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Electroviscous forces on a charged particle suspended in a flowing liquid

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The force on a charged solid particle (of general shape) suspended in a flowing polar fluid (e.g. an aqueous electrolyte solution) in the presence of a solid bounding wall (of general shape) is obtained for the situation in which the electrical double-layer thickness is very much smaller than the particle size (and the distance between particle and wall). The very general results so obtained are applied to the sedimentation of a charged spherical particle in an unbounded polar fluid (with no walls present) for which the drag force is found to be in complete agreement with Ohshima *et al*. (1984). However, there is disagreement between the present results and those obtained in a number of published papers owing to incorrect assumptions being made in the latter as to what physical mechanism gives rise to the dominant contribution to the electroviscous force on the particle.

1. Introduction

When two colloidal particles (or any two solid surfaces) in the presence of polar liquid (i.e. a liquid with positively and negatively charged ions present, such as an aqueous electrolyte solution) approach one another the forces between them consist of (*a*) a very short-range repulsive force, the Born repulsion, due to the interaction between the electron clouds of the molecules of the two surfaces, (*b*) a longer-range London–van der Waals force due to interactions between the electrical dipole moments of the molecules of the two surfaces, and (*c*) double-layer forces arising from an interaction between diffuse layers of electric charge in the liquid near each of the surfaces due to a higher concentration of positive ions (if the surface has a negative charge) or of negative ions (if the surface has a positive charge) (see, for example, Shaw 1986 or Everett 1988). The combined effects of the London–van der Waals and double-layer forces are given by the classical DLVO theory (Deryagin & Landau 1941; Verwey & Overbeek 1948).

Such forces between colloidal particles (or other solid surfaces) are of great importance since the manner in which they vary with distance between the surfaces will determine whether colloidal particles will coagulate (or whether a colloidal dispersion will be stable and not coagulate), whether colloidal particles will deposit on a solid boundary or whether they will deposit on the material of a filter.

When there is a fluid flow present, which may occur, for example, when one

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considers the interaction between a pair of colloidal particles approaching one another in a shear flow or the sedimentation of a single colloidal particle near a vertical solid wall, the double-layer forces mentioned above may be altered. This is because, in such situations, there is a coupling between the electrical and hydrodynamic equations with the ion concentrations being affected by the convection of ions by the flow and the flow being affected by electrical body forces. Thus, taking into account such electrohydrodynamic effects, Ohshima *et al.* (1984) derived the increased drag over and above the Stokes drag on a charged solid sphere sedimenting in a polar liquid.

In the present paper we consider the very general situation in which a charged solid particle P (of general shape) is suspended in a polar liquid bounded by a charged solid wall W (also of general shape). The liquid is moving due to either the motion of the particle or the wall or because of some prescribed motion (such as a shear flow at infinity). It is assumed that the thickness (κ^{-1}) of the electrical double layer is very much smaller than a characteristic dimension L (which may be taken as particle size or as distance of particle from wall) so that a singular perturbation expansion may be made in terms of the small parameter $\epsilon \equiv (\kappa L)^{-1}$. In this manner (§§2–12) the force on the particle is found to be the sum of the purely hydrodynamic force (of order ϵ^0) and an electrohydrodynamic or electroviscous force (of order ϵ^4), a recipe for obtaining the latter force being given in §13. The general results are applied (§14) to the particular case of a sedimenting charged sphere in an unbounded polar liquid (with no walls W present), with the drag force on the sphere being found to agree exactly with that obtained by Ohshima *et al.* (1984). However, disagreement was found to occur between our general results and the results obtained by a number of authors (Bike & Prieve 1990; Warszynski & van de Ven 1990, 1991; van de Ven, Warszynski & Dukhin 1993*a*, *b*) for particular problems because these authors calculated a force (of order ϵ^6) by considering only electrostatic forces and neglected hydrodynamic stresses which are predicted here to be of order ϵ^4.

2. General problem

Consider an electrically charged smooth solid particle P suspended in a liquid (such as an aqueous electrolyte solution) containing ionic charges with a charged smooth solid boundary wall W being present. The liquid is assumed to be moving due to either the motion of the particle P, the motion of the wall W or because there is some prescribed flow (such as a planar shear flow) of the liquid at infinity. The length scale and velocity scale of the flow are taken as L and V, respectively, (with L being, for example, the particle size or the distance between particle and wall).

At position $\boldsymbol{r}$ relative to some fixed origin and at time t, the velocity of the liquid is taken as $\boldsymbol{v}$ and the pressure as p. For simplicity, there are assumed to be just two species of ion present in the liquid (species 1 and 2) which have charges $+z_1 e$ and $-z_1 e$, respectively (where $z_1 = -z_2$ is the ion valency and e the charge of a proton), so that we consider only symmetric electrolytes (i.e. electrolytes in which both species of ion have the same valency z_1). The ion concentrations of species 1 and 2 are taken as n_1 and n_2, respectively, the electric potential as ψ and the charge density as ρ.

