Phoretic motion of spheroidal particles due to self-generated solute gradients

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Abstract. We study theoretically the phoretic motion of a spheroidal particle, which generates solute gradients in the surrounding unbounded solvent via chemical reactions active on its surface in a cap-like region centered at one of the poles of the particle. We derive, within the constraints of the mapping to classical diffusio-phoresis, an analytical expression for the phoretic velocity of such an object. This allows us to analyze in detail the dependence of the velocity on the aspect ratio of the polar and the equatorial diameters of the particle and on the fraction of the particle surface contributing to the chemical reaction. The particular cases of a sphere and of an approximation for a needle-like particle, which are the most common shapes employed in experimental realizations of such self-propelled objects, are obtained from the general solution in the limits that the aspect ratio approaches one or becomes very large, respectively.

1 Introduction

The increasing interest in the development of “lab on a chip” devices and of drug delivery systems has led to a stringent need of scaling standard machinery down to micro- and nano-scales. This reduction in length scale has raised a number of challenging issues, such as developing ways to enable small objects to perform autonomous, directional motion [1,2].

Although the experimental and theoretical research in this area is still in its early stages, several proposals for such “self-propellers” have already been tested experimentally (see, e.g., refs. [1–6]); a review of the recent progress in this field can be found in ref. [7]. These “proof of principle” proposals have generally employed particles with axial symmetry, i.e., cylindrical rods [1,2] or spheres [4–6], because they are relatively easy to manufacture, allow for a good control of the desired surface modifications, and their simple geometry is a significant bonus for the theoretical analysis of the experimental results. The underlying idea, as put forward by Whitesides and co-workers [1], is that an asymmetric decoration of the particle with a catalyst, which promotes an activated reaction in the surrounding liquid medium generating product molecules, can provide motility through a variety of mechanisms. As in the initial design proposed in ref. [1], the simplest example is the propulsion of mm-size objects due to the ejection and subsequent bursting of bubbles formed by the product molecules (O2 for PDMS plates with Pt catalyst tails placed in hydrogen peroxide (H2O2) aqueous solutions). As the size of the particle is decreased towards the micron scale or below, viscous and surface forces start to dominate and inertia-based mechanisms such as the “bubble ejection” propulsion become ineffective. If the product molecules remain dissolved in the surrounding liquid medium as, e.g., in the experiments reported in refs. [2, 4–6], the result of an asymmetric distribution of catalyst is that the chemical reaction gives rise to concentration gradients along the surface of the particle. It has therefore been argued [2,8] that in such cases the motion of the catalyst-covered “active” particle is rather phoretic, i.e., the result of the interactions between the particle and the non-uniformly distributed product molecules generated by the chemical reaction. For example, in the case of Au-Pt rods in H2O2-H2O mixtures [2] the product molecules O2 play the role of a solute the concentration gradient of which in the solution (formed by the H2O2-H2O mixture as the solvent and O2 as the solute) is the field that may induce phoretic motion.

In many cases the magnitude and the direction of the experimentally observed phoretic velocity of such “active” particles are compatible with a variety of microscopic mechanisms, such as surface tension gradients [2,3,9] (note that ref. [3] provides an elegant example that rotational motion can also be achieved), cyclic adsorption and desorption [7], electrokinetics [2,5–7,10],
or diffusio-phoresis [4,8,11,12]. (By using the notion of diffusio-phoresis, here we refer strictly to phoresis due to gradients of a solute, i.e., we do not consider the case of bimetallic particles [2,7] for which charge transfer and electro-chemistry may be the dominant effects. For simplicity, we focus here on the case of electrically neutral solutes, which in the literature is often also called “chemophoresis”.) Thus, understanding these systems and discriminating between these various possibilities require a careful, detailed theoretical analysis to predict the dependence of the velocity on the control parameters of the system, such as, e.g., the H$_2$O$_2$ content of the aqueous hydrogen peroxide solvent used in the experiments reported in refs. [2,4–6] or the fraction of the particle surface which is catalytically active. With the notable exception of ref. [11], which has used a microscopic description for the interfacial region at the expense of having to carry out numerically most of the analysis, the theoretical approach so far has been to map these systems onto the case of classic phoresis in an externally imposed gradient of a field such as, e.g., a solute concentration or an electric potential (see ref. [13] for a review of the theory of classic phoresis and additional references; a detailed discussion of the shortcomings of such a mapping is provided in ref. [14]).

