A NOTE ON THE ELECTROPHORESIS OF A UNIFORMLY CHARGED PARTICLE

by A. SELLIER[†]

(LMFA, CNRS UMR 5509, Ecole Centrale de Lyon/UCBL, France)

[Received 10 February 1999. Revises 7 February 2001 and 3 September 2001]

Summary

We examine the electrophoretic motion of a uniformly charged particle embedded in a varying electric field $\mathbf{E}_\infty$. If R and κ^{-1} respectively denote the typical radius of curvature of the particle's surface and the usual Debye–Hückel screening length we assume that $R \gg \kappa^{-1}$ and allow variations of $\mathbf{E}_\infty$ over lengths of order at least R. Under these assumptions, this paper shows that it is unnecessary to calculate the total electric field in the electrolyte when determining the rigid-body motion of the particle. The well-known Smoluchowski solution is thereafter readily recovered. Finally, we pay special attention to orthotropic and uniformly charged particles and detail the case of a solid ellipsoid.

1. Introduction and assumptions

Electrophoresis is defined as the transport of charged colloidal particles by an applied and possibly non-uniform electric field $\mathbf{E}_\infty$ (in this paper, $\mathbf{E}_\infty$ denotes the external electric field that would prevail when there is no particle). Many chemical and biological experimental applications, such as particle analysis or separation, actually consider the electrophoretic motion of solid particles in viscous electrolytes.

Except in the case of proximal boundaries (see for instance Keh and Anderson (**1**)), one may restrict the analysis to a single particle embedded in an unbounded viscous fluid. The charge on the surface of the particle S (see Fig. 1) is balanced by a diffuse cloud, C, of counter-ions surrounding the particle. Since the total charge is zero, one speaks of a double-layer for $S \cup C$ and we denote by S^+ the outer boundary of C.

At thermal equilibrium, for $\mathbf{E}_\infty = \mathbf{0}$ the particle and the electrolyte are motionless and the previous charges induce in the fluid domain an electrostastic potential ψ governed, for the Gouy–Chapman theory (see Hunter (**2**), Russel, Saville and Schowalter (**3**)) by the Poisson–Boltzmann equation. Accordingly, both ψ and the charge density ρ in C quickly decay away from the surface S and vanish at a distance of order of the Debye–Hückel screening length κ^{-1}. This typical length depends on the permittivity constant ϵ of the electrolyte, the thermal energy kT (with k the Boltzmann constant), the fundamental charge e and the concentration and valency of each type of ion far from the particle.

For a weak applied field $\mathbf{E}_\infty$ (of electrostatic potential ϕ_∞) the previous charge distributions approximately remain unchanged and the total electrostatic potential becomes $\psi + \phi$. Note that ϕ differs from ϕ_∞ since the charges in $S \cup C$ actually modify the applied field. Within the double

[†] Now at: LadHyX, Ecole Polytechnique, 91128 Palaiseau Cedex, France.

Q. Jl Mech. Appl. Math. (2002) 55 (4), 561–572

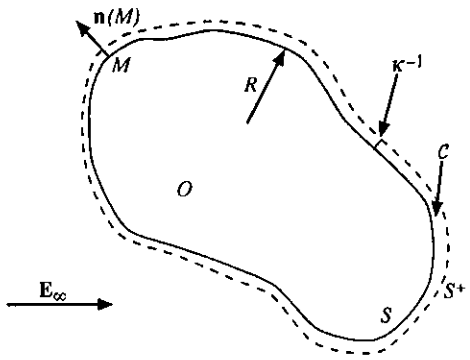

Fig. 1 A charged particle embedded in $\mathbf{E}_\infty$.

layer, the field $\mathbf{E} = -\nabla\phi$ induces a relative displacement of the diffuse cloud with respect to the surface S (except for polarization effects within the double layer (see for instance Fixman (**4**) and O'Brien (**5**)) this rearrangement does not affect the electric field **E**). Through viscous effects the solvent outside C, that is, in the outer domain, also moves but remains quiescent far from the particle. Consequently, for a steady fluid motion the particle experiences a rigid-body motion of unknown angular and translational velocities ω and **U** (where **U** designates the velocity of any origin O, see Fig. 1, attached to the particle). For a viscous electrolyte, the determination of $(\omega, \mathbf{U})$ requires solving the Poisson equation for **E** and, for the fluid motion, the quasistatic Stokes equations with $\rho\mathbf{E}$ as body force within the double layer. Such a task is very cumbersome. However, whenever the typical radius of curvature, R, of S is much larger than the Debye screening length ($\kappa R \gg 1$), the surface looks like a plane within the thin double layer. By combining the one-dimensional Stokes and Poisson's equations in the cloud layer, one thereafter obtains for the fluid velocity **u** in the outer domain, the following boundary condition (see Hunter (**2**), Anderson (**6**)) at each point M of the surface S^+:

$$\mathbf{u}(M) - (\mathbf{U} + \omega \wedge \mathbf{OM}) := \mathbf{u}^s(M) = -\frac{\epsilon\zeta(M)}{\mu}\mathbf{E}_t(M) \quad \text{on } S^+, \tag{1.1}$$

where this form for the 'slip velocity' $\mathbf{u}^s(M)$ is known as the Helmholtz–Smoluchowski equation, the subscript t denotes the tangential component, μ is the solvent viscosity and the so-called zeta potential ζ is equal to ψ on the shear surface (such a surface defined in Hunter (**2**) is approximated by S). The zeta potential plays a central role in electrical aspects of surface chemistry (see Adamson (**7**)). Through adequate models within the double layer (see Hiemenz and Rajagopalan (**8**)) it is possible to relate ζ to the charge density on S. In the outer domain, the electrostatic potential ϕ satisfies the Laplace equation and, for a non-conducting particle (that is, when the double layer admits no charge transfer across it) the boundary condition reads

$$\nabla\phi\cdot\mathbf{n}(M) = 0 \quad \text{on } S^+, \tag{1.2}$$

where $\mathbf{n}(M)$ denotes the outer unit normal on S^+. Note that the net charge of $S \cup C$ is zero and for a thin double layer the outer field **E** exerts zero force and torque on the particle (see Anderson (**6**)). Accordingly, one deduces ($\mathbf{U}, \omega$) by setting to zero the torque (about O for instance) and the force exerted by the outer fluid on S^+. For a uniform external field $\mathbf{E}_\infty$ and a uniformly charged particle (that is, of constant ζ potential) the celebrated result of Smoluchowski

$$\mathbf{U} = \frac{\epsilon\zeta}{\mu}\mathbf{E}_\infty, \qquad \omega = \mathbf{0} \tag{1.3}$$

holds. The solution (1.3) was first derived by Smoluchowski (**9**) for a sphere and further extended to an arbitrary shape by Morrison (**10**) and Teubner (**11**). Its validity rests on the following assumptions:

(i) the particle is both rigid and non-conducting,
(ii) the surrounding solvent is unbounded,
(iii) the typical radius of curvature R satisfies $\kappa R \gg 1$, that is, the 'slip velocity' model (1.1) applies,
(iv) the charge distributions within the double layer are not disturbed by the applied field $\mathbf{E}_\infty$,
(v) the zeta potential ζ is uniform over the surface of the particle,
(vi) the applied field $\mathbf{E}_\infty$ is uniform.

However, many practical applications require to relax at least one of these assumptions. For instance, one may assume that the particle is conducting. The colloquial piece of work of Henry (**12**) considers the case of a conducting sphere with a centrally-symmetrical charge density within the diffuse cloud. If γ' and γ respectively denote the sphere and electrolyte specific conductivity, Henry establishes that, under assumptions (ii) to (vi), $\omega = \mathbf{0}$ but this time $\mathbf{U} = 2\gamma\epsilon\zeta\mathbf{E}_\infty/(2\gamma + \gamma')\mu$. As the ratio γ'/γ vanishes, one of course recovers Smoluchowski's result (1.3). It is worth pointing out that Henry (**12**) also considers the case of a thick double-layer (actually by relaxing both assumptions (i) and (iii)) for a rigid and spherical particle. Increasing ζ results in a large change of ion densities within the thin double-layer. In such circumstances, the assumption (iv) breaks down and, for a spheroid, the reader is directed to the refined treatment of O'Brien and Ward (**13**)). Hence, for (1·3) to hold the zeta potential ζ must be sufficiently small. The effect of non-uniform zeta potential on the solution (1.3) has been also recently addressed for a sphere by Anderson (**14**), Keh and Anderson (**1**) and for a spheroidal particle by Fair and Anderson (**15**).

Our aim is to obtain the solution ($\mathbf{U}, \omega$) if the previous assumption (vi) is relaxed, more precisely when the applied field $\mathbf{E}_\infty$ may vary over lengths of order of the radius R. Note that Anderson (**14**) provides the answer for a sphere and shows that for such a particle (1.3) remains valid with $\mathbf{E}_\infty$ replaced by its value at the centre of the sphere.

Before tackling our problem it is worth adding a new assumption. As pointed out by one referee, each available work in the field of electrophoresis (at least to the author's very best knowledge) neglects the polarization body force $\mathbf{f} := (\mathbf{P}\cdot\nabla)\cdot\mathbf{E}$ that takes place in the electrolyte. This force may contribute to the net force and torque exerted by the electric field on the surface of the particle. Henceforth, we add a new assumption.

(vii) The net force and torque exerted on the surface of the particle by polarization effects in the electrolyte are neglected.

The paper is organized as follows. By applying the reciprocal theorem to the viscous fluid outside S^+, we derive our general solution in section 2. Section 3 deals with the more tractable case of orthotropic particles whilst a few concluding remarks in section 4 close the paper.

2. A solution solely expressed in terms of the applied field

Henceforth, we keep the assumptions (i) to (v) but weaken the condition (vi) by allowing the applied field $\mathbf{E}_\infty$ to vary over lengths of order at least $R \gg \kappa^{-1}$. This section derives, within this framework, the solution $(\mathbf{U}, \omega)$.

For $\kappa R \gg 1$, one actually approximates the outer surface S^+ by S and imposes the boundary conditions (1.1), (1.2) on S (this discards the case of variations of $\mathbf{E}_\infty$ on the κ^{-1} scale). Since we adopt the *quasi-static* form of the creeping motion equations for the electrolyte in the outer domain, the fluid velocity $\mathbf{u}$ and pressure p obey the following equations and boundary conditions

$$\mu\nabla^2\mathbf{u} = \nabla p \quad \text{in } \Omega_S, \tag{2.1}$$

$$\nabla\cdot\mathbf{u} = 0 \quad \text{in } \Omega_S, \tag{2.2}$$

$$(\mathbf{u}, p) \to (\mathbf{0}, 0) \quad \text{as } r \to \infty, \tag{2.3}$$

$$\mathbf{u} = \mathbf{u}_d \quad \text{on } S, \tag{2.4}$$

where Ω_S designates the unbounded domain outside S, $r := OM$ (with O the origin previously alluded to) and $\mathbf{u}_d$ is a vector-valued function. If $\phi' := \phi - \phi_\infty$ denotes the perturbation potential in the outer domain Ω_S the combination of (1.1) and (1.2) yields

$$\mathbf{u}_d(M) = \mathbf{U} + \omega \wedge \mathbf{OM} + \frac{\epsilon\zeta}{\mu}(\nabla\phi' - \mathbf{E}_\infty) \quad \text{on } S. \tag{2.5}$$

Under the usual Cartesian tensor summation convention, the symmetric stress tensor pertaining to the Stokes flow $(\mathbf{u}, p)$ reads $\sigma = \sigma_{ij}\mathbf{e}_i \otimes \mathbf{e}_j$ with

$$\sigma_{ij} = \sigma_{ij}(\mathbf{u}, p) = -p\delta_{ij} + \mu(\partial u_i/\partial x_j + \partial u_j/\partial x_i), \tag{2.6}$$

where δ_{ij} denotes the Kronecker delta and $\mathbf{OM} = x_i\mathbf{e}_i$.