The independent variables $\boldsymbol{r}$, t and dependent variables $\boldsymbol{v}$, p, n_1, n_2, ψ and ρ are expressed in terms of corresponding dimensionless quantities (shown with a tilde) by

$$\boldsymbol{r} = L\tilde{\boldsymbol{r}}, \quad t = (L/V)\,\tilde{t} \tag{2.1}$$

$$
\left.
\begin{aligned}
&\boldsymbol{v} = V\tilde{\boldsymbol{v}}, \quad p = \frac{\eta V}{L}\tilde{p}, \\
&n_i = n_\infty \tilde{n}_i \quad (i = 1, 2), \\
\text{and} \qquad &\psi = \frac{kT}{z_1 e}\tilde{\psi}, \quad \rho = 2n_\infty z_1 e\tilde{\rho},
\end{aligned}
\right\} \tag{2.2}
$$

where n_∞ is a characteristic value of the ion concentration (which will later be identified with the values of n_1 or n_2 at infinity), η is the liquid viscosity, k is Boltzmann's constant, and T is the absolute temperature.

The concentrations of the ions each satisfy a convective diffusion equation which may be written in terms of the dimensionless (tilde) variables as

$$\tilde{\boldsymbol{\nabla}} \cdot \{\tilde{\boldsymbol{\nabla}}\tilde{n}_1 + \tilde{n}_1 \tilde{\boldsymbol{\nabla}}\tilde{\psi} - Pe\, \tilde{n}_1 \tilde{\boldsymbol{v}}\} = Pe\, \partial\tilde{n}_1/\partial\tilde{t}, \tag{2.3a}$$

$$\tilde{\boldsymbol{\nabla}} \cdot \{\tilde{\boldsymbol{\nabla}}\tilde{n}_2 - \tilde{n}_2 \tilde{\boldsymbol{\nabla}}\tilde{\psi} - Pe\,(D_1/D_2)\, \tilde{n}_2 \tilde{\boldsymbol{v}}\} = Pe\,(D_1/D_2)\, \partial\tilde{n}_2/\partial\tilde{t}, \tag{2.3b}$$

where a tilde over an operator denotes evaluation with respect to the dimensionless position variable $\tilde{\boldsymbol{r}}$, D_1 and D_2 are the diffusion constants for ions 1 and 2, respectively, and Pe is a Péclet number defined as

$$Pe = VL/D_1. \tag{2.4}$$

In (2.3 *a*, *b*) the first, second and third terms in the curly brackets represent the negative of the flux due, respectively, to diffusion, to convection by the electric field and to convection by the fluid flow.

The electrostatic relationship between the electric potential and the electric charge density when written in terms of the dimensionless (tilde) variables becomes

$$\epsilon^2 \tilde{\nabla}^2 \tilde{\psi} = -\tilde{\rho}, \tag{2.5}$$

where

$$\epsilon = 1/\kappa L \tag{2.6}$$

is the ratio of the inverse of the Debye–Hückel parameter κ (i.e. the characteristic double-layer thickness) to the length scale L. Here κ is the quantity

$$\kappa = \left(\frac{2z_1^2 e^2 n_\infty}{\epsilon_r \epsilon_0 kT}\right)^{1/2}, \tag{2.7}$$

where ϵ_r is the relative permittivity of the liquid and ϵ_0 is the permittivity of a vacuum.

In terms of our definitions (2.2) of the dimensionless variables, the electric charge density may be written in terms of the ion concentrations as

$$\tilde{\rho} = \tfrac{1}{2}(\tilde{n}_1 - \tilde{n}_2). \tag{2.8}$$

We assume that the liquid is Newtonian and incompressible and that the Reynolds number (LV/ν) of the flow (where ν is the kinematic viscosity of the liquid) is very much smaller than unity so that inertia effects in the liquid flow may be neglected. The momentum and continuity equations for the liquid flow in terms of our dimensionless variables then become

$$\tilde{\nabla}^2 \tilde{\boldsymbol{v}} - \tilde{\boldsymbol{\nabla}}\tilde{p} = \lambda\tilde{\rho}\tilde{\boldsymbol{\nabla}}\tilde{\psi}, \quad \tilde{\boldsymbol{\nabla}} \cdot \tilde{\boldsymbol{v}} = 0, \tag{2.9a, b}$$

where λ is the parameter

$$\lambda = 2n_\infty kTL/\eta V \tag{2.10}$$

which measures the relative importance of the electrical forces on the liquid flow.

