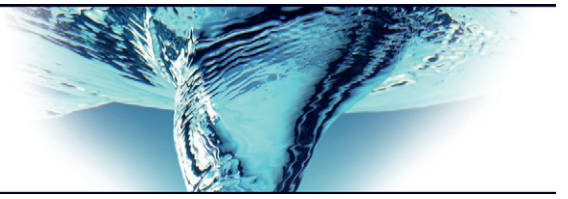
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A reciprocal theorem for Marangoni propulsion

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We study the Marangoni propulsion of a spheroidal particle located at a liquid–gas interface. The particle asymmetrically releases an insoluble surface-active agent and so creates and maintains a surface tension gradient leading to the self-propulsion. Assuming that the surface tension has a linear dependence on the concentration of the released agent, we derive closed-form expressions for the translational speed of the particle in the limit of small capillary, Péclet and Reynolds numbers. Our derivations are based on the Lorentz reciprocal theorem, which eliminates the need to develop the detailed flow field.

Key words: interfacial flows (free surface), low-Reynolds-number flows, propulsion

1. Introduction

The motion of interface-bound objects due to a gradient of surface tension, the so-called Marangoni propulsion (Bush & Hu 2006), appears in many biological and man-made systems (see Lauga & Davis 2012, and references therein). For instance, surface tension gradients can be induced externally or can be prompted by a form of activity taking place at the surface of the object. Biological examples of the latter case include water-walking insects that secrete surface-active materials to boost their walking speed in emergency situations (Bush & Hu 2006). Camphor boats are examples of synthetic systems in which the dissolution of camphor into the water gives rise to the self-propulsion (Rayleigh 1889; Nakata *et al.* 1997).

A primary feature of self-induced Marangoni propulsion is to relate the prescribed surface activity to the speed, which is useful for developing a continuum model for the collective dynamics of active surface-bound particles. Here, we consider

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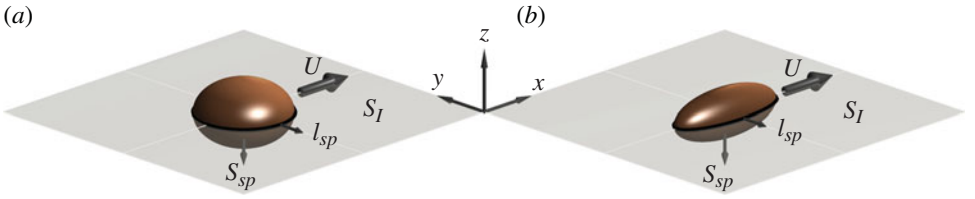


FIGURE 1. Oblate (*a*) and prolate (*b*) spheroids translating at a liquid–gas interface. Although it is not shown, we also consider the translation of the prolate spheroid in the y direction.

the Marangoni propulsion of an isolated spheroidal particle releasing an insoluble surface-active agent whose concentration has a linear relation with the surface tension. We assume that inertial effects are negligible, the transport of the released agent is dominated by diffusion and the surface tension is strong enough to keep the interface flat. We shall discuss the consequence of these assumptions in § 3.

In the conventional approach, calculating the self-propulsion speed entails solving the governing differential equations subject to the boundary conditions imposed by the surface activity (e.g. Lauga & Davis 2012). Alternatively, the Lorentz reciprocal theorem (e.g. Happel & Brenner 1965) can be used to facilitate the calculations by eliminating the need for developing the detailed flow field (e.g. Nadim, Haj-Hariri & Borhan 1990; Stone & Samuel 1996). Following this idea, in § 2, we derive closed-form expressions for the translational speed of spheroidal particles. We also present simplified expressions for the limiting cases of spheres, discs and rods.

2. Problem formulation and solution

Consider a solid spheroid located at a flat surface ($z = 0$) that bounds a half-space of Newtonian liquid with viscosity μ (see figure 1). The spheroid translates with the velocity $\boldsymbol{U} = U\boldsymbol{e}$ due to a non-uniformity in the surface tension γ stemming from the release of a rapidly diffusing insoluble agent. Here, $\boldsymbol{e}$ is the unit vector in the direction of motion. Also, the direction of unit vectors in the xyz coordinate system ($\boldsymbol{e}_x$, $\boldsymbol{e}_y$, $\boldsymbol{e}_z$) coincides with the principal axes of the spheroid whose semi-lengths are, respectively, a, b and c (see figure 1). The relations between the semi-lengths for oblate and prolate spheroids are, respectively, $a = b \geqslant c$ and $a \geqslant b = c$. To ensure that the self-propelling motion is restricted to translation, we assume that the release from the spheroid is symmetric about the direction of motion.

