known as diffusiophoresis [1, 2], finds dramatic application in the autonomous motility of active Janus colloids [3–7] which have an intrinsic polar axis determined by their catalyst patch. The localised catalyst generates the required solute gradient by decomposing a chemical species uniformly distributed in the ambient medium, and the resulting slip flow propels the colloid.

Interaction with an imposed non-uniform solute profile rotates the polar axis towards the parallel or antiparallel direction with respect to the gradient, and the colloid can thus move toward or away from regions of high concentrations [8–10]. It is this reorienting response, observed in a variety of phoretic systems [11–13], and not the classical Keller–Segel [14] rectification of run-and-tumble motion, which we will call chemotaxis in this article. In view of the growing appreciation of its relevance to active-colloid dynamics [15–17], here we explore its role in determining two-body interactions.

As active particles function under a sustained energy input within an ambient medium, their effective pair interactions are in general non-reciprocal and can systematically draw both linear and angular momentum from their surroundings. The roles of hydrodynamic flow [18–24], diffused solute [25–29], local phase change [30] and optical shadowing [31, 32] as mediators of these interactions have been studied, as well as guidance by nearby boundaries [33–35]. Unravelling the dependence of phoretic and chemotactic effects on the surface profiles of catalyst concentration and solute-colloid interaction [8, 36–38] and symmetry-based classifications of pair interactions [39] have opened up the possibility of engineering active colloids with desired behaviour.
We also note that time-periodic behaviours arising through the momentum-like role of the polar orientation [19, 42–44] have been observed in thermophoretic colloids in a diverging source of light [45] as well as in paramecium with multiple flagellated protrusions [46].

Our aim in this paper is to construct a directory of possible pair interactions and their relation to particle-scale features, with a focus on the resulting varieties of two-particle dynamics. These interactions are also the building blocks of the rich collective behaviour of catalytic colloids, including pattern formation, motility-induced phase separation, and chemotactic collapse [8–10, 32, 47–55].

Before we summarise our results, we need to introduce some definitions. Our pair of active colloids are spheres (i = 1, 2) of radius σ characterised by a catalytic coating of surface density $A(i)$ and a mobility $M(i)$. The mobility $M(i)$, defined as the proportionality coefficient between the local slip velocity $v_i$ and the local solute gradient $\nabla m$, parallel to the colloid surface, is determined by the interaction potential between the surface of the sphere and the product molecules. $A(i)$ and $M(i)$ are functions of location on the surfaces of the spheres, and can be decomposed in a Legendre polynomial basis (assuming, for simplicity, that they are axisymmetric about a common polar axis):

$$A^{(i)}(\theta_i) = a^{(i)} \sum_{\ell} \alpha^{(i)}_{\ell} P_{\ell}(\theta_i),$$

$$M^{(i)}(\theta_i) = m^{(i)} \sum_{\ell} \mu^{(i)}_{\ell} P_{\ell}(\theta_i),$$

where $a^{(i)}$ represents the overall scale of the production of product molecules per unit area, $m^{(i)}$ sets the scale of the mobility, and $\theta_i$ represent the polar angles on the two spheres. Each assignment $\{\alpha^{(i)}_{\ell}\}$, $\{\mu^{(i)}_{\ell}\}$ defines a distinct swimmer design. For our purposes it suffices to retain the components with $\ell = 0, 1, 2$; see below. We refer to $\mu^{(i)}_{1}$ and $\mu^{(i)}_{2}$ as polar and apolar mobilities. All results are presented using this simple model, whose validity we discuss at the end of the paper.

Here is a summary of our results. We consider two cases—(a) a swimmer interacting with a fixed source of solute, and (b) two swimmers that are both free to move. (i) A colloid which is (positively) chemotactic at every separation from the source, $\mu^{(i)}_{1} < 0$, $\mu^{(i)}_{2} < 0$, aligns with the gradient and is trapped by the source when self-propulsion and phoretic repulsion balance each other. (ii) A colloid that exhibits mixed response to the source, chemotactic at large separations and antichemotactic when within a few particle radii from the source, executes what appears to be periodic motion in closed orbits. (iii) Increasing the speed of the swimmer or increasing the impact parameter drives a transition from bound state to scattering. (iv) An anti-chemotactic colloid is always scattered. In the case of two swimmers we find: (v) Two interacting swimmers can form a stationary or moving dimer stabilised by a balance of self-propulsion and phoretic repulsion, with a fixed distance between them. (vi) Two swimmers, with at least one having a mixed chemotactic response to the other, can form bound states.
where they revolve around a common point on closed phase synchronised orbits while their polar axes are
locked at a finite inclination. (vii) Two anti-chemotactic swimmers always scatter from one another. The steady
states have been summarised in state diagrams (see figure 2) obtained by varying total surface activity \(a\) and
composition of the mobility coat. We also show that the bound states are robust to the presence of thermal or
other fluctuations, suggesting that signatures of these states should be observable in experiments. Finally, we
establish the validity of our approximations and the generality of our results by evaluating how the
fixed points and boundaries between states change when harmonics larger than \(\ell = 2\) are included or the chemical
field is calculated with greater precision. The varied dynamical behaviour is summarised in a schematic in figure 1.

Figure 2. 2D state diagrams categorising steady state dynamics are constructed by varying paired combinations of polar mobility \(\mu_1\) and total surface activity \(a\), keeping other parameters and initial conditions fixed (for details, see appendix B). Panels (a)–(c) on the left show the trapped, orbiting and scattered states observed when a swimmer interacts with a source, for three values of \(h_0 = a^{(1)}/a^{(2)}\). In figures (a) and (c) the source produces an isotropic distribution of product while in figure (b) the source distribution is anisotropic. Increasing \(h_0\), which is equivalent to increasing the speed of self-propulsion, tends to eliminate bound states by causing scattering. This can be seen from comparing figures (a) and (c) which differ in the value of \(h_0\) only. Panels (d)–(f) on the right show bound states for two mobile swimmers showing active dimers, binary-swimmers and scattering.
We emphasise that the results we present here are not anticipated in other work in this rather active area of research. First, the key ingredient in our work is the ‘chemotactic’ response, in the specific sense of reorientation of the polar axis in response to an external chemical gradient. All other work on interactions between phoretic colloids considered colloids whose mobility coefficient is constant on the surface, which rules out reorientation. Bound and scattering states have been observed in other work, but the periodic orbits and oscillating dimers are novel aspects, arising from the competition between two phoretic contributions—\(1/\rho^2\) from the polar and \(1/\rho^3\) from the apolar (uniaxial) contributions to the mobility; see equation (7)—to the angular velocity of one swimmer in the chemical field of another a distance \(r\) away. These compete with self-propulsion and phoretic repulsion in determining the final bound state. See the green regions in the state diagram, figure 2. The non-oscillatory dimers we observe are qualitatively different from those discussed in the literature so far as ours are stabilized by a short-ranged phoretic repulsion. The internal arrangement of the dimer configuration where the swimmers point either away from or towards each other and self-propel due to a net centre of mass velocity is a consequence of the angular motion and is therefore new. The dimers are produced only when the swimmers are positively chemotactic, as seen in the state space marked by magenta in figure 2. Other new features that emerge due to chemotactic alignment are the repulsive and attractive scattering trajectories (marked in white and blue in figure 2) that are determined solely by the sign of the angular velocity, the study of the role played by persistent self-propelled motion in destroying the bound states, and the transient revolutions before scattering that are reminiscent of a scattering resonance.

The article is organised as follows: in section 2 we present the equations of motion for the swimmers for a given separation and relative orientation and outline steps followed to obtain the dynamics. In section 3 we discuss the bound states obtained when one swimmer interacts with a source of solute. In section 4 we categorise the dynamics shown by two mobile swimmers.