Thus we have equations (2.3*a*, *b*), (2.5), (2.8), (2.9*a*, *b*) representing eight scalar equations for the eight dependent variables (given by $\tilde{\boldsymbol{v}}$, $\tilde{p}$, $\tilde{n}_1$, $\tilde{n}_2$, $\tilde{\psi}$ and $\tilde{\rho}$). It is to be noted that a possible solution of these equations for an unbounded liquid with no solid surfaces present is one with no volume charges present, i.e. the solution

$$\tilde{n}_1 = \tilde{n}_2 = \text{constant}, \quad \tilde{\rho} = 0,$$

with electric potential $\tilde{\psi}$ satisfying

$$\tilde{\nabla}^2 \tilde{\psi} = 0$$

and a purely hydrodynamic flow with

$$\tilde{\nabla}^2 \tilde{\boldsymbol{v}} - \tilde{\boldsymbol{\nabla}} \tilde{p} = \boldsymbol{0}, \quad \tilde{\boldsymbol{\nabla}} \cdot \tilde{\boldsymbol{v}} = 0.$$

Thus at large distances we will take a solution of this form with $\tilde{\psi} = 0$ (since we assume there is no applied electric field at infinity) which, if we take the characteristic ion concentration n_∞ to be that at infinity, we have, as $|\tilde{\boldsymbol{r}}| \to \infty$, the boundary conditions

$$\tilde{n}_1 \to 1, \quad \tilde{n}_2 \to 1, \tag{2.11a}$$

$$\tilde{\psi} \to 0, \quad \tilde{\boldsymbol{v}} \sim \text{(given flow at infinity)}. \tag{2.11b, c}$$

On the surface S_p of the particle P and on the surface S_w of the wall W we require the no-slip boundary condition to be satisfied so that if at a general point on S_p the velocity of the solid surface is $\boldsymbol{U}_p$ (and on S_w is $\boldsymbol{U}_w$), then we require

$$\tilde{\boldsymbol{v}} = \tilde{\boldsymbol{U}}_p \quad \text{on} \quad S_p, \quad \tilde{\boldsymbol{v}} = \tilde{\boldsymbol{U}}_w \quad \text{on} \quad S_w, \tag{2.11d}$$

where we have written

$$\tilde{\boldsymbol{U}}_p = \boldsymbol{U}_p / V \quad \text{and} \quad \tilde{\boldsymbol{U}}_w = \boldsymbol{U}_w / V \tag{2.12}$$

as the dimensionless velocity of the surface (S_p or S_w).

We assume that ions (of either species) on reaching a solid surface (S_p or S_w) do not give up their electric charge or in any way react with the surface so that the ion flux (of either species) normal to the surface (relative to the surface) must be zero. Thus

$$\boldsymbol{n} \cdot \{\tilde{\boldsymbol{\nabla}} \tilde{n}_1 + \tilde{n}_1 \tilde{\boldsymbol{\nabla}} \tilde{\psi}\} = 0 \quad \text{on} \quad S_p \text{ and } S_w, \tag{2.13a}$$

$$\boldsymbol{n} \cdot \{\boldsymbol{\nabla} \tilde{n}_2 - \tilde{n}_2 \tilde{\boldsymbol{\nabla}} \tilde{\psi}\} = 0 \quad \text{on} \quad S_p \text{ and } S_w, \tag{2.13b}$$

where $\boldsymbol{n}$ is the unit normal vector to the surface directed into the liquid. In deriving (2.13*a*) and (2.13*b*) it was noted that the convective flux due to the fluid relative to the solid surface is zero by (2.11*d*).

It is assumed that the surface potential of the particle is everywhere equal to a constant on S_p (and equals ψ_p say) and that of the wall is everywhere equal to another constant (and equals ψ_w say). Then we require

$$\tilde{\psi} = \tilde{\psi}_p \quad \text{on} \quad S_p, \quad \tilde{\psi} = \tilde{\psi}_w \quad \text{on} \quad S_w, \tag{2.14a, b}$$

where we have written

$$\tilde{\psi}_p = \psi_p \bigg/ \left(\frac{kT}{z_1 e}\right), \quad \tilde{\psi}_w = \psi_w \bigg/ \left(\frac{kT}{z_1 e}\right) \tag{2.15}$$

as the dimensionless surface potentials of the particle P and wall W.