Let $\boldsymbol{u}$ and $\boldsymbol{\sigma}$ denote, respectively, the velocity and stress fields, in $z \leqslant 0$, corresponding to the Marangoni-driven motion of the spheroid. Also, let $\hat{\boldsymbol{u}}$ and $\hat{\boldsymbol{\sigma}}$ denote, respectively, the velocity and stress fields corresponding to the translation with the velocity $\hat{\boldsymbol{U}} = \hat{U}\boldsymbol{e}$ of an identical spheroid at an otherwise clean interface (i.e. with no surface tension gradient). Then, in the absence of inertia, according to the reciprocal theorem

$$\int_{S_{sp}} (\boldsymbol{n}\cdot\boldsymbol{\sigma})\cdot\hat{\boldsymbol{u}}\,\mathrm{d}S + \int_{S_I} (\boldsymbol{n}\cdot\boldsymbol{\sigma})\cdot\hat{\boldsymbol{u}}\,\mathrm{d}S = \int_{S_{sp}} (\boldsymbol{n}\cdot\hat{\boldsymbol{\sigma}})\cdot\boldsymbol{u}\,\mathrm{d}S + \int_{S_I} (\boldsymbol{n}\cdot\hat{\boldsymbol{\sigma}})\cdot\boldsymbol{u}\,\mathrm{d}S, \qquad (2.1)$$

where S_{sp} is the surface area of the spheroid in contact with the liquid, S_I is the liquid–gas interface area (see figure 1) and $\boldsymbol{n}$ is the unit outward normal toS_{sp} and

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S_I. Integrals over bounding surfaces at infinity are zero since velocities decay at least as fast as the inverse distance in the far field.

Owing to the no-slip condition, $\boldsymbol{u} = U\boldsymbol{e}$ and $\hat{\boldsymbol{u}} = \hat{U}\boldsymbol{e}$ on S_{sp}. Given that all surface motions are planar, the balance of shear stress at the interface (i.e. the Marangoni stress condition) requires $(\boldsymbol{n}\cdot\boldsymbol{\sigma})\cdot\hat{\boldsymbol{u}} = -\nabla_s\gamma\cdot\hat{\boldsymbol{u}}$ and $(\boldsymbol{n}\cdot\hat{\boldsymbol{\sigma}})\cdot\boldsymbol{u} = 0$ on S_I, where ∇_s is the surface gradient operator. Since no net external force is applied on the spheroid, the viscous force $\int_{S_{sp}} \boldsymbol{n}\cdot\boldsymbol{\sigma}\,\mathrm{d}S$ exerted on S_{sp} is balanced by the surface tension force $F_{st}\boldsymbol{e} = \int_{\ell_{sp}} \gamma\boldsymbol{t}\,\mathrm{d}\ell$ acting along the triple-phase contact line ℓ_{sp}, where $\boldsymbol{t}$ is the unit vector tangent to S_I and normal to ℓ_{sp}. Taking the above relations into account, equation (2.1) reduces to

$$-\int_{\ell_{sp}} \gamma\boldsymbol{t}\,\mathrm{d}\ell\cdot\hat{\boldsymbol{U}} - \int_{S_I} \nabla_s\gamma\cdot\hat{\boldsymbol{u}}\,\mathrm{d}S = \int_{S_{sp}} \boldsymbol{n}\cdot\hat{\boldsymbol{\sigma}}\,\mathrm{d}S\cdot\boldsymbol{U}. \tag{2.2}$$

The second integral on the left-hand side of (2.2) represents the contribution of the Marangoni flow induced by the gradient of surface tension whereas the integral on the right-hand side of (2.2) denotes the fluid drag $\hat{F}_d\boldsymbol{e} = \int_{S_{sp}} \boldsymbol{n}\cdot\hat{\boldsymbol{\sigma}}\,\mathrm{d}S$ that the translating spheroid would have experienced in response to its motion at the interface had there been no Marangoni effect. Hence, equation (2.2) can be written succinctly as

$$U = -\frac{\hat{U}}{\hat{F}_d}\left[F_{st} + \int_{S_I} \frac{\hat{\boldsymbol{u}}}{\hat{U}}\cdot\nabla_s\gamma\,\mathrm{d}S\right]. \tag{2.3}$$

In effect, equation (2.3) is a general result for the translational velocity of an interface-bound spheroid for any distribution of surface tension along the interface. Note that $\hat{F}_d/\hat{U}$ is the drag coefficient of the particle.