2. Interacting active colloids

Consider two swimmers in a fluid medium constrained to move in a plane that also contains their polar axes. Reactants are converted into products when they come in contact with the enzyme coated colloidal surface, resulting in a spatiotemporal distribution \(\rho(\mathbf{r}, t)\) of products. The product diffuses freely in the bulk with diffusion coefficient \(D\). The quasi two-dimensional geometry is chosen to simplify the parametrization and visualisation of the problem, as it allows a better understanding of the mechanisms giving rise to the bound states. We also note that for the noise free system, the constraint of motion in two dimensions results from a choice of coplanar initial conditions for the colloid positions and polar axes. Rotations out of the plane are ruled out unless thermal fluctuations are taken into account.

The chemicals satisfy the diffusion equation in the bulk, whereas the normal flux of the product molecules on surfaces of the swimmers at every point \(\mathbf{r}_i\) is prescribed by \(A^{(i)}\):

\[
-D \nabla^2 \rho = 0, \quad -D \nabla_\perp \rho(\mathbf{r}_i, t) = A^{(i)}(\mathbf{r}_i). \tag{2}
\]

The activity \(A^{(i)}\) can depend on the local availability of the reactant depending on whether the chemical activity is diffusion-limited or reaction-limited. In the latter case it can be represented by the Michaelis–Menten rule [56]. In this work we do not consider this aspect and work with constant \(A^{(i)}\).

Under conditions of vanishing Reynolds number, the mobility and chemical gradient lead to the establishment of a slip velocity \(\mathbf{v}_i = \mathbf{M}^{(i)} \nabla_\perp \rho\). The slip velocity produces linear and angular velocities which for a sphere are given by the following surface integrals

\[
\mathbf{V}_i = -\frac{1}{4\pi \sigma_i^2} \int \mathrm{d}s \mathbf{v}_i(\mathbf{r}_i), \quad \mathbf{\omega}_i = \frac{3}{16\pi \sigma_i^4} \int \mathrm{d}s \mathbf{r}_i \times \mathbf{v}_i(\mathbf{r}_i). \tag{3}
\]

The linear velocity \(\mathbf{V}_i\) subsumes both self-propulsion and phoretic interactions, while \(\mathbf{\omega}_i\) is the angular velocity of the swimmer. The sign of \(\mathbf{\omega}_i\) determines the ‘chemotactic’ response of the swimmer i.e. whether it aligns to point up or down the gradient [8]. Equations of motion for the positions \(\mathbf{R}_{1,2}\) and orientations \(\theta_{1,2}\) of the swimmers in the lab frame are built by first solving equation (2) for \(\rho\). The solution for \(\rho\) gives \(\mathbf{v}_i\), which is inserted into equation (3) to calculate the velocities. Translation and rotation invariance of space restricts the dependence of these velocities on \(\mathbf{R}\) and the orientation of the polar axes, \(\Delta_1\) and \(\Delta_2\), measured with respect to the line joining the sphere centres (see figure 3). In appendix C we show that the field \(\rho\) can be calculated to a desired degree of precision as a perturbation series in powers of \(\sigma / R\), where \(\sigma\) is the colloid size. The calculation uses a method of reflections, analogous to the method of images used in electrostatics. For simplicity, we construct the dynamics for just one set of reflections; corrections from subsequent reflections contribute to progressively larger powers in \(\sigma / R\) and can be ignored. A systematic study of the effect of reflections is presented in appendices C and E.

The linear velocity of swimmer 1 in spherical polar coordinates in the frame of reference of swimmer 2 in terms of radial and angular velocities \(\mathbf{V}\) and \(\mathbf{\Omega}\) is, \(\mathbf{V}_1 = \mathbf{V} + \mathbf{\Omega} \mathbf{R} \hat{\mathbf{\beta}}_1\). \(\mathbf{R}\) and \(\hat{\mathbf{\beta}}_1\) are unit vectors in the radial and
tangential directions. We use the swimmer radius $\sigma$ to scale distances, while the velocities are scaled by $a^{(i)}m^{(i)}/D$. The equations of motion for swimmer 1 in terms of the separation $R$ and the relative orientations $\Delta_1 = \theta_{n1} - \beta_1$ and $\Delta_2 = \theta_{n2} - \beta_1 - \pi$ are

$$
\dot{\theta}_{n1} = \frac{a^{(1)}m^{(1)}}{D\sigma}\omega(\Delta_1, \Delta_2, R),
$$

$$
\dot{R}_1 = \frac{a^{(1)}m^{(1)}}{D}V(\Delta_1, \Delta_2, R),
$$

$$
\dot{\beta}_1 = \frac{a^{(1)}m^{(1)}}{D\sigma}\Omega(\Delta_1, \Delta_2, R).
$$

The velocity of swimmer 1 is a linear superposition of contribution from different harmonics of the catalytic coat of swimmer 2. We first write down the equations of motion for the case when $\alpha_1^{(2)} = 1$ and $\alpha_2^{(2)} = 0$ for $\ell > 0$. The angular velocity for the polar axis is

$$
\omega(\Delta_1, \Delta_2, R) = \frac{3\sigma^2\mu_1^{(1)}}{8R^2}\sin\Delta_1 + \frac{3\sigma^2\mu_2^{(1)}}{8R^2}\sin 2\Delta_1.
$$

At a given position, the polar axis rotates till it aligns parallel ($\Delta_1 = 0$) or anti-parallel ($\Delta_1 = \pi$) with the local concentration gradient. Note that the two terms that are controlled by $\mu_1^{(1)}$ and $\mu_2^{(1)}$ fall off with different powers of $R$, so that they influence the dynamics at different length scales. The second term is absent when a linear gradient is considered [8–10]. We discuss this aspect further in appendix C. The nature of the chemotactic response of the swimmer is determined by the sign of the factor $\mu_1^{(1)} + \mu_2^{(1)}/R$, for small deviations around alignment. When $\mu_1^{(1)}$, $\mu_2^{(1)}$ carry the same sign, the chemotactic response stays unchanged at all distances from the source, being chemotactic (anti-chemotactic) for negative (positive) sign. For $\mu_1^{(1)} < 0$ and $\mu_2^{(1)} > 0$, the response depends on radial distance and reverses when the swimmer approaches the source, leading to orbiting states which we will discuss in the next section. The radial and angular velocities are

$$
V(\Delta_1, \Delta_2, R) = -\frac{\sigma^2}{R^2}\left(\mu_0^{(1)} - \frac{\mu_1^{(1)}}{20}\right) + \frac{3\sigma^2\mu_1^{(1)}}{20R^2}\cos 2\Delta_1 - \frac{2\sigma^2\mu_3^{(1)}}{3R^3}\cos \Delta_1
$$

$$
- \frac{h_0}{15}(5\alpha_1^{(1)}\mu_0^{(1)} + 2\alpha_2^{(1)}\mu_1^{(1)} - \alpha_1^{(1)}\mu_2^{(1)})\cos \Delta_1,
$$

$$
\Omega(\Delta_1, \Delta_2, R) = \frac{\sigma^4\mu_1^{(1)}}{3R^4}\sin \Delta_1 + \frac{3\sigma^2\mu_2^{(1)}}{20R^3}\sin 2\Delta_1
$$

$$
- \frac{h_0}{15}(5\alpha_1^{(1)}\mu_0^{(1)} + 2\alpha_2^{(1)}\mu_1^{(1)} - \alpha_1^{(1)}\mu_2^{(1)})\sin \Delta_1,
$$

where the dimensionless parameter $h_0 = a^{(1)}/a^{(2)}$ is the ratio of the total catalytic activity of swimmers 1 and 2. In equations (8) and (9), the terms proportional to $h_0$ arise from self propulsion and the rest are due to phoretic
response to product field of swimmer 2. Since swimmer 1 responds to the product field generated by itself and that produced by swimmer 2 with the same mobility, $h_0$ measures the relative importance of self propulsion and interaction. The higher order terms in $\omega$ and $\mathbf{V}$ are always in the form of trigonometric functions of $p\Delta_1$, where $p$ is an integer.