The solution of the system of equations (2.3), (2.5), (2.8), (2.9) with boundary conditions (2.11), (2.13), (2.14) depend on, in addition to the shapes, relative positions and motions of the particle and wall (and flow at infinity), the following six parameters:

Pe, the Péclet number for ions of species 1 (see (2.4));

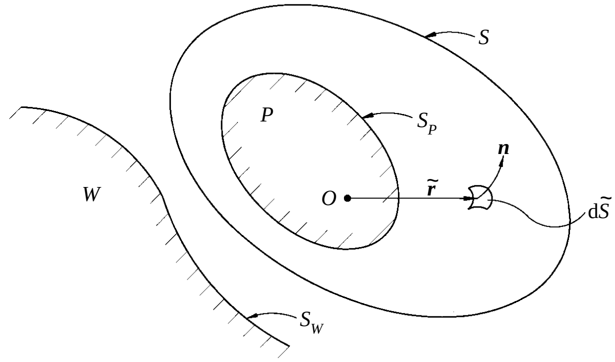

FIGURE 1. Surface S enclosing the particle P.

D_1/D_2, the ratio of diffusivities of the two species of ion;
ϵ, the ratio of double-layer thickness to L (see (2.6) and (2.7));
λ, the parameter measuring effect of electrical forces on flow (see (2.10));
$\tilde{\psi}_p$, the dimensionless particle surface potential (see (2.15));
$\tilde{\psi}_w$, the dimensionless wall surface potential (see (2.15)).

In the present work we consider the limit $\epsilon \to 0$ with all the other five parameters being held fixed and of order unity. Thus we are assuming that the double-layer thickness is very much smaller than particle size or the distance from particle to wall.

Since the total stress tensor σ_{ij} is the sum of the hydrodynamic and the electrostatic Maxwell stress tensors, we see that if we define a dimensionless stress tensor $\tilde{\sigma}_{ij}$ by

$$\sigma_{ij} = \frac{\eta V}{L}\tilde{\sigma}_{ij} \tag{2.16}$$

then $\tilde{\sigma}_{ij}$ is given as

$$\tilde{\sigma}_{ij} = -\tilde{p}\delta_{ij} + (\tilde{v}_{i,j} + \tilde{v}_{j,i}) + \lambda\epsilon^2(-\tfrac{1}{2}\tilde{\psi}_{,k}\tilde{\psi}_{,k}\delta_{ij} + \tilde{\psi}_{,i}\tilde{\psi}_{,j}), \tag{2.17}$$

where all derivatives are with respect to the $\tilde{r}_i$ variables. It may then, by using (2.5), (2.9), be readily shown that the total momentum equation

$$\tilde{\sigma}_{ij,j} = 0 \tag{2.18}$$

is satisfied. Thus, by using the divergence theorem, it is seen that the total force $\boldsymbol{F}$ acting on the particle P may be written in dimensionless form, using the dimensionless force $\tilde{\boldsymbol{F}}$ where

$$\boldsymbol{F} = \eta L V \tilde{\boldsymbol{F}}, \tag{2.19}$$

as

$$\tilde{F}_i = \int_{S_p} \tilde{\sigma}_{ij} n_j \,\mathrm{d}\tilde{S} = \int_S \tilde{\sigma}_{ij} n_j \,\mathrm{d}\tilde{S}, \tag{2.20}$$

where $\mathrm{d}\tilde{S}$ is an element of area, $\boldsymbol{n}$ is the unit normal vector to the surface directed outwards away from the particle and S is any closed surface completely surrounding the particle P and containing only liquid and the particle P itself, as shown in figure 1 (so that no part of the wall W is within S). Similarly the moment of force $\boldsymbol{G}$ on the particle P about a reference point O may be written, in terms of the dimensionless moment $\tilde{\boldsymbol{G}}$ where

$$\boldsymbol{G} = \eta L^2 V \tilde{\boldsymbol{G}}, \tag{2.21}$$

as
$$\tilde{G}_i = \int_{S_p} \epsilon_{ijk}\,\tilde{r}_j\,\tilde{\sigma}_{kl}\,n_l\,\mathrm{d}\tilde{S} = \int_{S} \epsilon_{ijk}\,\tilde{r}_j\,\tilde{\sigma}_{kl}\,n_l\,\mathrm{d}\tilde{S}, \tag{2.22}$$
where ϵ_{ijk} is the alternating tensor and $\tilde{r}_j$ is the position of the surface element relative to the reference point O.

3. Inner and outer regions

In solving the equations (2.3), (2.5), (2.8), (2.9) with the boundary conditions (2.11), (2.13), (2.14) for the limit $\epsilon \to 0$ we expand the dependent dimensionless (tilde) variables in terms of this parameter ϵ. In this manner we obtain an outer-region solution.