As explained in the previous section, the solvent remains at rest far from the particle and this justifies the condition (2.3) for $\mathbf{u}$. Moreover, if we require a constant pressure far from the particle the equations (2.1), (2.2) imply that, far from O, the pressure and stress tensor σ decay at least as fast as $1/r^2$ whilst the fluid velocity $\mathbf{u}$ decays at least as fast as $1/r$. The proof of these basic behaviours rests on the far-field expansion of the creeping motion equations (2.1), (2.2) in terms of spherical harmonics (see Lamb (**16**), Pozrikidis (**17**)). Accordingly, the flow satisfies (2.3). In addition, the Lorentz reciprocal theorem holds, that is, if $(\mathbf{u}, p, \sigma)$ and $(\mathbf{u}', p', \sigma')$ satisfy (2.1) to (2.4) respectively for data $\mathbf{u}_d$ and $\mathbf{u}'_d$ then

$$\int_S \mathbf{u}'_d\cdot\sigma\cdot\mathbf{n}dS = \int_S \mathbf{u}_d\cdot\sigma'\cdot\mathbf{n}dS. \tag{2.7}$$

Since it is available in standard textbooks (see Kim and Karrila (**18**), Pozrikidis (**17**)), the proof is not reproduced here. However, note that the derivations combine the reciprocal identity $\nabla(\sigma\cdot\mathbf{u}' - \sigma'\cdot\mathbf{u}) = 0$ in Ω_S and the previous behaviours far from S.

The requirement of zero net force $\mathbf{F} = F_i\mathbf{e}_i$ and torque $\Gamma = \Gamma_i\mathbf{e}_i$ (about the origin O) exerted by the fluid motion on the particle imposes, for $i \in \{1, 2, 3\}$,

$$F_i = \int_S \mathbf{e}_i\cdot\sigma\cdot\mathbf{n}dS = 0, \quad \Gamma_i = \int_S \mathbf{e}_i\cdot[\mathbf{OM} \wedge \sigma\cdot\mathbf{n}]dS = \int_S [\mathbf{e}_i \wedge \mathbf{OM}]\cdot\sigma\cdot\mathbf{n}dS = 0. \tag{2.8}$$

This latter form of Γ_i actually invokes the identity $\mathbf{a}\cdot(\mathbf{b}\wedge\mathbf{c}) = (\mathbf{a}\wedge\mathbf{b})\cdot\mathbf{c}$. If one introduces (see Happel and Brenner (**19**)), for $i \in \{1, 2, 3\}$, the translational motion $(\mathbf{u}_T^{(i)}, p_T^{(i)}, \sigma_T^{(i)})$ and the rotational motion $(\mathbf{u}_R^{(i)}, p_R^{(i)}, \sigma_R^{(i)})$ that satisfy the system (2.1) to (2.3) and the boundary conditions

$$\mathbf{u}_T^{(i)} = \mathbf{e}_i, \qquad \mathbf{u}_R^{(i)} = \mathbf{e}_i \wedge \mathbf{OM} \qquad \text{on } S, \tag{2.9}$$

then a legitimate choice of $\mathbf{u}_T^{(i)}$ and $\mathbf{u}_R^{(i)}$ for $\mathbf{u}'$ in applying the relation (2.7) makes it possible to cast the equalities (2.8) into the following forms (see (2.5)):

$$\int_S \mathbf{U}\cdot\sigma_T^{(i)}\cdot\mathbf{n}dS + \int_S [\omega\wedge\mathbf{OM}]\cdot\sigma_T^{(i)}\cdot\mathbf{n}dS = \frac{\epsilon}{\mu}\left\{\int_S \zeta\mathbf{E}_\infty\cdot\sigma_T^{(i)}\cdot\mathbf{n}dS - I_T^{(i)}\right\}, \tag{2.10}$$

$$\int_S \mathbf{U}\cdot\sigma_R^{(i)}\cdot\mathbf{n}dS + \int_S [\omega\wedge\mathbf{OM}]\cdot\sigma_R^{(i)}\cdot\mathbf{n}dS = \frac{\epsilon}{\mu}\left\{\int_S \zeta\mathbf{E}_\infty\cdot\sigma_R^{(i)}\cdot\mathbf{n}dS - I_R^{(i)}\right\}, \tag{2.11}$$

where the quantities $I_T^{(i)}$ and $I_R^{(i)}$ depend on the perturbation potential ϕ' and read

$$I_T^{(i)} := \int_S \zeta\nabla\phi'\cdot\sigma_T^{(i)}\cdot\mathbf{n}dS, \qquad I_R^{(i)} := \int_S \zeta\nabla\phi'\cdot\sigma_R^{(i)}\cdot\mathbf{n}dS. \tag{2.12}$$

Our main result is that the integrals $I_T^{(i)}$ and $I_R^{(i)}$ actually vanish as soon as ζ is uniform over the surface of the particle (assumption (v)).

First, we observe that the perturbation potential ϕ' obeys (see the previous section and (1.2)) the following well-posed boundary-value problem

$$\nabla^2\phi' = \mathbf{0} \qquad \text{in } \Omega_S, \tag{2.13}$$

$$\nabla\phi' \to \mathbf{0} \quad \text{as } r \to \infty, \tag{2.14}$$

$$\nabla\phi'\cdot\mathbf{n} = \mathbf{E}_\infty\cdot\mathbf{n} \qquad \text{on } S. \tag{2.15}$$

The boundary conditions (2.14), (2.15) are indeed sufficient to find a unique solution, ϕ', of Laplace's equation (2.13). Thus, one determines in $\Omega_S \cup S$ the field $\mathbf{v} := \nabla\phi'$. Assuming that $\mathbf{E}_\infty$ is induced by charges lying outside the particle, the condition (2.15) yields $\int_S \mathbf{v}\cdot\mathbf{n}dS = 0$. Accordingly, one deduces the refined far-field behaviour

$$|\mathbf{v}| \sim 1/r^3 \qquad \text{as } r \to \infty. \tag{2.16}$$

Morrison (**11**) exploits the fact that any potential flow satisfies the Navier–Stokes equations (with pressure and fluid velocity related by Bernoulli's equation). Here, we observe that, since the flow is potential, $\mathbf{v}$ obeys the creeping motion equations (2.1), (2.2) with a constant pressure. The behaviour (2.14) and previous remarks actually show that this constant is zero. Thus, for the Stokes flow $(\mathbf{v}, 0)$ the stress tensor $\sigma(\phi') := \sigma(\mathbf{v}, 0)$ becomes (see (2.6))

$$\sigma(\phi') = 2\mu\frac{\partial^2\phi'}{\partial x_i\partial x_j}\mathbf{e}_i\otimes\mathbf{e}_j. \tag{2.17}$$