Regardless of the value of $h_0$, self propulsion is the leading term in equation (8), which implies that when swimmer 1 is farther than a few radii from swimmer 2, the influence of 2 on 1 is negligible. The angular velocity, however, originates from the interaction alone and the alignment of the polar axis begins before the $R^{-2}$ term in equation (8) influences the linear velocity. Assuming this separation of time scale between the radial position and the polar axis, the velocity along the line joining the colloid centres (influenced by equilibrated alignment) can be obtained by substituting $\Delta_1 = 0$ in equation (8). The non-monotonic radial velocity opens the possibility that it can vanish at finite $R_0$, leading to bound states where both attraction and repulsion are generated by the mechanism of phoresis. For $\mu_0(1) > 0$, the $R^{-2}$ term drives the swimmers apart. Further, if $\alpha(1) < 0$, self-propulsion drives two swimmers pointing towards one another further towards one another, thus leading to the formation of a bound state. The details of these calculations are presented in the next sections. A particularly interesting situation arises when this separation of time scales is no longer true. In this case, the coupled dynamics of the angular and linear degrees of freedom leads to orbits.

Finally, we write down a few of the terms in $\omega$ that are present when the anisotropy of chemical field produced by swimmer 2 is considered, and present the full equations in the appendix

$$\omega \approx \frac{3\sigma \mu^{(1)}}{32R^3} [\sin \Delta_1 + 3 \sin (\Delta_1 + \Delta_2)] - \frac{3\sigma \mu^{(1)}}{64R^4} [5 \sin (\Delta_1 + 2\Delta_2) + \sin (\Delta_1 - 2\Delta_2) + 2 \sin \Delta_1].$$

The colloid is a micron sized particle subject to fluctuations due to thermal as well as non-thermal sources, so that the dynamics should be supplemented with appropriate noises. We present a discussion on the effect of noise on the dynamics in a later section. In the next section we can discuss two possible bound states and explore swimmer designs that lead to one or the other.

3. Single active colloid near a source of product molecules

We first consider the case when, $m^{(2)} = 0$ and $m^{(1)} = 0$; i.e. swimmer 1 interacts with a tethered swimmer 2, that we now call source. An isotropic source is uniformly coated active colloid, $\alpha^{(2)} = 0$ for $\ell > 0$; an anisotropic source has at least one non-zero $\alpha^{(2)}$ for $\ell > 0$. The numerical simulations have been carried out in mathematica™ using the package NDSolve to solve the equations (6) with suitable initial conditions.

3.1. Bound final state

We first discuss a bound state formed by a swimmer with mobility $\mu^{(1)} < 0$ and $\mu^{(1)} < 0$. It is trapped at points where both translational and angular velocities vanish. A swimmer that impinges on a source with an arbitrary initial orientation of its polar axis aligns with the local concentration gradient, provided it spends enough time in its vicinity. It is trapped if the radial velocity vanishes. For an isotropic source, the trapping surface is a circle of radius $R_0$ centred at the source. The final orientation is $\Delta_1 = 0$, so that $R_0$ satisfies the condition $V(0, 0, R_0) = 0$. Using equation (8), and ignoring terms of order higher than $\sigma^2/R_0^2$, we find

$$R_0 \approx \sqrt{\frac{3}{h_0}} \left( -\alpha^{(1)} - \frac{2\alpha^{(2)} \mu^{(1)}}{5 \mu^{(1)} - \mu^{(2)}} \right)^{-\frac{1}{2}} .$$

Swimmers that are designed such that a positive value of $R_0$ is allowed by equation (11) will be trapped. $R_0$ depends on swimmer design and can be tuned by varying the ratio $\alpha^{(1)} / \alpha^{(2)}$, for example. Swimmers of distinct designs are thus trapped at different distances from the source. This provides a method for sorting the colloids experimentally.

The motion of the swimmer in a chemical field can be equivalent to colloid motion in an externally applied attractive force field in a dissipative medium. This is seen as follows: with the assumption that $\Delta_1$ has relaxed to its stationary value, the equation of motion of the colloid for deviations away from $R_0$, denoted by $\delta R$ is

$$\delta \dot{R}(t) = V(0, 0, R = R_0 \pm \delta R) \equiv -\nabla \psi .$$

The source produces a confining potential $\psi(R) = \int_{R_0}^R dR' V(0, 0, R')$, when $\partial^2 R \psi(R) > 0$. An isotropic source produces a radially symmetric potential, see figure 4(c). Near an anisotropic source, $\omega$ vanishes when $\theta_{\alpha_1} - \theta_{\alpha_2} = \pi$, thus creating an anisotropic confining potential with two traps along the polar axis of the source. The swimmer gets trapped in one or the other depending on the initial conditions. To illustrate the strength of
the confinement we plot the anisotropic potential produced along the source axis in figure 4(d). The region of state space where the bound state is formed is shown in pink in figures 2(a)–(c). Note a swimmer is trapped either when both \(0 \leq \mu_1, \mu_2 < 0\) or either one of them is both negative and sufficiently larger in magnitude than the other.

### 3.2. Orbits

A swimmer with \(\mu_2 > 0\) and \(\mu_1 < 0\), executes persistent periodic orbits around the source for a small enough value of \(h_0\). This particular choice of parameters ensures that the swimmer is chemotactic at large distance and anti-chemotactic near the source. Close to an isotropic source, it tries to align with the local gradient and becomes trapped in a limit cycle at a constant distance \(R_0\) (indicated in green in figures 2(a) and (b)) while maintaining a constant angle \(\Delta_{10}\) with the line joining its centre with the source. The angle \(\Delta_{10}\) and radius \(R_0\) are determined from conditions

\[
\omega(\Delta_{10}, 0, R_0) - \Omega(\Delta_{10}, 0, R_0) = 0, \quad V(\Delta_{10}, 0, R_0) = 0.
\]

In an anisotropic chemical field, we find non-circular orbits of two distinct types—trajectories that resemble a figure of 8 and do not enclose the source and non-circular orbits that do (see figure 5(b) and brown regions of state diagram in figure 2(b)). These oscillations can occur in this inertia-less regime because of the dynamics of the internal degree of freedom, namely, the polar axis.
3.3. Effect of fluctuations on bound states
To check the stability of the bound states to thermal fluctuations, we add Gaussian white noise terms to the dynamics in equations 7–9 with the strength chosen as appropriate for a free swimmer of Péclet number 15. The noisy trajectories so obtained and distributions of $R$, $\Delta_1$ and $\beta$ are shown in figure 6. The values of $R_\sigma^{-1}$ indicated on the axes are the mean values computed from the distribution and they match the deterministic values of $R_0$ shown in figures 4 and 5.

