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Particle self-diffusiophoresis near solid walls and interfaces

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Abstract The purpose of this paper is to explore, from a theoretical viewpoint, the mechanisms whereby locomotion of low-Reynolds-number organisms and particles is affected by the presence of nearby no-slip surfaces and free capillary surfaces. First, we explore some simple models of the unsteady dynamics of low-Reynolds-number swimmers near a no-slip wall and driven by an arbitrarily imposed tangential surface slip. Next, the self-diffusiophoresis of a class of two-faced Janus particles propelled by the production of gradients in the concentration of a solute diffusing into a surrounding fluid at zero Reynolds and Péclet numbers is studied, both in free space and near a no-slip wall. The added difficulty now is that the tangential slip is not arbitrarily chosen but is given by the solution of a separate boundary value problem for the solute concentration. Finally, an analysis of a model system is used to identify a mechanism whereby a non-self-propelling swimmer can harness the effects of surface tension and deformability of a nearby free surface to propel itself along it. The challenge here is that it is a free boundary problem requiring determination of the surface shape as part of the solution.

Keywords: self-diffusiophoresis, Janus particle, no-slip wall

1. Introduction

An important technological challenge, for drug-delivery systems and in micromechanics, is to develop ways to enable small-scale objects to perform autonomous controlled motion. A promising route for producing such artificial microswimmers, or "nanomotors", is to endow a particle of fixed shape with anisotropically patterned physico-chemical properties. Among the many examples are so-called Janus colloids which are chemically reactive beads or rods consisting of one of more portions of their boundaries, or "faces", having different chemical, electrical or thermomechanical properties. These particles take advantage of self-phoretic effects where gradients of solute concentration, electric or temperature fields interact with the particle's surface properties to create slip velocities that lead to net propulsion and rotation by virtue of the constraints that the particle is free of any net force or torque. On the other hand, micro-organisms or biological "swimmers", such as bacteria, can propel themselves in a qualitatively similar manner by using the concerted action of surface-based cilia to produce a net surface slip velocity (or a surface stress).

2. Wall-bounded motion

There has been much recent interest in the effect of no-slip walls on the dynamics of low-Reynolds-number organisms. For example, the motility of sperm has been of particular interest and many investigators have been interested in assessing how the vicinity of nearby walls can affect it. In this spirit, simple mathematical models based on singularity theory for Stokes flows have been devised to explain the dynamics – observed both experimentally and by means of numerical simulations – of a class of artificial "swimmers" made up of networks of rotating spheres connected by rigid rods. While it is common to model a low-Reynolds-number swimmer as a stresslet singularity, a key observation of the work of Crowdy & Or [*Phys. Rev. E*, **81**, 036313, (2010)] is to iden-

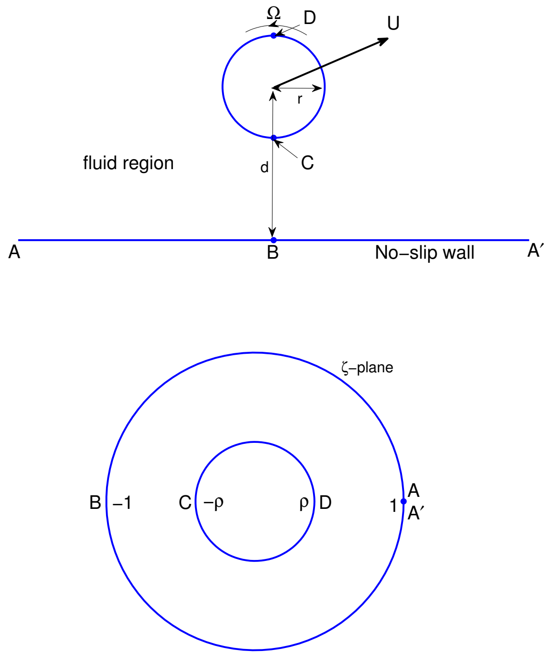

Figure 1: A circular swimmer translating with complex speed U and rotating with angular velocity Ω near a no-slip wall. The interior of the annulus $\rho < |\zeta| < 1$ (shown right) is transplanted, under the mapping $z(\zeta)$ given in (5), to the fluid region in the z-plane above the no-slip wall and outside the moving swimmer. Points labelled with the same letter correspond under the mapping (5).

tify the important role played by the irrotational quadrupole singularity contribution. Although it is of higher order than the stresslet, and so generally expected to be less important, it is found to play a decisive role in promoting locomotion along a wall. Indeed they show that while a pure point stresslet will simply crash into a wall, a superposition of a stresslet with an irrotational quadrupole can lead to nonlinear periodic orbits involving net locomotion along the wall direction.