Next, we make the assumption that the surface tension γ has a linear dependence on the surface concentration of the active agent ϕ, so that

$$\gamma = \gamma_0 + \kappa\phi, \tag{2.4}$$

where γ_0 and κ are constants (Acree 1984; Adamson 1990; Lauga & Davis 2012). Therefore, to determine the distribution of γ, we must solve for ϕ. Neglecting advection, a quasi-static distribution of ϕ satisfies the Laplace equation ($\nabla_s^2\phi = 0$). The general solution for ϕ can be obtained by the method of separation of variables and eigenfunction expansions in polar and elliptic coordinates for oblate and prolate spheroids, respectively (Morse & Feshbach 1953).

Since the interface is flat (which also requires the triple-phase contact angle to be 90°), $\hat{\boldsymbol{u}}$ and $\hat{\boldsymbol{\sigma}}$ in $z \leqslant 0$ are equal to, respectively, the velocity and stress fields generated by a spheroid translating in an otherwise unbounded liquid. Then, $\hat{F}_d$ is half the Stokes drag experienced by a translating spheroid in a quiescent liquid. Hence, we can look up $\hat{\boldsymbol{u}}$ and $\hat{F}_d$ (Happel & Brenner 1965) and substitute them along with (2.4) and the solution for ϕ in (2.3) to calculate the translational speed U. Below, we present the derivation of U for oblate and prolate spheroids, respectively. For the latter, we consider the translation along and normal to the axis of revolution.

2.1. *Oblate spheroid*

For the oblate spheroid, we set the direction of motion to $\boldsymbol{e} = \boldsymbol{e}_x$. Therefore, given that the release is symmetric about the x direction and that the surface concentration of

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the active agent vanishes at infinity, the general solution of ϕ in the polar coordinates (r, θ) can be written as

$$\phi(r, \theta) = A_0 + 2\sum_{n=1}^{\infty} A_n r^{-n} \cos n\theta \quad \text{for } r \geqslant 1, \tag{2.5}$$

where $r = \sqrt{x^2 + y^2}/a$, $\theta = \tan^{-1}(y/x)$ and A_n are coefficients determined by the prescribed boundary condition at the contact line. Substituting (2.5) into (2.4) and integrating γ along the contact line, we obtain

$$F_{st} = 2\pi\kappa a A_1. \tag{2.6}$$

The Stokes flow past a translating ellipsoid is well known (e.g. Happel & Brenner 1965, §§ 5–11, pp. 220–224). In particular, the Stokes drag on an oblate spheroid moving normal to its axis of revolution is

$$\hat{F}_d = -8\pi\mu a \varepsilon^3 \chi \hat{U}, \tag{2.7}$$

where $\chi = [(1 + 2\varepsilon^2)\sin^{-1}\varepsilon - \varepsilon\sqrt{1-\varepsilon^2}]^{-1}$ and $\varepsilon = \sqrt{1 - (c/a)^2}$. In addition, Happel & Brenner (1965) report the velocity field $\hat{\boldsymbol{u}}$ in Cartesian coordinates and it is straightforward to use their results to obtain the velocity representation in other coordinates. Considering equation (2.5), we rewrite $\hat{\boldsymbol{u}}$ at the $z = 0$ plane in polar coordinates as

$$\frac{\hat{u}_r}{\hat{U}} = \chi\left[\frac{\varepsilon^3(r^2-1)}{r^2\sqrt{r^2-\varepsilon^2}} - \frac{\varepsilon\left(1-\varepsilon^2\right)}{\sqrt{r^2-\varepsilon^2}} + \left(1+2\varepsilon^2\right)\sin^{-1}\left(\frac{\varepsilon}{r}\right)\right]\cos\theta, \tag{2.8a}$$

$$\frac{\hat{u}_\theta}{\hat{U}} = \chi\left[\frac{\varepsilon\sqrt{r^2-\varepsilon^2}}{r^2} - \left(1+2\varepsilon^2\right)\sin^{-1}\left(\frac{\varepsilon}{r}\right)\right]\sin\theta. \tag{2.8b}$$