3.4. Scattering
For large enough $h_0$, a chemotactic swimmer interacts briefly with the source before escaping it following paths that resemble scattering off an attractive centre, see figure 7(a). The scattering angle defined as $\Theta_{\text{sc}} = \lim_{t \to \infty} \theta_{\text{sc}}(t)$ is calculated by varying $h_0$ and the impact parameter $b_0$. $b_0$ is the initial lateral separation between the swimmer and the source. For a chemotactic swimmer at fixed $h_0$, there exists a threshold value of $b_0$ below which the swimmer is trapped in one of the two bound states. Above a maximum $h_0$, the swimmer is scattered for all $b_0$. Figure 7(b) shows $\Theta_{\text{sc}}$ for two different values of $h_0$. A swimmer that can form orbits revolves around the source several times before escaping which results in non-monotonic dependence of the scattering angle $\Theta_{\text{sc}}$ on $h_0$. An anti-chemotactic swimmer constantly turns away from the source and gets repelled, see figures 7(c), (d).

3.5. Fixed points in an isotropic source
To identify the two fixed points discussed so far, we will calculate the flow into these points (see figure 8). We consider an isotropic source only, as the fixed points and phase portrait in this case can be exactly represented in 2D space spanned by $R$ and $\Delta_1$. Close to fixed point $(R_0, \Delta_{10})$, the linearised equations can be written as $(\delta R, \delta \Delta_1) = \mathcal{M} \cdot (\delta R, \delta \Delta_1)$. The signs of the real parts of the two eigenvalues of the dynamical matrix $\mathcal{M}$ determine system stability. At low $h_0$ the fixed point is stable node, see figure 8(a), characterised by two unequal negative real eigenvalues. With increasing $h_0$ the system undergoes a pitchfork bifurcation to a stable spiral, see figure 8(b), i.e. the two eigenvalues are complex conjugate of each other with negative real parts. On increasing $h_0$ further, the system undergoes a spiral-saddle bifurcation as the real part of the eigenvalues, with the eigenvector
predominantly along $R_i$ turns positive causing $R_i$ to grow unboundedly, see figure 8(h). At this value of $h_0$ a transition occurs from a bound to a scattered state. The other eigenvalue remains negative and $\Delta_1$ reaches the fixed value $\pi$ as seen in figure 8(i).

4. Two mobile swimmers

The concepts developed in section 3 related to the motion of one swimmer when the other is fixed, are now useful for studying two mobile swimmers. For a system with momentum conservation, a Galilean transformation to relative frame of reference reduces the two-body problem to a one-body problem, making it solvable. In this dissipative system, possibility of such a transformation is ruled out, so that the two particle interactions studied in this section are distinct from those of the single swimmer discussed in section 3.

The phoretic slip velocity propels the swimmer while also generating long-ranged fluid flows in an unbounded medium. The pair of swimmers we consider are advected by these flows. We have incorporated these advective terms in the expressions for velocities equations (7)–(9); see appendix F. The general treatment of hydrodynamics would involve either a numerical solution of the problem with prescribed boundary conditions or a use of the method of reflections. As there is evidence to suggest that the far-field approximation provides a reasonably accurate description of these effects [57], we treat the hydrodynamics using the far-field description accompanied by Fäxén’s law and augment it with one reflection. Note that our setup is fundamentally different from a strictly two-dimensional formulation of the problem that is considered in [24].

We find that the final state is independent of the microscopic details and can be sorted into three broad classes: (1) Active dimers, whose relative distance stays fixed while the centre of mass translates uniformly (2), Binary swimmers, whose polar axes become phase-locked, so that they revolve around a common centre in synchronised closed circular orbits while maintaining a fixed distance between their centres, like planetary orbits.
under gravity (3), Scattering states, where the swimmers interact for a finite period of time and then take off at an angle to one another.

The translational velocities of the swimmers 1 and 2 are

\[ \mathbf{V}_1 = V_1(\Delta t_1, \Delta t_2, R) \mathbf{R} + \Omega_1(\Delta t_1, \Delta t_2, R) \mathbf{R} \mathbf{\hat{R}}, \]

\[ \mathbf{V}_2 = -V_2(\Delta t_2, \Delta t_1, R) \mathbf{R} + \Omega_2(\Delta t_2, \Delta t_1, R) \mathbf{R} \mathbf{\hat{R}} \]

and the angular velocities are

\[ \dot{\theta}_{11} = \omega_1(\Delta t_1, \Delta t_2, R), \]

\[ \dot{\theta}_{12} = \omega_2(\Delta t_2, \Delta t_1, R). \]

\[ R = |R_1 - R_2| \]

is the separation between the two swimmers and \( \mathbf{R} \) is the unit vector pointing from swimmer 2 to 1. The trajectories shown in the rest of this section are produced by solving the equations of motion with initial conditions

\[ \theta_{11}(0) - \theta_{22}(0) = 0, \]

\[ X_{1}(0) - X_{2}(0) = b_0, \]

where \( b_0 \) is the impact parameter, and

\[ Z_{1}(0) - Z_{2}(0) = 10^3 \sigma. \]

The numerical calculations have been carried out in mathematica\textsuperscript{TM} using the package ND Solve.

The interactions between the swimmers are not reciprocal. We now discuss the three different types of dynamics in detail keeping in mind the non-reciprocity of interactions.

4.1. Active dimers

Two mutually chemotactic or mixed swimmers form a stable bound state where their relative separation freezes at a constant value \( R_0 \) and their polar axes align. We call this final state which can be translating or stationary, an active dimer. Two mutually chemotactic swimmers form an active dimer with their polar axes pointing inwards along the line joining their centres and their relative velocity vanishes, so that \( R_0 \) satisfies

\[ V_1(0,0, R_0) + V_2(0,0, R_0) = 0. \]

The dimer translates with the centre of mass velocity, defined in this inertia-less regime as the sum of the individual velocities given by

\[ V_1(0,0, R_0) - V_2(0,0, R_0). \]

A chemotactic–antichemotactic pair also forms a dimer in a similar way, with the difference that one of them points towards the other while the other points away,
as seen in figure 9(b). The separation $R_0$ satisfies $V_1(0,0,R_0) + V_2(0,\pi,R_0) = 0$ and the translation velocity is $V_1(0,0,R_0) - V_2(0,\pi,R_0)$, where 1 is attracted to 2, but 2 is repelled by 1.

Bound states due to forces derived from a potential are formed when a particle sits in the minima of the effective potential produced by the other. As discussed in section 3.1, a tethered swimmer can trap a mobile one. The dimers are formed when at least one of the two swimmers traps the other by creating an anisotropic trapping potential. In this system, long-ranged attractive and short-ranged repulsive drift velocities are generated by a balance between attraction due to chemotaxis and repulsion due to phoresis. This can be contrasted with other propelling clusters where the symmetry is broken by the shape of the cluster [37, 38, 53, 58]. For two identical attractive swimmers, the condition to form a stationary dimer is $V(0,0,R_0) = 0$, as seen in figure 9(a). The centre of mass of this system remains static always while the swimmers forms a stable dimer as ‘forces’ balance.

### 4.2. Binary swimmers

Two swimmers can go around a common point in synchronised circular orbits while maintaining fixed orientations $\Delta_1 = \Delta_{10}$ and $\Delta_2 = \Delta_{20}$ and a constant distance $R_0$ between their centres. This is formed when at least one of them is designed such that it can orbit around a stationary source, i.e. $\mu_1^{(0)} < 0$, $\mu_2^{(0)} > 0$; see section 3.2. We call this bound pair a binary swimmer as it resembles binary stars formed due gravitational attraction that also varies with separation as $R^{-2}$.