However such a solution is not uniformly valid for all $\tilde{\boldsymbol{r}}$ because of ϵ^2 multiplying the highest-order derivatives in (2.5). Thus at each point on the solid surfaces S_p and S_w we must form an inner (double-layer) region expansion in ϵ. Thus at a completely general point Q at position $\tilde{\boldsymbol{r}}_Q$ on the surface S_p (or on the surface S_w) we define locally a set of orthogonal coordinates $(\xi, \tilde{\eta})$ lying within the surface S_p with unit metric tensor in terms of the outer variables (so that distance ds between $(\tilde{\xi}, \tilde{\eta})$ and $(\tilde{\xi}+\mathrm{d}\tilde{\xi}, \tilde{\eta}+\mathrm{d}\tilde{\eta})$ is $L[(\mathrm{d}\tilde{\xi})^2+(\mathrm{d}\tilde{\eta})^2]^{1/2}$. Then at Q we define local outer-region Cartesian coordinates $(\tilde{x}, \tilde{y}, \tilde{z})$ with $\tilde{z}$ normal to S_p and directed into the liquid and the $\tilde{x}$- *and* $\tilde{y}$-axes tangent to the $\tilde{\xi}$- and $\tilde{\eta}$-coordinate lines at Q, as shown in figure 2. Inner-region variables (denoted as barred variables) for the inner region at Q are then defined by
$$\tilde{x} = \epsilon^{1/2}\bar{x}, \quad \tilde{y} = \epsilon^{1/2}\bar{y}, \quad \tilde{z} = \epsilon\bar{z}, \quad \tilde{t} = \bar{t}, \tag{3.1}$$
and
$$\left.\begin{aligned} &\tilde{\boldsymbol{v}} = \tilde{\boldsymbol{U}} + \tilde{\boldsymbol{\Omega}} \times \tilde{\boldsymbol{r}} + \bar{\boldsymbol{v}}, \quad \tilde{p} = \bar{p}, \\ &\tilde{n}_i = \bar{n}_i \quad (i = 1, 2), \\ &\tilde{\psi} = \bar{\psi}, \quad \tilde{\rho} = \bar{\rho}, \end{aligned}\right\} \tag{3.2}$$
where $\tilde{\boldsymbol{U}}$ here is the dimensionless velocity of the particle at Q (equal to either $\tilde{\boldsymbol{U}}_p$ or $\tilde{\boldsymbol{U}}_w$ at Q), $\tilde{\boldsymbol{\Omega}}$ is the dimensionless angular velocity of the surface ($= \boldsymbol{\Omega}/(V/L)$) where $\boldsymbol{\Omega}$ is the dimensional angular velocity) and $\tilde{\boldsymbol{r}}$ here is the position relative to Q in outer variables, so that
$$\left.\begin{aligned} \tilde{v}_x &= \tilde{U}_x + \bar{v}_x - \epsilon^{1/2}\tilde{\Omega}_z\,\bar{y} + \epsilon\tilde{\Omega}_y\,\bar{z}, \\ \tilde{v}_y &= \tilde{U}_y + \bar{v}_y + \epsilon^{1/2}\tilde{\Omega}_z\,\bar{x} - \epsilon\tilde{\Omega}_x\,\bar{z}, \\ \tilde{v}_z &= \tilde{U}_z + \bar{v}_z + \epsilon^{1/2}(\tilde{\Omega}_x\,\bar{y} - \tilde{\Omega}_y\,\bar{x}). \end{aligned}\right\} \tag{3.3}$$

The solution procedure will be to solve as an expansion in ϵ in the outer region (2.3), (2.5), (2.8), (2.9) with the boundary conditions (2.11), (2.13), (2.14) at infinity. Then at each point Q on the surfaces S_p and S_w an inner-region expansion in ϵ is made by solving the same equations with the same boundary but written entirely in terms of the inner-region (barred) variables. These solutions are matched asymptotically by requiring that the inner-region solution at Q for $\bar{z} \to \infty$ be identical to the outer-region solution as the point Q is approached.

The shape of the particle surface S_p (or wall surface S_w) in the neighbourhood of the point Q may, using the local outer coordinates $\tilde{x}, \tilde{y}, \tilde{z}$ at Q, be written as
$$\begin{aligned} \tilde{z} = a_{11}\,\tilde{x}^2 + 2a_{12}\,\tilde{x}\tilde{y} + a_{22}\,\tilde{y}^2 &+ (\text{cubic terms in } \tilde{x}, \tilde{y}) \\ &+ (\text{quartic terms in } \tilde{x}, \tilde{y}) + \ldots, \end{aligned} \tag{3.4}$$
where the constants a_{11}, a_{12} and a_{22} are of order unity and have values dependent on the point Q chosen (and on the choice of $(\tilde{\xi}, \tilde{\eta})$-coordinates).

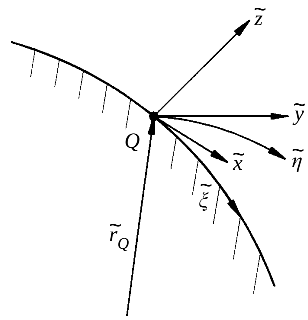

FIGURE 2. Definition of $\tilde{x}, \tilde{y}, \tilde{z}$ coordinates with origin at Q.