For a constant zeta potential ζ, the behaviour (2.16) makes it possible to employ the reciprocal identity (2.7) when calculating the terms $I_T^{(i)}/\zeta$ and $I_R^{(i)}/\zeta$. By invoking (2.17), one thereafter obtains

$$\frac{I_T^{(i)}}{\zeta} = \int_S \mathbf{e}_i \cdot \sigma(\phi') \cdot \mathbf{n} dS = 2\mu \int_S \frac{\partial}{\partial x_j}\left(\frac{\partial \phi'}{\partial x_i}\right) n_j dS, \tag{2.18}$$

$$\frac{I_R^{(i)}}{\zeta} = \int_S [\mathbf{e}_i \wedge \mathbf{OM}] \cdot \sigma(\phi') \cdot \mathbf{n} dS = 2\mu \int_S \left[\epsilon_{kin} x_n \frac{\partial^2 \phi'}{\partial x_k \partial x_j}\right] n_j dS, \tag{2.19}$$

where ϵ_{kin} designates the completely antisymmetric permutation tensor. For r sufficiently large, we denote by $\Omega(r)$ the region that is enclosed by the particle surface S and the surface $S_r := \{M;\ OM = r\}$. Owing to the divergence theorem, it follows that

$$\frac{I_T^{(i)}}{2\mu\zeta} = -\int_{\Omega(r)} \frac{\partial}{\partial x_i}(\nabla^2 \phi') d\Omega + \int_{S_r} \frac{\partial^2 \phi'}{\partial x_i \partial x_j} \frac{x_j}{r} dS, \tag{2.20}$$

$$\frac{I_R^{(i)}}{2\mu\zeta} = -\int_{\Omega(r)} \frac{\partial}{\partial x_j}\left[\epsilon_{kin} x_n \frac{\partial^2 \phi'}{\partial x_k \partial x_j}\right] d\Omega + \int_{S_r} \frac{\epsilon_{kin} x_n x_j}{r} \frac{\partial^2 \phi'}{\partial x_k \partial x_j} dS. \tag{2.21}$$

Since $\epsilon_{kij} + \epsilon_{jik} = 0$ and (2.13) holds, the volume integrals on the right-hand sides of (2.20), (2.21) vanish. In addition, in virtue of (2.16) the surface integrals over S_r go to zero as $r \to \infty$ (the reader may actually check that this remains true whenever $|\nabla\phi'| \sim 1/r^2$). The external electrostatic potential ϕ_∞ does not decay as fast as $1/r$ far from the particle and this feature prevents us from applying the same treatment to the remaining right-hand sides of (2.10), (2.11). In other words, there exists a Stokes flow satisfying (2.1) to (2.4) with $\mathbf{u}_d = \nabla\phi_\infty$ but this flow is not $(\nabla\phi_\infty, 0)$.

Following Happel and Brenner (**19**), we introduce the widely employed translation tensor **K**, rotation tensor Ω and coupling tensors **C** and **D** whose Cartesian components obey

$$-\mu K_{ij} = \int_S \mathbf{e}_j \cdot \sigma_T^{(i)} \cdot \mathbf{n} dS, \quad -\mu \Omega_{ij} = \int_S [\mathbf{e}_j \wedge \mathbf{OM}] \cdot \sigma_R^{(i)} \cdot \mathbf{n} dS, \tag{2.22}$$

$$-\mu C_{ij} = \int_S [\mathbf{e}_j \wedge \mathbf{OM}] \cdot \sigma_T^{(i)} \cdot \mathbf{n} dS; \quad -\mu D_{ij} = \int_S \mathbf{e}_j \cdot \sigma_R^{(i)} \cdot \mathbf{n} dS. \tag{2.23}$$

These tensors characterize the resistance of the particle to a rigid-body motion and depend on the location of the origin O (except for **K**) and on the particle shape. In terms of this notation, the equalities (2.10), (2.11) become

$$\mathbf{K} \cdot \mathbf{U} + \mathbf{C} \cdot \omega = -\frac{\epsilon\zeta}{\mu^2}\left[\int_S \mathbf{E}_\infty \cdot \sigma_T^{(i)} \cdot \mathbf{n} dS\right] \mathbf{e}_i, \tag{2.24}$$

$$\mathbf{D} \cdot \mathbf{U} + \Omega \cdot \omega = -\frac{\epsilon\zeta}{\mu^2}\left[\int_S \mathbf{E}_\infty \cdot \sigma_R^{(i)} \cdot \mathbf{n} dS\right] \mathbf{e}_i. \tag{2.25}$$

Hence, $(\mathbf{U}, \omega)$ obeys a system of six linear algebraic equations whose associated 6×6 square matrix, denoted by **M**, is usually referred as the resistance matrix. By exploiting once more the reciprocal theorem, Happel and Brenner (**18**) have shown that the tensors **K** and $\mathbf{\Omega}$ are symmetric whilst $\mathbf{C} = \mathbf{D}^T$. Thus, **M** is a symmetric matrix. Moreover, the condition of positive energy dissipation (see Happel and Brenner (**19**)) requires the matrices **M**, **K** and $\mathbf{\Omega}$ to be positive-definite and thereby invertible. Accordingly, (2.24), (2.25) admits a unique solution.

If $\mathbf{E}_\infty$ is uniform one readily recovers the Smoluchowski solution (1.3) by using the system (2.24), (2.25). Our results (2.24), (2.25) also show that, under the assumptions (i) to (v), the determination of $(\mathbf{U}, \omega)$ does not require calculation of the perturbed electric field $\mathbf{E}$ even if the applied field $\mathbf{E}_\infty$ admits variations (over lengths at least of order of the typical radius of curvature R).

3. Application to orthotropic bodies

Despite the simple form of the system (2.24), (2.25) only a numerical determination of $(\mathbf{U}, \omega)$ remains thinkable for a particle of arbitrary shape (as soon as $\mathbf{E}_\infty$ is not uniform). However, it is worth considering how simple variations of the external field $\mathbf{E}_\infty$ (for instance, a linearly varying field) affect the Smoluchowski solution.