Figure 10(a) shows a binary system formed by two swimmers. The swimmers at position A and B and the centre O form a triangular configuration AOB, shown in figure 10(a). The triangle is defined by $R_0$, angles $\phi_{10,20}$ and the relative orientations $\Delta_{10,20}$. The conditions of fixed relative distance and orientation are satisfied when

\[
\begin{align*}
V_1(\Delta_{10}, \Delta_{20}, R_0) + V_2(\Delta_{20}, \Delta_{10}, R_0) &= 0, \\
\Omega_1(\Delta_{10}, \Delta_{20}, R_0) - \omega_1(\Delta_{10}, \Delta_{20}, R_0) &= 0, \\
\Omega_2(\Delta_{20}, \Delta_{10}, R_0) - \omega_2(\Delta_{20}, \Delta_{10}, R_0) &= 0.
\end{align*}
\]

The swimmers orbit around the centre O with in circular orbits with angular frequency $\omega(\Delta_{10}, \Delta_{20}, R_0)$. We find that this angular frequency lies between the frequencies of the orbits when either is held stationary. The total linear velocity of the swimmer in this bound state is perpendicular to the line joining their centres to the common centre. This condition provides the following relations for angles $\phi_{10}$ between the sides of length $R_0$ and $R_1$

\[
\tan \phi_{10} = \frac{V_1(\Delta_{10}, \Delta_{20}, R_0)}{R_0 \Omega_1(\Delta_{10}, \Delta_{20}, R_0)}, \quad \tan \phi_{20} = \frac{V_2(\Delta_{20}, \Delta_{10}, R_0)}{R_0 \Omega_2(\Delta_{20}, \Delta_{10}, R_0)}.
\]
Equations (14) and (15) are solved in order to obtain the 5 unknowns: the stationary angles $\Delta_{10}$, $\Delta_{20}$, $R_0$ and $\phi_{10,20}$.

For swimmer mobilities $m^{(1)} > m^{(2)}$, we obtain loopy trajectories as seen in figures 10(c), (d). The frequencies of orbital motion when either one is held fixed differ by nearly an order of magnitude in both cases. These are cycloidal trajectories that is a locus of a circle moving on another cycle.

For two identical swimmers, symmetry dictates that $\Delta_{10} = \Delta_{20}$. Thus identical binary swimmers are exactly like binary stars, as the component of their velocities parallel to the line joining their centres is zero and the non-zero perpendicular component leads to the rotation of the swimmers about a common point, see figure 10(b).

4.3. Effect of fluctuations on bound states
We end the discussion of bound states by testing the stability of these states to fluctuations. In order to do so, we add Brownian noise to the equations of motion for the dry system. The resulting distributions of $R_0$ and $\theta_{\text{rel}}$ are shown in figure 11. The distributions peak at values of $R_0$ and $\Delta_{10} + \Delta_{20}$ as calculated for the noise-free dynamics.

4.4. Scattering
Two mutually attractive or mixed swimmers scatter apart if the combination of self-propulsion and interaction along their centres is enough to separate them, see figure 12(a). Two anti-chemotactic swimmers continuously anti-align and scatter away, see figure 12(b). The active dimers and binary-swimmers discussed in the sections 4.1 and 4.2 unbind for a large enough $b_0$, figure 12(d). The region of the state diagram in figure 2 where the swimmers scatter apart following trajectories typical of attractive or repulsive interactions are shown in white and blue respectively in figure 2.

Figure 10. Trajectories of binary-swimmers that rotate in synchronised orbits around a common point. Polar axes of swimmers 1 and 2 are represented using cyan and brown arrows respectively; paths followed by 1 and 2 are shown in grey and black points. Panel (a) shows two mutually attractive swimmers bound in a binary pair, panel (b) shows a pair of identical swimmers that rotate with $R_0$ equal to orbit diameter. Panels (c) and (d) shows looping trajectories obtained when mobility of swimmer 1 is an order of magnitude larger than swimmer 2. The mobility of coat of all the swimmers in the figure are same as ones in figure 5(a). The catalytic coat parameters are $\{1, -0.5, 0\}$ and $\{3, -0.25, 0\}$ for 1 and 2 in panel (a), $\{1, -0.125, 0\}$ in panels (b) and (d) for both 1 and 2, $\{1, -0.15, 0\}$ and $\{2, -0.25, 0\}$ for 1 and 2 in figure (c).
5. Conclusions

We have explored theoretically the varieties of dynamics exhibited by polar self-diffusiophoretic colloids, focusing on the case where the motion is planar. Gradients in the diffusing chemical species—generated by other colloids—affect the motion of the colloids, directly by translating them, and indirectly by rotating their polar axes and thus their self-propelling velocities. These effects cooperate and compete, with remarkable dynamical consequences ranging from trapping, scattering and simple orbits around a fixed source to complex pairs of dances, which are the main results presented in this paper. The interactions are mediated by a diffusing field and are therefore naturally long-ranged. A distinguishing feature of our treatment is that the short-range inter-particle repulsion is also dynamically generated by phoretic mechanisms. We have tested the robustness of our results with respect to the precision with which the states are computed, the existence of hydrodynamic interactions, and thermal fluctuations. Specifically, we find that hydrodynamic interactions shift the phase boundary while the topology of the state diagram stays same as the ‘dry’ system.

A comparison to the Newtonian mechanics of particles interacting via central force fields is natural: the concentration of diffusing species plays a role similar to a potential, and the polar orientation resembles a momentum, endowing the dynamics with a character similar to inertia as it determines the direction of persistent motion (see [59] for another Stokesian driven system with an effective inertia). This is why, despite their vanishingly small Reynolds number, their behaviour bears some similarity to scattering in Newtonian...
mechanics. The analogy is incomplete as there is no equivalent of Newton’s III law. The absence of a conserved centre-of-mass momentum gives rise to the non-trivial joint motions of dimers discussed in section 3.4. It would appear therefore that there is no reduction of effective degrees of freedom in the two-body problem; could it then show chaos? We do not see evidence for this in our numerical calculations. Possibly this is because the relaxational dynamics partially slaves some of the orientational degrees of freedom to each other and to the separation vectors; see equations (7) and (9).

We have pointed out the fixed points that underlie the dynamical transitions. These results are expected to hold in higher dimensions as well. In recent works, chemical [60] and magnetic [61] interactions have been shown to compete against instabilities originating from hydrodynamic interactions. Therefore, it is important to examine how hydrodynamic effects modify the dynamics (especially in the case of bound states) that we have described in this work under more realistic geometries such as a Hele–Shaw cell.

Whereas we have concentrated on the two-body problem, the implications of non-mutual pair interactions between dissimilar particles for the collective behaviour of active binary mixtures remain to be explored. Another interesting extension, would be the case of non-planar, i.e. three-dimensional, motion. Meanwhile, our predictions for the planar case can be tested in suitable microfluidic setups [62]. We expect our work to inspire efforts to fabricate particles with a range of catalytic and mobility coat patterns, using shape [63, 64] as an additional control parameter. This will allow a test of our predictions through exploration of our dynamical state diagrams. We also note that the chemotactic alignment mechanisms discussed here have been found to play a key role in determining the behaviour of trail-following bacteria such as *Pseudomonas aeruginosa*, both at the level of single-particle trajectories [65] and collective self-organisation and micro-colony formation [66].

**Figure 12.** Two identical swimmers scatter off one another when self propulsion is stronger than the attraction. Figure (a) shows typical trajectories of two mutually chemotactic swimmers and figure (b) shows two mutually anti-chemotactic swimmers. The final polarity $\Theta_{n1}, \Theta_{n2}$ and the relative scattering angle $\Delta \Theta$ are shown as a function of the impact parameter for three cases: (c) two swimmers that scatter apart for all $b_0$, (d) two swimmers that form dimers for $b_0/\sigma < 13$, (e) two mutually anti-chemotactic swimmers.
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Appendices

The appendix is organised in five sections: in (A) we present details of the parameters chosen to construct the state diagrams in figure 2; in (B) we outline the steps leading to the equations of motion in equations (7)–(9) and discuss the approximations in detail; in (C) we calculate the velocity field relevant for the pair interactions; in (D) we discuss the effects of higher resolution of the surface patterns in determining bound states and in (E) the full equations of motion are written down.