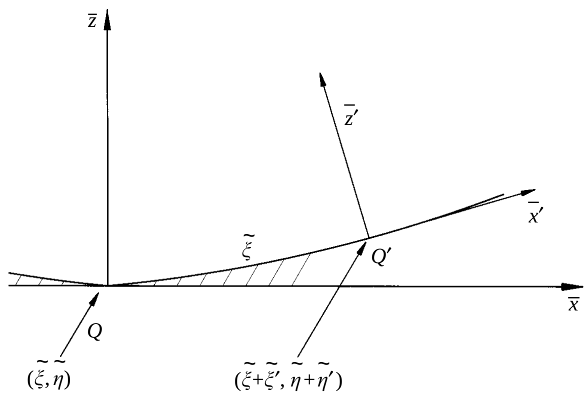

FIGURE 3. Coordinates $\bar{x}, \bar{y}, \bar{z}$ at $Q(\tilde{\xi}, \tilde{\eta})$ and coordinates $\bar{x}', \bar{y}', \bar{z}'$ at $Q'(\tilde{\xi}+\tilde{\xi}', \tilde{\eta}+\tilde{\eta}')$.

Within the inner region we will, for simplicity, solve for the dependent variable only on the $\bar{z}$-axis (where $\bar{x} = \bar{y} = 0$) since if we have the value of any dependent variable ($\bar{f}$ say) as a function of $\bar{z}$ in the inner region at all points Q (so that $\bar{f}$ is also a function of $\tilde{\xi}$ and $\tilde{\eta}$), then $\bar{f}$ and also its $\bar{x}$ and $\bar{y}$ derivatives must be completely determined. Thus we write

$$\bar{f} = \bar{f}(\bar{z}; \tilde{\xi}, \tilde{\eta}). \tag{3.5}$$

Consider coordinates $(\bar{x}, \bar{y}, \bar{z})$ used in the inner region at Q (at position $(\tilde{\xi}, \tilde{\eta})$ on the surface S_p and the coordinates $(\bar{x}', \bar{y}', \bar{z}')$ used in the inner region at a neighbouring point Q' (at position $(\tilde{\xi}+\tilde{\xi}', \tilde{\eta}+\tilde{\eta}')$), as shown in figure 3. The $\bar{x}, \bar{y}, \bar{z}$ coordinates of a point at $\bar{x}' = \bar{y}' = 0$ on the $\bar{z}'$-axis at Q' are readily seen as being given by

$$\left.\begin{aligned} \epsilon^{1/2}\bar{x} &= \tilde{\xi}' - 2\epsilon\bar{z}'(a_{11}\tilde{\xi}' + a_{12}\tilde{\eta}') + (\text{cubic}) + \epsilon\bar{z}'(\text{quadratic}), \\ \epsilon^{1/2}\bar{y} &= \tilde{\eta}' - 2\epsilon\bar{z}'(a_{12}\tilde{\xi}' + a_{22}\tilde{\eta}') + (\text{cubic}) + \epsilon\bar{z}'(\text{quadratic}), \\ \epsilon\bar{z} &= \epsilon\bar{z}' + (a_{11}\tilde{\xi}'^2 + 2a_{12}\tilde{\xi}'\tilde{\eta}' + a_{22}\tilde{\eta}'^2) + (\text{cubic}) + \epsilon\bar{z}'(\text{quadratic}), \end{aligned}\right\} \tag{3.6}$$

where the terms (cubic) and (quadratic) are, respectively, cubic and quadratic polynomials of $\tilde{\xi}'$ and $\tilde{\eta}'$. The result (3.6) may be inverted (for $\epsilon \to 0$) to give $\tilde{\xi}', \tilde{\eta}', \bar{z}'$ in terms of $\bar{x}, \bar{y}, \bar{z}$, and hence one may obtain the values of first-order partial derivatives (such as $\partial\tilde{\xi}'/\partial\bar{x}$, etc.) and second-order partial derivatives (such as $\partial^2\tilde{\xi}'/\partial\bar{x}^2$, etc.) on the $\bar{z}$-axis (i.e. where $\bar{x} = \bar{y} = 0$). These may then be used to calculate on the $\bar{z}$-axis the partial derivatives of a function $\bar{f}$ of the form (3.5) with respect to $\bar{x}$ and $\bar{y}$ as expansions in ϵ:

$$\left.\frac{\partial \bar{f}}{\partial \bar{x}}\right|_{\bar{x}=\bar{y}=0} = \epsilon^{1/2}\frac{\partial \bar{f}}{\partial \tilde{\xi}} + O(\epsilon^{3/2}), \quad \left.\frac{\partial \bar{f}}{\partial \bar{y}}\right|_{\bar{x}=\bar{y}=0} = \epsilon^{1/2}\frac{\partial \bar{f}}{\partial \tilde{\eta}} + O(\epsilon^{3/2}), \tag{3.7 a, b}$$

$$\left.\frac{\partial^2 \bar{f}}{\partial \bar{x}^2}\right|_{\bar{x}=\bar{y}=0} = -2a_{11}\frac{\partial \bar{f}}{\partial \bar{z}} + O(\epsilon), \quad \left.\frac{\partial^2 \bar{f}}{\partial \bar{x}\,\partial \bar{y}}\right|_{\bar{x}=\bar{y}=0} = -2a_{12}\frac{\partial \bar{f}}{\partial \bar{z}} + O(\epsilon), \tag{3.8 a, b}$$

$$\left.\frac{\partial^2 \bar{f}}{\partial \bar{y}^2}\right|_{\bar{x}=\bar{y}=0} = -2a_{22}\frac{\partial \bar{f}}{\partial \bar{z}} + O(\epsilon), \tag{3.8 c}$$

where $\partial \bar{f}/\partial \tilde{\xi}$, $\partial \bar{f}/\partial \tilde{\eta}$ and $\partial \bar{f}/\partial \bar{z}$ are calculated with $\bar{f}$ of the form (3.5) with $\tilde{\xi}$ and $\tilde{\eta}$ having values corresponding to the point Q. Thus

$$\left.\left(\frac{\partial^2 \bar{f}}{\partial \bar{x}^2} + \frac{\partial^2 \bar{f}}{\partial \bar{y}^2}\right)\right|_{\bar{x}=\bar{y}=0} = -\alpha\frac{\partial \bar{f}}{\partial \bar{z}}, \tag{3.8 d}$$

where

$$\alpha = 2(a_{11}+a_{22}) \tag{3.9}$$

is the dimensionless sum of the principal curvatures of the surface at the point Q under consideration. Note that α is negative for convex surfaces (like a sphere) and positive for concave ones (such as a spherical cavity).

With appropriate interpretation all of the above results (3.7)–(3.9) are equally valid for the point Q lying on the wall surface S_w as on the particle surface S_p.

4. Solution to the electrical problem

We consider here a special case of the problem discussed in §2 in which we have a steady state with the fluid velocity $\boldsymbol{v}$ being everywhere zero. This implies that the velocity $\boldsymbol{U}$ of the surfaces S_p and S_w of particle and wall must also be zero and that $\boldsymbol{v} \to \boldsymbol{0}$ at infinity. We use variables with a subscript E to denote all dependent variables for this case (i.e. we use $\tilde{n}_{1E}, \tilde{n}_{2E}, \tilde{\psi}_E, \tilde{\rho}_E, \tilde{p}_E$), the equations (2.3), (2.5), (2.8), (2.9 a) then becoming (with (2.9 b) automatically satisfied)

$$\tilde{\nabla}^2\tilde{n}_{1E} + \tilde{\boldsymbol{\nabla}}\cdot(\tilde{n}_{1E}\tilde{\boldsymbol{\nabla}}\tilde{\psi}_E) = 0, \quad \tilde{\nabla}^2\tilde{n}_{2E} - \tilde{\boldsymbol{\nabla}}\cdot(\tilde{n}_{2E}\tilde{\boldsymbol{\nabla}}\tilde{\psi}_E) = 0, \tag{4.1 a, b}$$

$$\epsilon^2\tilde{\nabla}^2\tilde{\psi}_E = -\rho_E, \quad \tilde{\rho}_E = \tfrac{1}{2}(\tilde{n}_{1E}-\tilde{n}_{2E}), \quad -\tilde{\boldsymbol{\nabla}}\tilde{p}_E = \lambda\tilde{\rho}_E\tilde{\boldsymbol{\nabla}}\tilde{\psi}_E, \tag{4.1 c–e}$$

with the boundary conditions (2.11 a, b), (2.13), (2.14) becoming (with (2.11 c, d) automatically satisfied)

$$\tilde{n}_{1E} \to 1, \quad \tilde{n}_{2E} \to 1, \qquad \tilde{\psi}_E \to 0 \tag{4.2 a, b}$$

as $|\tilde{\boldsymbol{r}}| \to \infty$ with

$$\boldsymbol{n}\cdot\{\tilde{\boldsymbol{\nabla}}\tilde{n}_{1E} + \tilde{n}_{1E}\tilde{\boldsymbol{\nabla}}\tilde{\psi}_E\} = 0 \quad \text{on} \quad S_p \quad \text{and} \quad S_w, \tag{4.2 c}$$

$$\boldsymbol{n}\cdot\{\tilde{\boldsymbol{\nabla}}\tilde{n}_{2E} - \tilde{n}_{2E}\tilde{\boldsymbol{\nabla}}\tilde{\psi}_E\} = 0 \quad \text{on} \quad S_p \quad \text{and} \quad S_w, \tag{4.2 d}$$

$$\tilde{\psi}_E = \tilde{\psi}_p \quad \text{on} \quad S_p, \qquad \tilde{\psi}_E = \tilde{\psi}_w \quad \text{on} \quad S_w. \tag{4.2 e, f}$$