Starting from the model system proposed in refs. [2,8], here we study the phoretic motion of a spheroidal particle which generates number density gradients of product molecules emerging from chemical reactions, which are active on the surface of the particle in a cap-like region centered at one of the poles. The product molecules diffuse into the surrounding unbounded three-dimensional Newtonian liquid solvent. Similar to the earlier studies in refs. [8,12,14,15], our work is based on adopting the standard theory of phoresis for the present case, in which the gradients are self-generated rather than being produced and maintained by external sources [16]. The motivation for this work is to provide a unified description (within the standard theory) for the diffusio-phoretic motion of objects belonging to an extended class of geometrical shapes relevant to experimental studies [2,4–6,17,18]. The previously studied spherical and needle-like-shaped objects are recovered as particular limiting cases. We note that here we focus on the case of rigid particles. If the body is actually soft and deformable, various additional phenomena, such as a transfer between translational and rotational motion upon shape changes, may occur (see, e.g., ref. [19]).

The outline of the paper is as follows. In sect. 2 we define the model. Section 3 is devoted to the derivation of the diffusio-phoretic velocity; it includes also the computation of the distribution of the product molecules which induces the phoretic motion. The results, as well as the connections with the previous studies in refs. [2,8,12,9], are discussed in sect. 4. We conclude with a brief summary in sect. 5.

2 The model

The system we consider is shown in fig. 1(a). It consists of an impermeable, spheroidal, rigid particle of polar and equatorial semi-axes $R_1$ and $R_2$, respectively. At one of the poles there is a cap-like region (the black area in fig. 1) covered by a catalyst (depicted as a black area). The aspect ratio of the particle is $s_1 = R_2/R_1$; $s_1 < 1$ (shown here) corresponds to a prolate shape, while $s_1 > 1$ to an oblate one. $s_1 = 1$ corresponds to a sphere. The product molecules of diameter $a$ are shown as small hatched circles. “O” denotes the geometric center of the particle from which the number density $\rho(r,t)$ of product molecules is measured.

(b) and (c) show cuts of the $xz$ plane through the prolate and oblate iso-surfaces in terms of prolate (\(\zeta, \phi, \eta\)) and oblate (\(\xi, \phi, \chi\)) spherical coordinates, respectively (see, e.g., eqs. (7)-(12) and eqs. (20)-(24), respectively). $\xi_0$ and $\phi_0$ denote the values of the prolate $\xi$ and oblate $\zeta$ coordinates, respectively, for which the corresponding iso-surfaces coincide with the surface of the particle (shown as a thick gray line; the thick black line at the lower pole indicates the catalyst-covered region).

Fig. 1. (a) An impermeable, spheroidal particle of polar and equatorial semi-axes $R_1$ and $R_2$, respectively, with a cap-like part of the surface covered by a catalyst (depicted as a black area). The aspect ratio of the particle is $s_1 = R_2/R_1$; $s_1 < 1$ (shown here) corresponds to a prolate shape, while $s_1 > 1$ to an oblate one. $s_1 = 1$ corresponds to a sphere. The product molecules of diameter $a$ are shown as small hatched circles. “O” denotes the geometric center of the particle from which the number density $\rho(r,t)$ of product molecules is measured.

(b) and (c) show cuts of the $xz$ plane through the prolate and oblate iso-surfaces in terms of prolate (\(\zeta, \phi, \eta\)) and oblate (\(\xi, \phi, \chi\)) spherical coordinates, respectively (see, e.g., eqs. (7)-(12) and eqs. (20)-(24), respectively). $\xi_0$ and $\phi_0$ denote the values of the prolate $\xi$ and oblate $\zeta$ coordinates, respectively, for which the corresponding iso-surfaces coincide with the surface of the particle (shown as a thick gray line; the thick black line at the lower pole indicates the catalyst-covered region).