Appendix A. Parameters for the state diagram

The state diagram is constructed by evaluating the trajectories for swimmers of different designs until a steady state is reached. Initial conditions are unchanged in evaluating a particular state diagram. Initial conditions for the single swimmer state diagrams in figures 2(a), (b) and (c) are as follows: \( b_{\text{swim}}(0) = \pi \) and \( Z_i(0) = 10^3 \sigma \), while \( b_{\text{swim}} = 0.5\sigma \) for figures 2(a) and (b) and \( b_{\text{swim}} = 2\sigma \) for figure 2(c). Design parameters for single swimmer state diagrams: in figure 2(a) The source is isotropic with catalytic coat \{1, 0, 0\}. The swimmer catalytic coat design parameters are \{1, 1, 0\} and mobility \( \mu_0^{(1)} = 0.3 \). \( \mu_1^{(1)} \) and \( \mu_2^{(1)} \) are varied in the range \((-0.4, 0.25)\) and \((-1, 1)\) in steps of 0.025. In figure 2(b) we use swimmer parameters same as in figure 2(a), in presence of an anisotropic source with catalytic coat \{1, 1, 0\}. \( \mu_1^{(1)} \) and \( \mu_2^{(1)} \) are varied in the range \((-0.4, 0.25)\) and \((0.6, 1.2)\) in steps of 0.01. In figure 2(c) The swimmer and source design are the same as in figure 2(a); and \( h_0 = 1 \) is larger than the value 0.587 for which we find bound states. The impact parameter is \( b_0 = 2\sigma \). Note that only figure 2(c) is sensitive to the choice of \( h_0 \). This is because given the choice of \( h_0 \), the capture length for the swimmer is finite. If the impact parameter is increased larger than 30\( \sigma \), the bound states disappear completely.

The trajectories for two swimmers are evaluated for \( \theta_{\text{swim}} - \theta_{\text{swim}} = 2\pi \) and \( Z_i - Z_i = 2 \times 10^3 \sigma \). Parameters for two swimmer state diagrams: in figure 2(d), we consider two identical swimmers with \( \mu_0^{(1)} = 0.3 \), \( \mu_1^{(1)} = -0.5 \), and \( \mu_2^{(1)} \) is varied. The total catalytic activity \( \alpha^{(1)} \) is varied, the catalytic coat design is \{1, 1, 0\} and \( b_0 = 2 \). In figure 2(e) we consider two swimmers with mobility \[0.3, -0.5, 1\], catalytic coat \{1, 1, 0\}, \( b_0 = 4\sigma \) and surface activities \( \sigma^{(1)} \) and \( \sigma^{(2)} \) are varied. In figure 2(f) The total surface activity and \( \sigma^{(2)} \) is varied with other parameters being the same as in figure 2(e).

Appendix B. Evaluation of the chemical field

In this section we outline a method of reflections to calculate the chemical field \( \rho \) produced by two swimmers of any orientation and a separation \( R \). \( \rho \) satisfies Neumann boundary condition on the swimmer surfaces, (equation (2) in the main text).

\[
\nabla^2 \rho = 0, \tag{16}
\]

\[
-D \nabla_i \rho(\mathbf{r}) = A^{(1)}(\mathbf{r}). \tag{17}
\]

\( \rho \) is a linear sum of contributions from both \( A^{(1)} \), so it suffices to outline the calculation of \( \rho \) for \( A^{(1)} = 0 \). The solution can be split into two parts—\( \rho \equiv \rho_{(2)} + \rho \), where \( \rho_{(2)} \) is the solution of the Poisson equation with the boundary condition equation (34) on colloid 2 assuming colloid 1 to be absent. \( \rho \) is the correction due to presence of colloid 1 that we want to calculate. \( \rho \) is solved by a method of reflection, where at every order \( n \), the boundary condition equation (34) is enforced first on colloid 1 and then on 2. \( \rho \) is decomposed as follows

\[
\rho = \sum_n \rho_n^{(1)} + \sum_n \rho_n^{(2)}. \tag{18}
\]

The convexity of the spherical surface rules out multiple reflections at a given order \( n \), meaning that equation (18) is an exact solution for \( \rho \) in a given background concentration. \( \rho_n^{(1)} \) satisfies the diffusion equation \( \nabla^2 \rho_n^{(1)} = 0 \) with boundary conditions
\[-\nabla_i \rho_1^{(1)}(r) = \sum_{k=1}^{n-1} \sum_{j=1}^{2} \nabla_i \rho_k^{(1)}(r), \tag{19}\]
\[-\nabla_i \rho_2^{(2)}(r) = \sum_{k=1}^{n'} \sum_{j=1}^{2} \nabla_i \rho_k^{(1)}(r), \tag{20}\]

where \(n' = n\) for \(i = 1\) and \(n' = n - 1\) for \(i = 2\). Also note that \(\rho_0^{(1)} = 0\). Equations (19) and (20) are further simplified to obtain the following boundary conditions

\[-\nabla_i \rho_1^{(1)}(r) = \nabla_i \rho_1^{(2)}(r), \tag{21}\]
\[-\nabla_i \rho_2^{(2)}(r) = \nabla_i \rho_2^{(1)}(r), \tag{22}\]

\(\nabla_i \rho_1^{(i)}(r)\) is decomposed into surface harmonics as follows

\[-\nabla_i \rho_1^{(i)}(r) = \sum_{\ell m} A_{\ell m}^{(i)} Y_{\ell m}(r). \tag{23}\]

Substituting equation (23) in equations (21) and (22), we derive the following recursion relation for coefficients \(A_{\ell m}^{(1)}\)

\[A_{\ell m}^{(1)} = A_{\ell m}^{(2)} N_{\ell m}^{12}, \tag{24}\]

where \(N_{\ell m}^{12}\) is a geometrical factor that can be calculated as follows. Recall from the main text, that the swimmers have radii \(\sigma\), polar axes \(\theta_n\). In figure B1, the frames of reference \(\Sigma_1\) and \(\Sigma_2\) are in the body fixed axes of the colloids and their z axes are parallel to the line joining their centres. \(\Sigma'_1\) is the lab frame with its origin coinciding with that of \(\Sigma_1\). We use spherical coordinates \((R_1, \theta_1, \phi_1)\) and \((R_2, \theta_2, \phi_2)\) in frames \(\Sigma_1\) and \(\Sigma_2\) respectively. The unit vectors representing polar axes are \((1, \theta_n, 0)\) and \((1, \theta_n, 0)\), see figure B1. The expression for \(\rho_n^{(1)}\) satisfying boundary conditions equation (23) is

\[\rho_1^{(2)} = \sum_{\ell m} \frac{1}{(\ell + 1)R_{\ell + 1}^{2}} Y_{\ell m}(\theta, \phi) A_{\ell m}^{(2)}, \tag{25}\]

The following transformations connect coordinates in \(\Sigma_1\) and \(\Sigma_2\)

\[\theta_2(\theta_1, R_1, R) = \cos^{-1}\left(\frac{R_1 \cos \theta_1 - R}{\sqrt{R_1^2 + R^2 - 2R_1 R \cos \theta_1}}\right),\]
\[R_2(\theta_1, R_1, R) = \sqrt{R_1^2 + R^2 - 2R_1 R \cos \theta_1},\]
\[\phi_2 = \phi_1. \tag{26}\]