The idea of posing a singularity distribution comprising a stresslet-quadrupole combination was inspired by asking about the far-field effective singularity distribution associated with a purely circular swimmer with a certain imposed tangential velocity distribution. This imposed tangential slip is intended to emulate the effect of the concerted motion of cilia on the swimmer surface. Crowdy & Or chose to study a particular tangential slip velocity that would lead to *no net locomotion* of the swimmer if in free space, away from any walls; that way, they isolated the net effect of the presence of the wall on the swimmer locomotion. Having found the far-field singularity description associated with such a swimmer, they determined the motion of such a stresslet-quadrupole singularity combination near a wall and found excellent qualitative agreement with experiments and numerical simulations.

It was discovered, in later work [Crowdy, *Int. J. Nonlin. Mech.*, **46**, (2011)], that the problem of a circular swimmer with an arbitrary imposed tangential velocity can in fact be solved in closed analytical form without any need to approximate the swimmer by an effective singularity description. This remarkable analytical discovery resulted from combining two mathematical ideas: the reciprocal theorem of Stokes flow, and a known exact solution for the so-called "dragging problem" for a rigid circular cylinder near a wall. These new analytical insights have prompted further investigations into how more complex swimmer types evolve near a nearby no-slip wall.

3. Mathematical results

A key ingredient for our analysis is a complex variable formulation, and use of conformal mapping techniques. These mathematical ideas are largely ignored by the low-Reynolds-number community, but they are nevertheless relevant to two-dimensional Stokes flow modelling and have enormous technical advantages. In two dimensions it is known that an incompressible Stokes flow is describable in terms of a streamfunction ψ which satisfies the biharmonic equation

$$\nabla^4 \psi = 0. \tag{1}$$

Complex analysis enters the analysis on noticing that the general solution of (1) can be written as

$$\psi = \mathrm{Im}[\bar{z}f(z) + g(z)], \qquad (2)$$

where $f(z)$ and $g(z)$ are two functions that are analytic functions of $z = x + \mathrm{i}y$ in the fluid region. These two so-called *Goursat functions* are determined by the boundary conditions on the flow. For a solid wall, these are no-slip conditions taking the form

$$-\overline{f(z)} + \bar{z}f'(z) + g'(z) = 0, \text{ on the wall.} \qquad (3)$$

The usual fundamental singularities of Stokes flows, such as the stokeslet, stresslets and rotlets, now manifest themselves as isolated singularities of these two analytic functions. For example, as shown by Crowdy & Or , a point stresslet of complex strength λ, say, at a point z_0 requires that, near this point, $f(z)$ and $g'(z)$ have the local form

$$\begin{aligned} f(z) &= \frac{\lambda}{z - z_0} + \text{locally analytic}, \\ g'(z) &= \frac{\lambda \overline{z_0}}{(z - z_0)^2} + \text{locally analytic}. \end{aligned} \qquad (4)$$

Conformal mapping theory can also aid the analysis. For motion near an infinite straight wall it is convenient to consider a preimage domain comprising the concentric annulus $\rho < |\zeta| < 1$ in a parametric ζ-domain. The conformal mapping of this region to the doubly connected fluid region exterior to a circular swimmer near to – but not touching – a plane wall is given by the linear-fractional mapping

$$z(\zeta) = \mathrm{i}R\left[\frac{\zeta + 1}{\zeta - 1}\right] \qquad (5)$$

where both parameters R and ρ depend on the radius of the swimmer s and its distance d from the wall according to

$$\begin{aligned} \rho &= \frac{d}{s} - \sqrt{\left(\frac{d}{s}\right)^2 - 1}, \\ R &= d\left[\frac{\rho^2 - 1}{\rho^2 + 1}\right]. \end{aligned} \qquad (6)$$

Figure 1 shows a schematic illustrating the fluid domain and the preimage ζ annulus.