This section examines such a question for an orthotropic particle, that is, a particle admitting three mutually perpendicular symmetry planes. For our orthotropic body we take as origin O the intersection of the planes of symmetry and for $\mathbf{e}_1, \mathbf{e}_2$ and $\mathbf{e}_3$ vectors normal to these planes. Under these choices (**19**), the coupling tensors $\mathbf{C}$ and $\mathbf{D}$ vanish whilst $\mathbf{K}$ and Ω become diagonal. According to (2.24), (2.25), one thereafter separately determines each component of the translation and rotation velocities $\mathbf{U}$ and ω (recall that $\mathbf{U}$ is the velocity at point O).

In computing $\mathbf{K}$, Ω and the right-hand sides of (2.24), (2.25) one needs the values of the surface forces $\sigma_T^{(i)}\cdot\mathbf{n} = \mu\mathbf{f}_T^{(i)}$ and $\sigma_R^{(i)}\cdot\mathbf{n} = \mu\mathbf{f}_R^{(i)}$ exerted by the fluid on the particle for the previously introduced translational and rotational motions. Note that neither $\mathbf{f}_T^{(i)}$ nor $\mathbf{f}_R^{(i)}$ depends on the fluid viscosity μ. For a sphere of radius a about O (the simplest orthotropic particle), one obtains

$$\mathbf{f}_T^{(i)}(M) = -\frac{3}{2a}\mathbf{e}_i; \qquad \mathbf{f}_R^{(i)}(M) = -\frac{3}{a}(\mathbf{e}_i \wedge \mathbf{OM}). \tag{3.1}$$

The reader may actually check these formula by invoking Lamb (**16**) for $\mathbf{f}_T^{(i)}$ and Jeffery (**20**) for $\mathbf{f}_R^{(i)}$ (see also (3.16) and (3.18)). For our sphere, it follows that (no summation over i in (3.2))

$$K_{ii} = 6\pi a; \qquad \int_S \mathbf{E}_\infty\cdot\mathbf{f}_T^{(i)} dS = -\frac{3}{2a}\int_S \frac{\partial\phi_\infty}{\partial x_i} dS, \tag{3.2}$$

$$\int_S \mathbf{E}_\infty\cdot\mathbf{f}_R^{(i)} dS = -3\int_S (\mathbf{E}_\infty \wedge \mathbf{e}_i)\cdot\mathbf{n} dS = -3\int_{B(a)} \epsilon_{ijk}\frac{\partial^2\phi_\infty}{\partial x_j \partial x_k} d\Omega = 0 \tag{3.3}$$

if $B(a) := \{M;\ \ OM < a\}$. Moreover, since $\partial\phi_\infty/\partial x_i$ is harmonic in the sphere $B(a)$, one deduces (see Kellogg (**21**)) that $[\partial\phi_\infty/\partial x_i](O)$ is the arithmetic mean of $\partial\phi_\infty/\partial x_i$ over S. Thus, the combination of (2.24), (2.25) and (3.2), (3.3) yields, for any external field $\mathbf{E}_\infty$,

$$\mathbf{U} = \frac{\epsilon\zeta}{\mu}\mathbf{E}_\infty(O), \qquad \omega = \mathbf{0}. \tag{3.4}$$

This result recovers the conclusions of Anderson (**13**) and Keh and Anderson (**1**): for a sphere one has only to replace $\mathbf{E}_\infty$ by $\mathbf{E}_\infty(O)$ in the Smoluchowski solution (1.3). For other orthotropic particles, we use for $\mathbf{E}_\infty$ its Taylor polynomial expansion about the origin O. By superposition we restrict ourselves to the case

$$\mathbf{E}_\infty = \mathbf{E}_\infty^{(n)} := \sum_{i_1,i_2,i_3}^{n} a_{i_1,i_2,i_3}^{n,j} x_1^{i_1} x_2^{i_2} x_3^{i_3} \mathbf{e}_j, \qquad n \geqslant 1 \tag{3.5}$$

and denote by $(\mathbf{U}^{(n)}, \omega^{(n)})$ the associated solution $(\mathbf{U}, \omega)$. The previous symbol $\sum_{k,l,m}^{n}$ indicates a summation over positive integers k, l and m such that $k + l + m = n$. Note that the properties $\nabla \wedge \mathbf{E}_\infty = \mathbf{0}$ and $\nabla^2 \phi_\infty = 0$ impose relations between the real families $(a^{n,j}_{i_1,i_2,i_3})$ which can be expressed in terms of derivatives of the electrostatic potential ϕ_∞ at O. Since $\mathbf{E}^{(0)}_\infty = \mathbf{E}_\infty(O)$, the solution $(\mathbf{U}^{(0)}, \omega^{(0)})$ is given by (3.4). For $n \geqslant 1$, it is worth taking into account the symmetry properties of surface forces $\sigma^{(i)}_T \cdot \mathbf{n}$ and $\sigma^{(i)}_R \cdot \mathbf{n}$. As the Appendix shows, for an orthotropic particle the following properties hold, for $M(x_1, x_2, x_3)$ belonging to S,

$$\mathbf{e}_1 \cdot \mathbf{f}^{(1)}_T(x_1, x_2, x_3) = \mathbf{e}_1 \cdot \mathbf{f}^{(1)}_T(|x_1|, |x_2|, |x_3|), \tag{3.6}$$

$$\mathbf{e}_j \cdot \mathbf{f}^{(1)}_T(x_1, x_2, x_3) = \mathrm{sgn}(x_1)\mathrm{sgn}(x_j)[\mathbf{e}_j \cdot \mathbf{f}^{(1)}_T](|x_1|, |x_2|, |x_3|) \quad \text{for } j \in \{2, 3\}, \tag{3.7}$$

$$\mathbf{e}_1 \cdot \mathbf{f}^{(1)}_R(x_1, x_2, x_3) = \mathrm{sgn}(x_1)\mathrm{sgn}(x_2)\mathrm{sgn}(x_3)[\mathbf{e}_1 \cdot \mathbf{f}^{(1)}_R](|x_1|, |x_2|, |x_3|), \tag{3.8}$$

$$\mathbf{e}_j \cdot \mathbf{f}^{(1)}_R(x_1, x_2, x_3) = \mathrm{sgn}(x_j)\mathrm{sgn}(x_2)\mathrm{sgn}(x_3)[\mathbf{e}_j \cdot \mathbf{f}^{(1)}_R](|x_1|, |x_2|, |x_3|), \quad j \in \{2, 3\}, \tag{3.9}$$

where $\mathrm{sgn}(x) := x/|x|$ for any non-zero value of x. Morevoer $dS(\pm x_1, \pm x_2, \pm x_3) = dS(x_1, x_2, x_3)$. Accordingly, many integrals encountered when calculating the right-hand sides of (2.24), (2.25) for $i = 1$ and $\mathbf{E}^{(n)}_\infty$ actually vanish. Two different cases occur for the solution $(\mathbf{U}^{(n)}, \omega^{(n)})$.