Using equation (26) in equation (25), we obtain \(\rho_0^{(1)}\) in \(\Sigma_1\). Define

\[N_{\ell m}^{12} = \sigma \Gamma_{\ell m} \int Y_{\ell m}(\theta, \phi) \frac{Y_{\ell m}(\theta_2(\theta_1, R_1, R), \phi_2)}{R_2(\theta_1, R_1, R)^{\ell + 1}} \, d\mathbf{r}, \tag{27}\]

Figure B1. Figure showing two swimmers at a fixed distance and orientation and coordinate axes necessary for calculating the chemical field.
A similar set of coefficients \( N_{d,m}^{21} \) are defined by exchanging indices 1 and 2 in equation (27). The recursion relations equations (24) and (25) are solved to obtain the field to any degree of precision. In order to obtain the equations of motions presented in the main text we truncate the expansion at \( n = 1 \). For a uniformly coated colloid 2 with \( \alpha_2^{(2)} = 1 \) we have the following result consistent with the potential due to a charge next to a sphere (see [67])

\[
\rho_0 + \rho_1^{(1)} = \frac{d^{(2)} \sigma}{D} \sum_{\ell_m} \frac{4\pi}{2\ell + 1} \left[ \frac{\sigma R_0^2}{R^{\ell + 1}} + \frac{\ell}{\sigma (\ell + 1)} \left( \frac{\sigma^2}{R R_1} \right)^{\ell + 1} \right] Y_{\ell_m}(\theta, \phi) Y_{\ell_m}^*(\beta, 0).
\] (28)

To test the validity of our approximations we calculate the chemical field to a larger degree of precision than in the main text. We calculate \( \rho_0^{(2)} + \rho_1^{(2)}, \rho_1^{(3)} + \rho_2^{(3)}, \) the leading terms of which are proportional to \( R^{-4} \) and \( R^{-3} \), respectively. These terms are of order \( n = 1 \) and \( n = 3 \) in reflections. Swimmer 1 generates a chemical field \( \rho_0^{(1)} \), which leads to its self-propulsion, that is reflected off swimmer 2 before it is sensed by 1 again. This contributes a correction whose leading order term varies as \( R^{-2} \). This is the correction of order \( n = 2 \). In appendix E the effect of these two additional terms on the bound states is investigated.

The angular and linear velocities are obtained by evaluating the surface integrals in equation (3). For the angular velocity this involves evaluation of integrals of the following form

\[
A' \equiv \int d\theta d\phi \sin \theta Y_{\ell_m}(\theta, \phi) \left[ \cos \phi \partial_\phi Y_{\ell_m}(\theta, \phi) - \cot \theta \sin \phi \partial_\theta Y_{\ell_m}(\theta, \phi) \right],
\] (29)

where the primed harmonics are contributions from the chemical field in equation (28) and the unprimed are due to \( M^{(i)} \). Using properties of spherical harmonics, we find that \( A' = 0 \) for \( \ell \neq L \) and \( |m| \neq |M| \neq 0 \). This leads to a pair wise coupling between harmonics of the mobility coat and corresponding harmonic of the chemical field. This is the reason why the \( \mu_0^{(1)} \) couples to the \( \ell' = 1 \) term in equation (28) that decays as \( R^{-2} \) and \( \mu_2^{(2)} \) couples to the \( \ell' = 2 \) term in equation (28) that decays as \( R^{-3} \); thereby leading to the two terms in equation (7).

**Appendix C. Fluid flows due to self-propulsion**

In this Appendix, we calculate the flow field produced by a single swimmer held at the origin. The slip velocity generated on the colloid surface due to its own catalytic activity alone is axisymmetric about the polar axis and can be written as \( v_{(i)} = v^{(i)}(\theta) \hat{v}, v^{(i)}(\phi) \) is expanded as follows

\[
v^{(i)}(\theta) = v_1^{(i)} \sin \theta + v_2^{(i)} \sin 2\theta,
\] (30)

where \( v_1^{(i)} \) and \( v_2^{(i)} \) are the following linear combinations of harmonics of \( A^{(i)} \) and \( M^{(i)} \)

\[
\begin{align*}
v_1^{(i)} & = \frac{\alpha_1^{(i)} \mu_0^{(i)} + 3\alpha_2^{(i)} \mu_1^{(i)}}{2} - \frac{\alpha_2^{(i)} \mu_2^{(i)}}{4}, \\
v_2^{(i)} & = \frac{\alpha_1^{(i)} \mu_0^{(i)} + 3\alpha_2^{(i)} \mu_1^{(i)}}{2} + \frac{3\alpha_2^{(i)} \mu_2^{(i)}}{4}.
\end{align*}
\] (31)

The first term in equation (30) leads to colloid motion relative to fluid produces a velocity field that decays as \( r^{-3} \), where \( r \) is the radial distance from swimmer centre. The second term does not contribute to net motion and produces a symmetric velocity field around the colloid that varies as \( r^{-2} \). This term determines whether the swimmer is a pusher or puller. The stream function \( \chi \) [68], is written as

\[
\chi^{(i)} = \left( C_0 r^2 + \frac{C_2}{r} \right) \sin^2 \theta - \cos \theta \sin^2 \theta \left( C_3 + \frac{C_4}{r^2} \right).
\] (32)

The radial and angular components of \( v^{(i)} \) are obtained from \( \chi \) as follows

\[
\begin{align*}
v_r^{(i)}(r, \theta) & = - \frac{1}{r^2 \sin \theta} \frac{\partial \chi^{(i)}}{\partial \theta}, \\
v_\theta^{(i)}(r, \theta) & = - \frac{1}{r \sin \theta} \frac{\partial \chi^{(i)}}{\partial r}.
\end{align*}
\] (33)

The coefficients \( C_i \) are evaluated using the following boundary conditions

\[
v_1^{(i)}(\sigma, \theta) = 0, v_2^{(i)}(\sigma, \theta) = v^{(i)}(\theta).
\] (34)

Using equations (32)–(34) we obtain the following expressions for the two components of velocity in the body frame of the swimmer
The velocity in the lab-frame is obtained by a change of the frame of reference. Swimmer 2 is thus advected by swimmer 1 through the following velocity and vorticity following Faxén’s laws [68]

\[
\begin{align*}
v_{ad}^{(i)}(\sigma, \theta) &= \frac{2v_{(1)}^{(i)}}{3} \left(1 - \frac{\sigma^3}{r^3}\right) \cos \theta - \frac{v_{(2)}^{(i)}}{2} \left(1 + 3 \cos 2\theta\right) \\
v_{ad}^{(j)}(\sigma, \theta) &= \frac{2v_{(1)}^{(j)}}{3} \left(1 + \frac{\sigma^3}{2r^3}\right) \cos \theta + \frac{v_{(2)}^{(j)}}{2} \frac{\sigma^4}{r^4} \sin 2\theta.
\end{align*}
\]

The velocity in the lab-frame is obtained by a change of the frame of reference. Swimmer 2 is thus advected by swimmer 1 through the following velocity \(v_{ad}^{(2)}(r, t)\) and vorticity \(\omega_{ad}^{(2)}(r, t)\) following Faxén’s laws [68]

\[
\begin{align*}
v_{ad}^{(2)}(r, t) &= v^{(1)} + \frac{\sigma^3}{6} \nabla v^{(1)} \\
\omega_{ad}^{(2)}(r, t) &= \frac{1}{2} \nabla \times v^{(1)}.
\end{align*}
\]

Appendix D. How do experimentally realistic swimmers move?