Suppose a smooth tangential velocity profile imposed on the boundary of the particle (i.e. on $|\zeta| = \rho$) has the form

$$b_n\zeta^n + \overline{b_n}\frac{\rho^{2n}}{\zeta^n}, \quad n \geq 0 \qquad (7)$$

for some complex coefficient b_n. This quantity is real on $|\zeta| = \rho$ and it is important to note that *any* smooth imposed tangential velocity field can be represented as an infinite sum of such terms – the result is just the Laurent expansion of the velocity profile valid on $|\zeta| = \rho$. On use of the reciprocal theorem, and computation of the resulting integrals by means of the residue theorem, we find the remarkable result that

$$(U', V', \Omega') = \begin{cases} (0, 0, -b_0/s), \quad (n = 0) \\ \left(\rho\mathrm{Re}[b_1], -\frac{\rho(1-\rho^2)}{(1+\rho^2)}\mathrm{Im}[b_1], \right. \\ \left. -\frac{2\rho^2}{s(1+\rho^2)}\mathrm{Re}[b_1]\right), (n = 1) \\ (0, 0, 0), \quad (n > 1). \end{cases} \qquad (8)$$

Therefore, only the two modes with $n = 0$ and 1 of the tangential velocity profile, expressed as a Laurent expansion in ζ, lead to *any* nontrivial particle velocities U', V' and Ω' with the $n = 0$ term serving only to alter the particle's angular velocity. We believe this observation is significant. Mathematically it means that, for an arbitrary imposed tangential slip, only its projection onto these *two* modes are relevant to its locomotive properties.

4. Janus particle models

We now give details of a theoretical investigation of the self-diffusiophoresis of a class of two-faced, two-dimensional Janus particles propelled by the production of gradients in the concentration of a solute diffusing into a surrounding fluid at zero Reynolds and Pclet numbers. Those concentration gradients produce a tangential boundary slip resulting in translation and rotation of the particle, as a consequence of the fact that it is free of both force and torque. Mathematically, the additional complication is that it is now necessary to simultaneously solve a boundary value problem for the solute concentration and then couple it to the Stokes flow problem.

Our model Janus particle as an isolated two-faced circular particle which is a zero net source of solute; that solute diffuses around the particle at zero Péclet number with diffusion coefficient D. Let the solute concentration exterior to the particle be denoted by $c(x,y)$. In the zero Péclet number limit the boundary value problem for $c(x,y)$ is to solve Laplace's equation

$$\nabla^2 c = 0 \tag{9}$$

outside the particle with the Neumann boundary condition

$$-D\,\mathbf{n}.\nabla c = A, \tag{10}$$

where D is the diffusion coefficient and A is the local surface activity. Positive values of surface activity A correspond to solute emitting surfaces. We assume that there is no solute in the far-field. The particle is situated in fluid of viscosity μ assumed to be in the zero Reynolds number régime. Once the solute concentration has been found from the above boundary value problem the local phoretic slip velocity $\mathbf{u_s}$ on the boundary is

$$\mathbf{u_s} = M(\mathbf{I}-\mathbf{nn}).\nabla c, \tag{11}$$

where M is the surface mobility, and it is this surface velocity that will drive a local Stokes flow around the particle. We therefore understand that, unlike the swimmer problems considered previously where the tangential surface slip was simply imposed arbitrarily, now the tangential slip is given by the solution of another boundary value problem.

We make the special choice of piecewise constant surface activity A and mobility M given by

$$(A,M) = \begin{cases} (A_1,M_1), & \text{on } C_1, \\ (A_2,M_2), & \text{on } C_2, \end{cases} \tag{12}$$

where A_i, M_i for $i = 1,2$ are constants; the portion of the boundary with $\arg[z] \in [-\theta,\theta]$ is denoted by C_1 while the remainder of the boundary is C_2 as shown in Figure 2.

A natural first step is to consider such a swimmer in isolation (away from any walls). We analyze this case and show that if the particle is actuated by a ratio r of its surface having uniform surface mobility M_1 and surface activity A_1, with the remainder having mobility M_2, then the (reduced) particle speed is

$$\frac{U}{U_0} = -\frac{\sin \pi r}{\pi}\left[\frac{r+\lambda(1-r)}{1-r}\right], \tag{13}$$

where

$$U_0 = \frac{A_1 M_1}{D}, \qquad \lambda = \frac{M_2}{M_1}. \tag{14}$$

The direction of travel is shown in Figure 2. Notice already that the locomotion speed is a complicated nonlinear function of the ratio r. The mathematical details here are complicated by the presence of discontinuities in the surface properties, and these have to be properly accounted for. But, again, complex variable methods can be used to find the explicit results above.

Confinement effects are then investigated by placing the same Janus particle just described near a straight no-slip wall. The mathematical difficulties associated with discontinuities in the surface properties have to be accounted for, but, in combination with the result (8) cited above, it has been found that the governing nonlinear dynamical system can be established in completely explicit form. The resulting nonlinear system is used to study how the geometry, location and orientation of the particle relative to the wall affect its motion. It is found that if the particles do not hit the wall in finite time they are eventually repelled away from it. In particular, no steadily translating or periodic orbits along the wall could be found suggesting that it is unlikely that such swimmers will be able to move along the wall.