(i) If $n = 2m \geqslant 2$, then $\omega^{(n)}_1 = \mathbf{0}$ and $\mathbf{U}^{(n)}_1$ is given by

$$K_{11}\mathbf{U}^{(n)}_1 = -\frac{\epsilon\zeta}{\mu}\left\{ \sum_{j_1,j_2,j_3}^{m} \int_S a^{n,1}_{2j_1,2j_2,2j_3} x_1^{2j_1} x_2^{2j_2} x_3^{2j_3} [\mathbf{e}_1 \cdot \mathbf{f}^{(1)}_T] dS \right.$$
$$\left. + \sum_{j_1,j_2,j_3}^{m-1} \sum_{j=2}^{3} \int_S a^{n,j}_{2j_1+1,2j_2+\delta_{j2},2j_3+\delta_{j3}} x_1^{2j_1+1} x_2^{2j_2+\delta_{j2}} x_3^{2j_3+\delta_{j3}} [\mathbf{e}_j \cdot \mathbf{f}^{(1)}_T] dS \right\}. \tag{3.10}$$

Remember (see (2.6)) that δ designates the Kronecker delta.

(ii) If $n = 2m + 1 \geqslant 1$, then $\mathbf{U}^{(n)}_1 = \mathbf{0}$ and $\omega^{(n)}_1$ is given by

$$\Omega_{11}\omega^{(n)}_1 = -\frac{\epsilon\zeta}{\mu}\left\{ \delta'_{n1} \sum_{j_1,j_2,j_3}^{m-1} \int_S a^{n,1}_{2j_1+1,2j_2+1,2j_3+1} x_1^{2j_1+1} x_2^{2j_2+1} x_3^{2j_3+1} [\mathbf{e}_1 \cdot \mathbf{f}^{(1)}_R] dS \right.$$
$$\left. + \sum_{j_1,j_2,j_3}^{m} \sum_{j=2}^{3} \int_S a^{n,j}_{2j_1,2j_2+\delta'_{j2},2j_3+\delta'_{j3}} x_1^{2j_1} x_2^{2j_2+\delta'_{j2}} x_3^{2j_3+\delta'_{j3}} [\mathbf{e}_j \cdot \mathbf{f}^{(1)}_R] dS \right\} \tag{3.11}$$

where $\delta'_{kl} := 1 - \delta_{kl}$.

It is straightforward to deduce the solution $(\mathbf{U}^{(n)}, \omega^{(n)})$ by applying cyclical changes of indices to our formulae (3.10), (3.11). Thus, only even or odd values of n respectively contribute to the translational and angular velocities. However, even and odd values of n indirectly interact since the rotation changes the external field felt by the particle and thereafter modifies the translational velocity as the particle moves. Case (i) indicates, for instance, that an orthotropic particle embedded in a quadratic electric field does not rotate. For a linear external field (not necessarily vanishing at O) such a particle translates at velocity $\mathbf{U} = \epsilon\zeta\mathbf{E}_\infty(O)/\mu$ and rotates at the angular velocity $\omega = \omega_i \mathbf{e}_i$ such that (apply (3.11) for $n = 1$)

$$\omega_1 = \frac{\epsilon\zeta}{\mu\Omega_{11}} \frac{\partial^2\phi_\infty}{\partial x_2 \partial x_3}(O) \int_S [x_3\mathbf{e}_2 + x_2\mathbf{e}_3]\cdot\mathbf{f}_R^{(1)} dS, \tag{3.12}$$

$$\omega_2 = \frac{\epsilon\zeta}{\mu\Omega_{22}} \frac{\partial^2\phi_\infty}{\partial x_1 \partial x_3}(O) \int_S [x_3\mathbf{e}_1 + x_1\mathbf{e}_3]\cdot\mathbf{f}_R^{(2)} dS, \tag{3.13}$$

$$\omega_3 = \frac{\epsilon\zeta}{\mu\Omega_{33}} \frac{\partial^2\phi_\infty}{\partial x_1 \partial x_2}(O) \int_S [x_2\mathbf{e}_1 + x_1\mathbf{e}_2]\cdot\mathbf{f}_R^{(3)} dS. \tag{3.14}$$

Of course, for a sphere one recovers $\omega = \mathbf{0}$ (employ (3.1)).

Before closing this section we address the case of an ellipsoidal particle whose surface, $\mathcal{E}$, is defined by

$$x_1^2/a_1^2 + x_2^2/a_2^2 + x_3^2/a_3^2 = 1 \quad \text{for} \quad M(x_1, x_2, x_3) \in \mathcal{E}. \tag{3.15}$$

For this specific body, note that Oberbeck (**22**) and Edwardes (**23**) (further corrected by Perrin (**24**)) respectively provide the diagonal tensors $\mathbf{K}$ and Ω but discard the surface forces $\sigma_T^{(i)}\cdot\mathbf{n}$ and $\sigma_R^{(i)}\cdot\mathbf{n}$. The solutions $\mathbf{f}_T^{(i)}$ and $\mathbf{f}_R^{(i)}$ are actually available in Jeffery (**20**). The results (26) of this latter paper however suffer from misprint errors (γ_0 to be replaced by γ_0' in the numerators of H and H' and similar corrections for other terms F, F', G and G'). One thereafter obtains, for $M(x_1, x_2, x_3) \in \mathcal{E}$ (without summation over i)

$$\mathbf{f}_T^{(i)}(M) = -\frac{4s(M)}{[\chi + a_i^2\alpha_i]}\mathbf{e}_i, \qquad \mathbf{f}_R^{(i)}(M) = -\frac{4s(M)}{[\chi - a_i^2\alpha_i]}(\mathbf{e}_i \wedge \mathbf{OM}), \tag{3.16}$$

where, if we set $\Delta(t) := \{(a_1^2 + t)(a_2^2 + t)(a_3^2 + t)\}^{1/2}$, then

$$\chi := a_1a_2a_3 \int_0^\infty \frac{dt}{\Delta(t)}, \qquad \alpha_i := a_1a_2a_3 \int_0^\infty \frac{dt}{(a_i^2 + t)\Delta(t)} \tag{3.17}$$

and, if we adopt usual ellipsoidal coordinates $\phi \in [0, \pi]$ and $\theta \in [0, 2\pi]$, the functions s and dS obey, on $\mathcal{E}$,

$$s(M) := \{x_1^2/a_1^4 + x_2^2/a_2^4 + x_3^2/a_3^4\}^{-1/2}, \qquad s(M)dS = a_1a_2a_3 \sin\phi d\phi d\theta. \tag{3.18}$$