Given the form of $\hat{\boldsymbol{u}}$, the integral in (2.3) is only non-zero for $n = 1$. Theoretical studies on self-diffusiophoresis of particles share the same feature that only specific modes of boundary data induce self-propulsion (e.g. Crowdy 2013). Substitution of (2.4)–(2.8) into (2.3) yields, after some manipulations,

$$U = \left(\frac{\kappa A_1}{\mu}\right)\left(\frac{\sin^{-1}\varepsilon - \varepsilon\sqrt{1-\varepsilon^2}}{2\varepsilon^3}\right). \tag{2.9}$$

Equation (2.9) reduces to $U = \kappa A_1 \pi/4\mu$ and $U = \kappa A_1/3\mu$ for discs ($\varepsilon \to 1$) and spheres ($\varepsilon \to 0$), respectively. Our expression for the velocity of discs is identical to that obtained by Lauga & Davis (2012) after solving for both the velocity and pressure fields.

2.2. *Prolate spheroid moving along its axis of revolution*

First, we consider the case where the prolate spheroid translates along the x direction ($\boldsymbol{e} = \boldsymbol{e}_x$). Hence, the general solution for ϕ in elliptic coordinates (λ, ζ) may be expressed as

$$\phi(\lambda, \zeta) = A_0 + 2\sum_{n=1}^{\infty} A_n \exp[-n(\lambda - \lambda_0)]\cos n\zeta \quad \text{for } \lambda \geqslant \lambda_0, \tag{2.10}$$

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where $x + \mathrm{i}y = \sqrt{a^2 - b^2}\cosh(\lambda + \mathrm{i}\zeta)$ (Happel & Brenner 1965), $\lambda_0 = \ln[(a+b)/(a-b)]/2$ and A_n are again prescribed coefficients. This formulation satisfies both the symmetry condition about the x direction and the zero concentration condition at infinity, and leads to

$$F_{st} = 2\pi\kappa a A_1 \sqrt{1-\varepsilon^2}, \tag{2.11}$$

where $\varepsilon = \sqrt{1-(b/a)^2}$. The Stokes drag $\hat{F}_d$ on a prolate spheroid translating along its axis of revolution is

$$\hat{F}_d = -8\pi\mu a \varepsilon^3 \alpha \hat{U}, \tag{2.12}$$

where $\alpha = \{-2\varepsilon + (1+\varepsilon^2)\ln[(1+\varepsilon)/(1-\varepsilon)]\}^{-1}$. For the prolate spheroid, we rewrite the velocity field at the interface in elliptic coordinates as

$$\frac{\hat{u}_\lambda}{\hat{U}} = \left(\frac{\alpha}{\sqrt{\sinh^2\lambda + \sin^2\zeta}}\right)\left[\left(1+\varepsilon^2\right)\sinh\lambda \ln\left(\frac{\cosh\lambda + 1}{\cosh\lambda - 1}\right) - 2(1-\varepsilon^2)\coth\lambda\right]\cos\zeta, \tag{2.13a}$$

$$\frac{\hat{u}_\zeta}{\hat{U}} = \left(\frac{\alpha}{\sqrt{\sinh^2\lambda + \sin^2\zeta}}\right)\left[-\left(1+\varepsilon^2\right)\cosh\lambda \ln\left(\frac{\cosh\lambda + 1}{\cosh\lambda - 1}\right) + 2\right]\sin\zeta. \tag{2.13b}$$

Again, the integral in (2.3) is zero for $n \neq 1$. Substituting (2.4) and (2.10)–(2.13) into (2.3), we obtain

$$U = \left(\frac{\kappa A_1}{\mu}\right)\left(\frac{1+\sqrt{1-\varepsilon^2}}{4\varepsilon^3}\right)\left\{\left(1-\varepsilon^2\right)\ln\left(\frac{1+\varepsilon}{1-\varepsilon}\right) + 2\varepsilon\left[2\left(1-\sqrt{1-\varepsilon^2}\right) - 1\right]\right\}. \tag{2.14}$$

Equation (2.14) reduces to $U = \kappa A_1/2\mu$ for rods ($\varepsilon \to 1$), indicating that the speed remains finite despite the fact that F_{st} approaches zero faster than $\hat{F}_d$ as ε approaches one (see (2.11) and (2.12)). Indeed, (2.14) recovers $U = \kappa A_1/3\mu$ for spheres ($\varepsilon \to 0$), as found above.