D.G. Crowdy, Wall effects on self-diffusiophoretic Janus particles: a theoretical study, *J. Fluid Mech.*, **735**, 473-498, (2013).

5. Motion near a free surface

Other types of low-Reynolds-number swimmers have been found to locomote parallel to

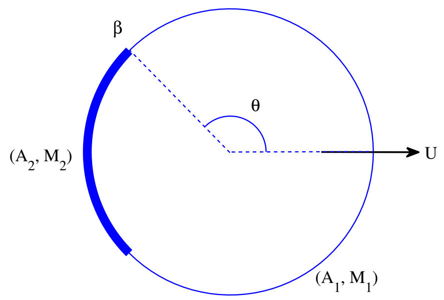

Figure 2: A circular Janus particle C_1 occupying $r = \theta/\pi$ of the surface and C_2 (the thick line portion) occupying the remainder. Its locomotion speed is given in (13) as a function of r and surface mobility ratio λ.

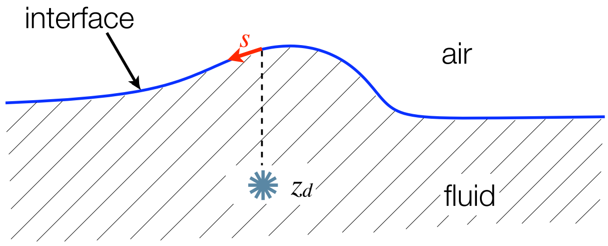

Figure 3: Model of a swimmer, as a point singularity at z_d, beneath a deformable free surface.

free surfaces. What is surprising here is that, unlike no-slip surfaces, free surfaces cannot support any shear stress so the way in which an organism makes use of the nearby surface to assist its locomotion must be fundamentally different. We have attempted to investigate this using the same two-dimensional models already discussed in the context of no-slip walls.

The analysis is, however, significantly more complicated owing to the deformation of the free surface: it is a *free boundary problem* requiring that the shape of the free surface be determined as part of the solution. Given this difficulty we have only investigated the existence of possible steady states in which the swimmer is travelling uniformly at constant speed in the direction parallel to the undisturbed free surface. Moreover, given these complications with the free surface, it is natural to resort back to a singularity model of the swimmer comprising a stresslet and superposed quadrupole (rather than thinking of a circular swimmer with an imposed tangential slip).

Similar mathematical techniques based on complex analysis are useful here too. By adapting mathematical techniques used by Jeong & Moffatt [*J. Fluid Mech.*, **241**, (1992)] to study free surface cusps induced by counter-rotating rollers, we have been able to analyze this problem and find the required steadily translating state in terms of closed form formulas. The methods again rest on strategic use of a complex variable formulation of the Stokes flow problem with conformal mapping theory used to describe deformation of the free surface. Owing to the fact that the swimmer is modelled as a singularity at a single point, without any spatial extent, the fluid region is now simply connected, implying that the required conformal mapping function can be taken from the unit disc, rather than the doubly connected annulus (i.e. this is the limit $\rho \to 0$ for the preimage ζ annulus shown in Figure 1). This affords a major simplification since now the flow is bounded only by the free surface with a point singularity sitting in the fluid region at some point z_d beneath it. Figure 3 shows a schematic.

A non-zero surface tension T is taken to be active on the free surface and, in this case, the statement of the stress balance on the free surface takes the modified form

$$\overline{f(z)} + \bar{z} f'(z) + g'(z) = \frac{\mathrm{i}T}{2} \overline{\frac{dz}{ds}}, \quad \text{on the surface,} \tag{15}$$

where s denotes arclength along the free surface as shown in Figure 3. This relation determines the unknown Goursat functions $f(z)$ and $g(z)$. In this case, a non-dimensional capillary number Ca can be defined that governs the balance between surface tension and viscous effects generated by the local motion induced by the swimmer. By virtue of an asymptotic analysis of the system as $Ca \to 0$, a new mechanism of locomotion is identified. Its origin is a subtle balance of surface tension and free surface deformation.

Full details of this analysis have been published in:
D.G. Crowdy, S. Lee, O. Samson, E. Lauga and A.E. Hosoi, A two-dimensional model of low-Reynolds number swimming beneath a free surface, *J. Fluid. Mech.*, **681**, 24-47, (2011).