By substituting (3.16) into (2.22) it follows that (no summation over i)

$$K_{ii} = \frac{16\pi a_1a_2a_3}{[\chi + a_i^2\alpha_i]}, \qquad \Omega_{ii} = \frac{16\pi a_1a_2a_3[a_1^2 + a_2^2 + a_3^2 - a_i^2]}{3[\chi - a_i^2\alpha_i]}. \tag{3.19}$$

Accordingly, simplifications occur for (3.10) and (3.11). For instance, (3.10) becomes

$$\mathbf{U}^{(n)} = \frac{\epsilon\zeta}{4\pi\mu} \sum_{j_1,j_2,j_3}^{n/2} a^{n,i}_{2j_1,2j_2,2j_3} a_1^{2j} a_2^{2j_2} a_3^{2j_3} \left[\int_{S_1} x_1^{2j_1} x_2^{2j_2} x_3^{2j_3} dS_1\right]\mathbf{e}_i, \qquad n = 2m \geqslant 2, \tag{3.20}$$

where $S_1 = \{M(x_1, x_2, x_3); x_i x_i = 1\}$ denotes the unit sphere in $\mathbb{R}^3$. Moreover, when embedded in a linear external field $\mathbf{E}_\infty$ the ellipsoidal particle experiences a rigid-body motion $(\mathbf{U}, \omega)$ (see (3.12) to (3.14)) given by (no summation over i)

$$\mathbf{U} = \frac{\epsilon\zeta}{\mu}\mathbf{E}_\infty(O), \qquad \omega\cdot\mathbf{e}_i = -\frac{\epsilon\zeta}{\mu[a_1^2 + a_2^2 + a_3^2 - a_i^2]}\{\nabla \wedge [(a_j^2\mathbf{e}_j)\cdot\mathbf{E}_\infty]\}(O)\cdot\mathbf{e}_i. \tag{3.21}$$

For a spheroid whose axis of revolution is $\mathbf{e}_k$, note that $\omega_k = 0$.

4. Concluding remarks

The present work also applies to the osmosis (transport by gradients of solute) of a particle embedded in a non-electrolyte (see Anderson *et al.* (**25**)). The concentration of neutral molecules C plays the role of the electrostatic potential ϕ (with ∇C_∞ the possibly non-uniform external field and C_∞ the given and undisturbed solute concentration). The function C obeys Laplace's equation with the condition (1.2) on S (no transport of molecules across the particle surface) and the 'slip velocity' (see Anderson (**6**))

$$\mathbf{u}^s(M) = -\frac{kT}{\mu}KL^*(\nabla C)_t(M), \tag{4.1}$$

where kT, K and L^* respectively designate the constant thermal energy, a positive 'adsorption' length and first (positive or negative) moment of the solute distribution in the vincinity of S. Both quantities K and L^* may be related to the zeta potential ζ on the particle surface through adequate models (for instance, see Koh and Anderson (**26**)). The length $|L^*|$ is the range of the solute–particle interaction and plays the role of κ^{-1}.

If $|L^*| \ll R$ and ζ is constant over S, the material developed in sections 2 and 3 immediately yields the particle's rigid-body motion $(\mathbf{U}, \omega)$ for possibly non-uniform external fields ∇C_∞.

Acknowledgements

The author is indebted to a referee who drew his attention to the basic work of Henry (**12**) and also questioned the role played by the polarization body force in the electrolyte (thereby suggesting the assumption (vii)).

References

1. H. Keh and J. L. Anderson, Boundary effects on electrophoretic motion of colloidal spheres, *J. Fluid. Mech.* **153** (1985) 417–439.
2. R. J. Hunter, *Zeta Potential in Colloid Science* (Academic Press, New York 1981).
3. W. B. Russel, D. A. Saville and W. R. Schowalter, *Colloidal Dispersions* (Cambridge University Press, Cambridge 1989).
4. J. Fixman, Charged macromolecules in external fields. I. The sphere, *J. Chem. Phys.* **72** (1980) 5177–5186.
5. R. W. O'Brien, The solution of the electrokinetic equations for colloidal particles with thin double layers, *J. Colloid. Interface Sci.* **92** (1983) 204–216.
6. J. L. Anderson, Colloid transport by interfacial forces, *Ann. Rev. Fluid. Mech.* **21** (1989) 61–99.