To check the validity of our approximations we now can now calculate the phase diagram for a partially coated active colloids. Figure 2 suggests that \(\mu_2^{(i)} > 0, \rho_2^{(i)} < 0\) and \(|\rho_2^{(i)}| > |\rho_1^{(i)}|\) facilitates formation of orbiting states. This suggests a colloid with a band in the centre, or equivalently, one with two catalytic caps with uniform mobility and catalytic activity so that the apolar component of activity and mobility are significant. \(\mu^{(i)}\) and \(\alpha^{(i)}\) can thus be written using the Heaviside theta function as follows (see figure D1(a) for a schematic):

\[
\begin{align*}
M^{(i)}(\Theta) &= (\rho_{mid}^{(i)} - \rho_{cap}^{(i)}) \Theta(\theta - \theta_{top}^{(i)}) \left[1 - \Theta(\theta - \theta_{bottom}^{(i)})\right] + \rho_{cap}^{(i)} \\
A^{(i)}(\Theta) &= (\alpha_{mid}^{(i)} - \alpha_{cap}^{(i)}) \Theta(\theta - \theta_{top}^{(i)}) \left[1 - \Theta(\theta - \theta_{bottom}^{(i)})\right] + \alpha_{cap}^{(i)}.
\end{align*}
\]
The angular momentum is

\[ \ell = 5 \quad n = 3 \]

Using these expressions \( \mu^{(i)} \), \( \alpha^{(i)} \) are calculated up to \( \ell = 9 \) using equation (1). The recursion relations in equation (27) are then used to calculate the contributions from different orders of reflection \( n \) (see discussion after equation (28)) and thus \( V \) and \( \omega \). Using NDsolve in Mathematica\textsuperscript{TM} the final state is determined for both the source-swimmer system and the pair of mobile swimmers. We construct state diagrams to determine the effect of the harmonics higher than \( \ell = 2 \), higher orders of reflection. For the pair of swimmers, we also evaluate the effect of fluid flows on the state diagram. Our results are summarised in figures D1 and D2 for source-swimmer and pair dynamics respectively.

We quote a few numbers to compare the stationary state for truncation at \( \ell = 2 \) and \( \ell = 9 \): for \( \theta^{(1)}_{\text{bottom}} = 2\pi/3 \) and \( h_0 = 0.05 \), the radius of the circular orbit of the swimmer in an isotropic source changes from 7.23\( \sigma \) to 6.8\( \sigma \) for \( h_0 = 0.05 \), while the angular velocity changes from 0.05\( \sigma \) to 0.02\( \sigma \). Using NDsolve in Mathematica\textsuperscript{TM} the final state is determined for both source-swimmer and pair dynamics respectively. Panel (a) is for the dry system with maximum \( \ell = 5 \) and the order of reflection \( n = 1 \). Panel (b) is for the dry system with maximum \( \ell = 2 \) and \( n = 1 \). Panel (c) is constructed including fluid flows in the dynamics and for maximum \( \ell = 2 \) and \( n = 3 \). As noted in figure D1, the phase boundaries shift as higher order corrections are included, both in the number of harmonics and the order of reflection but the qualitative nature of the state diagrams are similar. A large part of the parameter space where we find dimers in panels (b) and (c), we find oscillatory dimers in (a). This region is denoted by bright purple in panel (a). The inclusion of hydrodynamic interactions changes the phase boundaries only slightly. Also note that the dimer formation is more robust to the change in approximations than the binary-swimmers.

**Appendix E. Complete equations of motion**

The angular momentum is

\[
\omega(\Delta_1, \Delta_2, r) = \frac{3\sigma^2 \alpha^{(2)} \mu^{(1)}_1}{8R^2} \sin \Delta_1 + \frac{3\sigma^2 \alpha^{(2)} \mu^{(1)}_2}{8R^2} \sin 2\Delta_1 - \frac{3\sigma^2 \alpha^{(2)} \mu^{(1)}_1}{32R^3} [\sin \Delta_1 - 3 \sin (\Delta_1 + \Delta_2)] \\
- \frac{3\sigma^2 \alpha^{(2)} \mu^{(1)}_2}{32R^4} [5 \sin (2\Delta_1 + \Delta_2) - \sin (2\Delta_1 - \Delta_2)] \\
+ \frac{3\sigma^2 \alpha^{(2)} \mu^{(1)}_1}{64R^5} [5 \sin (\Delta_1 + 2\Delta_2) + 2 \sin \Delta_1 + \sin (\Delta_1 - 2\Delta_2)] \\
+ \frac{\sigma^2 \alpha^{(2)} \mu^{(1)}_2}{64R^5} [3 \sin (2\Delta_1 - 2\Delta_2) + 35 \sin (2\Delta_1 + 2\Delta_2) + 10 \sin 2\Delta_1].
\] (38)
The radial velocity is

\[
V(\Delta_1, \Delta_2, r) = -\left(\mu_0^{(1)} - \frac{\mu_2^{(1)}}{2}\right)\frac{\sigma^{\alpha_0^{(2)}}}{R^2} + \frac{3\sigma^{\alpha_1^{(2)}}}{20R^2}\cos 2\Delta_1,
\]

\[
- \frac{2\sigma^{\alpha_1^{(2)}}}{3R^3}\cos \Delta_1 + \frac{\sigma^{\alpha_1^{(2)}}}{R^3}\cos \Delta_2
\]

\[
+ \frac{\sigma^{\alpha_2^{(2)}}}{80R^3}[9\cos(2\Delta_1 + \Delta_2) + 3\cos(2\Delta_1 - \Delta_2) + 4\cos \Delta_2]
\]

\[
+ \frac{\sigma^{\alpha_1^{(2)}}}{4R^3}[3\cos(\Delta_1 + \Delta_2) + \cos(\Delta_1 - \Delta_2)] - \frac{\sigma^{\alpha_1^{(2)}}}{4R^3}[1 + 3\cos 2\Delta_2]
\]

\[
+ \frac{\sigma^{\alpha_1^{(2)}}}{160R^4}[6\cos 2\Delta_1 + 15\cos(2\Delta_1 + \Delta_2) + 3\cos(2\Delta_1 - \Delta_2) + 6\cos 2\Delta_2 + 2]
\]

\[
- \frac{\sigma^{\alpha_2^{(2)}}}{6R^3}[2\cos \Delta_1 + 5\cos(\Delta_1 + \Delta_2) + \cos(\Delta_1 - \Delta_2)].
\]

(39)

The orbital angular velocity is

\[
\Omega(\Delta_1, \Delta_2, r) = \frac{3\sigma^{\alpha_1^{(2)}}}{20R^3}\sin 2\Delta_1 + \frac{\sigma^{\alpha_1^{(2)}}}{3R^4}\sin \Delta_1 - \frac{\mu^{\alpha_1^{(2)}}}{2R^5}\sin \Delta_2
\]

\[
\frac{\sigma^{\alpha_1^{(2)}}}{80R^4}[2\sin \Delta_1 - 9\sin(2\Delta_1 + \Delta_2) - 3\sin(2\Delta_1 - \Delta_2)]
\]

\[
- \frac{\mu^{\alpha_1^{(2)}}}{2R^5}\sin(\Delta_1 + \Delta_2) + \frac{\sigma^{\alpha_2^{(2)}}}{2R^3}\sin 2\Delta_2
\]

\[
\frac{\sigma^{\alpha_1^{(2)}}}{160R^4}[6\sin(2\Delta_2) + 15\sin(2\Delta_2 + \Delta_2) + 3\sin(2\Delta_2 - \Delta_2) - 4\sin 2\Delta_2]
\]

\[
+ \frac{\sigma^{\alpha_1^{(2)}}}{24R^5}[2\sin(\Delta_1) + 15\sin(\Delta_1 + \Delta_2) - \sin(\Delta_1 - \Delta_2)].
\]

(40)

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