2.3. *Prolate spheroid moving normal to its axis of revolution*

Following the same procedure as in § 2.2, for a prolate spheroid translating along the y direction ($\boldsymbol{e} = \boldsymbol{e}_y$), we have

$$\phi(\lambda, \zeta) = A_0 + 2\sum_{n=1}^{\infty} A_n \exp[-n(\lambda - \lambda_0)]\sin n\zeta \quad \text{for } \lambda \geqslant \lambda_0, \tag{2.15}$$

$$F_{st} = 2\pi\kappa a A_1, \tag{2.16}$$

$$\hat{F}_d = -16\pi\mu a \varepsilon^3 \delta \hat{U}. \tag{2.17}$$

The corresponding components of velocity $\hat{\boldsymbol{u}}$ are

$$\frac{\hat{u}_\lambda}{\hat{U}} = \left(\frac{\delta}{\sqrt{\sinh^2\lambda + \sin^2\zeta}}\right)\left[\left(3\varepsilon^2 - 1\right)\cosh\lambda \ln\frac{\cosh\lambda + 1}{\cosh\lambda - 1} - 2\left(1-\varepsilon^2\right)\coth^2\lambda + 4\right]\sin\zeta, \tag{2.18a}$$

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$$\frac{\hat{u}_\zeta}{\hat{U}} = \left(\frac{\delta}{\sqrt{\sinh^2\lambda + \sin^2\zeta}}\right)\left[\left(3\varepsilon^2 - 1\right)\sinh\lambda \ln\frac{\cosh\lambda + 1}{\cosh\lambda - 1} + 2\left(1 - \varepsilon^2\right)\coth\lambda\right]\cos\zeta, \tag{2.18b}$$

where $\delta = \{2\varepsilon + (3\varepsilon^2 - 1)\ln[(1+\varepsilon)/(1-\varepsilon)]\}^{-1}$. Hence, using (2.3), (2.4), and (2.15)–(2.18) we find

$$U = \left(\frac{\kappa A_1}{\mu}\right)\left(\frac{1}{8\varepsilon^3}\right)\left[\left(3\varepsilon^2 - 1\right)\left(1 + \sqrt{1-\varepsilon^2}\right)\ln\left(\frac{1+\varepsilon}{1-\varepsilon}\right) + 2\,\varepsilon\left(1 + \sqrt{1-\varepsilon^2} - 4\varepsilon^2\right)\right]. \tag{2.19}$$

Equation (2.19) approaches $U = \kappa A_1/3\mu$ as $\varepsilon \to 0$ and diverges logarithmically as $\varepsilon \to 1$. The divergence is due to the fact that $\hat{F}_d$ logarithmically decays to zero while F_{st} remains unchanged as ε approaches one (see (2.16) and (2.17)).

3. Discussion

We have derived exact analytical expressions for the Marangoni propulsion of spheroidal particles induced by the release of an insoluble surface-active agent from the particle. Our calculations utilized the reciprocal theorem so did not involve solving for the flow field, which considerably simplified the analyses. As articulated clearly by Lauga & Davis (2012), the calculation we have outlined makes the assumptions of small capillary, Péclet and Reynolds numbers. Thus, we expect the results to be valid when

$$C_a = \frac{\mu U}{\gamma_0} = \frac{\kappa A_1}{\gamma_0} \ll 1, \tag{3.1a}$$

$$P_e = \frac{aU}{D} = \frac{a\kappa A_1}{\mu D} \ll 1, \tag{3.1b}$$

$$R_e = \frac{\rho U a}{\mu} = \frac{\rho\kappa A_1 a}{\mu^2} \ll 1, \tag{3.1c}$$

where D is the diffusivity of the active agent and ρ is the liquid density.

Our approach is not restricted to a particular choice of boundary condition for the concentration of the active agent at the contact line, since the results can be applied to both systems with a prescribed rate of release at the boundary (Zhang *et al.* 2013) and systems with a fixed concentration at the boundary (Lauga & Davis 2012). In either situation, the coefficients A_n would be determined (see (2.5), (2.10) and (2.15)) and only A_1 enters the final formulae (see (2.9), (2.14) and (2.19)). Finally, although we considered the self-propulsion of single particles in this work, our study is the first step in developing a continuum model for the collective Marangoni propulsion of a swarm of active particles.

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