7. A. W. Adamson and A. Gast, *Physical Chemistry of Surfaces* (Wiley, New York 1997).
8. P. C. Hiemenz and R. Rajagopalan, *Principles of Colloid and Surface Chemistry* (Dekker, New York 1986).
9. M. V. Smoluchowski, In *Handbuch der Elektrizität und des Magnetismus* (ed. L. Graetz and J. A. Barth; Leipzig, 1921).
10. F. A. Morrison, Electrophoresis of a particle of arbitrary shape, *J. Colloid. Interface Sci.* **34** (1970) 210–214.
11. M. Teubner, The motion of charged colloidal particles in electric fields, *J. Chem. Phys.* **76** (1982) 5564–5573.
12. D. C. Henry, The cataphoresis of a sphere, *Proc. R. Soc.* A **133** (1931) 106–129.
13. R. W. O'Brien and D. N. Ward, The electrophoresis of a spheroid with a thin double layer, *J. Colloid. Interface Sci.* **121** (1988) 402–413.
14. J. L. Anderson, Effect of nonuniform zeta potential on particle movements in electric fields, *ibid.* **105** (1985) 45–54.
15. M. C. Fair and J. L. Anderson, Electrophoresis of nonuniformly charged ellipsoidal particles, *ibid.* **127** (1989) 388–400.
16. H. Lamb, *Hydrodynamics*, 6th edn (Cambridge University Press, Cambridge 1932).
17. C. Pozrikidis, *Boundary Integral and Singularity Methods for Linearized Viscous Flow* (Cambridge University Press, Cambridge 1992).
18. S. Kim and S. Karrila, *Microhydrodynamics: Principles and Selected Applications* (Butterworth, London 1991).
19. J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics* (Martinus Nijhoff, The Hague 1973).
20. G. B. Jeffery, The motion of ellipsoidal particles immersed in a viscous fluid, *Proc. R. Soc.* A **102** (1922) 161–179.
21. O. D. Kellogg, *Foundations of Potential Theory* (Dover, New York 1954).
22. Oberbeck, Uber stationare Flussigkeitsbewegungen mit Berucksichtigung der inneren Reibung, *J. Reine Angew. Math.* **81** (1876) 62–80.
23. B. A. Edwardes, Steady motion of a viscous liquid in which an ellipsoid is constrained to rotate about a principal axis, *Quart. J. Math.* **26** (1892) 70–78.
24. F. Perrin, Mouvement Brownien d'un ellipsoide (I). Dispersion diélectrique pour des molécules ellipsoidales, *J. Phys. Radium.* **5** (1934) 497–519.
25. J. L. Anderson, M. E. Lowell and D. C. Prieve, Motion of a particle generated by chemical gradients. Part 1. Non-electrolytes, *J. Fluid. Mech.* **117** (1982) 107–121.
26. W. H. Koh and J. L. Anderson, Diffusion of neutral molecules in charged pores, *J. Colloid Interface Sci.* **64** (1978) 57–67.

APPENDIX

This Appendix examines the properties exhibited by the surface forces $\sigma_T^{(1)}\cdot\mathbf{n}$ and $\sigma_R^{(1)}\cdot\mathbf{n}$ for an orthotropic particle whose surface S obeys the equation $F(x_1, x_2, x_3) = F(|x_1|, |x_2|, |x_3|) = 0$. This assumption shows that, for $M(x_1, x_2, x_3) \in S$, the unit normal vector $\mathbf{n}(M)$ satisfies

$$n_i(x_1, x_2, x_3) = \mathrm{sgn}(x_i) n_i(|x_1|, |x_2|, |x_3|). \tag{5.1}$$

The associated translational motion $(\mathbf{u}, p)$ is the unique solution of the following equations and boundary conditions:

$$\mu\nabla^2\mathbf{u} - \nabla p = \mathbf{0} \quad \text{and} \quad \nabla\cdot\mathbf{u} = 0 \quad \text{in } \Omega_S, \tag{5.2}$$

$$(\mathbf{u}, p) \to (\mathbf{0}, 0) \quad \text{as } r \to \infty \text{ and } \mathbf{u} = \mathbf{e}_1 \text{ on } S. \tag{5.3}$$

For $\mathbf{v} = v_j\mathbf{e}_j$, the reader may check that the flow $(\mathbf{u}', p')$ such that, for $M \in \Omega_S \cup S$,

$$u_1'(x_1, x_2, x_3) = u_1(-x_1, x_2, x_3), \quad p'(x_1, x_2, x_3) = -p(-x_1, x_2, x_3), \tag{5.4}$$

$$u_2'(x_1, x_2, x_3) = -u_2(-x_1, x_2, x_3), \quad u_3'(x_1, x_2, x_3) = -u_3(-x_1, x_2, x_3), \tag{5.5}$$

also obeys (5.2), (5.3). Thus, $(\mathbf{u}, p) = (\mathbf{u}', p')$ and one thereafter deduces properties of the flow $(\mathbf{u}, p)$ by replacing $(\mathbf{u}', p')$ by $(\mathbf{u}, p)$ in (5.4), (5.5). The same procedure holds when changing x_2 in $-x_2$ and x_3 in $-x_3$. For $M(x_1, x_2, x_3) \in \Omega_S \cup S$, it follows that

$$u_1(M) = u_1(|x_1|, |x_2|, |x_3|), \quad p(M) = \text{sgn}(x_1)p(|x_1|, |x_2|, |x_3|), \tag{5.6}$$

$$u_j(M) = \text{sgn}(x_1)\text{sgn}(x_j)u_j(|x_1|, |x_2|, |x_3|) \quad \text{for } j \in \{2, 3\}. \tag{5.7}$$

Finally, one obtains the results (3.6), (3.7) from (2.6), (5.1) and (5.6), (5.7). The rotational motion $(\mathbf{u}'', p'')$ satisfies on $S : \mathbf{u}(M) = -x_3\mathbf{e}_2 + x_2\mathbf{e}_3$. How the change of x_1 in $-x_1$ affects the solution $(\mathbf{u}'', p'')$ is obtained by noting that the fluid motion $(-\mathbf{u}', -p')$ (introduced by (5.4), (5.5)) obeys the same problem as $(\mathbf{u}'', p'')$. This is also the case of the fluid motion $(\mathbf{u}''', p''')$ such that, for $M(x_1, x_2, x_3) \in \Omega_S \cup S$,

$$u_2'''(x_1, x_2, x_3) = u_2''(x_1, -x_2, x_3), \quad p'''(x_1, x_2, x_3) = -p''(x_1, -x_2, x_3), \tag{5.8}$$

$$u_1'''(x_1, x_2, x_3) = -u_1''(x_1, -x_2, x_3), \quad u_3'''(x_1, x_2, x_3) = -u_3''(x_1, -x_2, x_3). \tag{5.9}$$

If one replaces x_3 by $-x_3$ other properties are deduced for $(\mathbf{u}'', p'')$. Hence the reader can check that, for $M(x_1, x_2, x_3) \in \Omega_S \cup S$ and if $|M| := (|x_1|, |x_2|, |x_3|)$,

$$u_2''(M) = \text{sgn}(x_3)u_2''(|M|), \quad p''(M) = \text{sgn}(x_2)\text{sgn}(x_3)p''(|M|), \tag{5.10}$$

$$u_3''(M) = \text{sgn}(x_2)u_3''(|M|), \quad u_1''(M) = \text{sgn}(x_1)sgn(x_2)\text{sgn}(x_3)u_1''(|M|). \tag{5.11}$$

The properties (5.10), (5.11) yield the relations (3.8), (3.9).