If we write

$$\tilde{\boldsymbol{q}}_{1E} = \tilde{\boldsymbol{\nabla}}\tilde{n}_{1E} + \tilde{n}_{1E}\tilde{\boldsymbol{\nabla}}\tilde{\psi}_E \tag{4.3}$$

as the dimensionless flux of the ions of species 1, we see that (4.1 a) becomes

$$\tilde{\boldsymbol{\nabla}}\cdot\tilde{\boldsymbol{q}}_{1E} = 0. \tag{4.4}$$

If we multiply this by $\tilde{\psi}_E$ and integrate over the liquid volume V contained within a

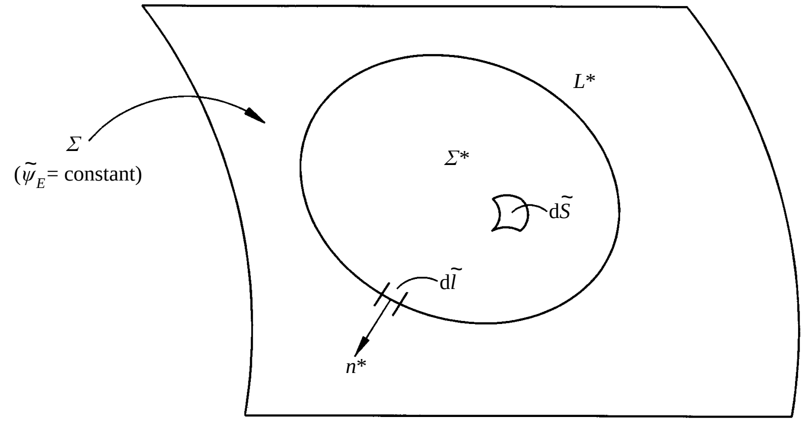

FIGURE 4. Area Σ^* bounded by the line L^* and lying in the surface Σ defined by $\tilde{\psi}_E$ = constant.

large sphere S_R of radius R (so that V is bounded by S_p, S_w and S_R) we obtain, upon using the divergence theorem, the energy equation for the ions of species 1 as

$$-\int_{S_p+S_w+S_R} \tilde{\psi}_E\, \tilde{\boldsymbol{q}}_{1E} \cdot \boldsymbol{n}\, \mathrm{d}\tilde{S} = \int_V \tilde{\boldsymbol{q}}_{1E} \cdot \tilde{\boldsymbol{\nabla}}\tilde{\psi}_E\, \mathrm{d}\tilde{V}, \tag{4.5}$$

where $\mathrm{d}\tilde{S}$ and $\mathrm{d}\tilde{V}$ are elements of surface area and volume (in our dimensionless tilde variables) and $\boldsymbol{n}$ is the unit normal to the surface (S_p, S_w or S_R) drawn into the liquid. The boundary conditions (4.2a–c) then show that (so long as $\tilde{n}_{1E}, \tilde{n}_{2E}, \tilde{\psi}_E$ tend to their respective limits sufficiently rapidly as $|\tilde{\boldsymbol{r}}| \to \infty$) the integral on the left-hand side of (4.5) is zero. Thus

$$\int_v \tilde{\boldsymbol{q}}_{1E} \cdot \tilde{\boldsymbol{\nabla}}\tilde{\psi}_E\, \mathrm{d}\tilde{V} = 0. \tag{4.6}$$

Since the quantity $(-\tilde{\boldsymbol{q}}_{1E} \cdot \tilde{\boldsymbol{\nabla}}\tilde{\psi}_E)$ is the dimensionless rate of energy conversion into heat per unit volume (assuming the species 1 of ions have a positive charge) it must be a strictly non-negative quantity. Thus

$$\tilde{\boldsymbol{q}}_{1E} \cdot \tilde{\boldsymbol{\nabla}}\tilde{\psi}_E = 0 \tag{4.7}$$

everywhere. Consider now any equipotential surface Σ given by $\tilde{\psi}_E$ = constant. By (4.7), $\tilde{\boldsymbol{q}}_E$ has zero component normal to Σ, whilst by (4.3), it has components in the plane of Σ given by

$$\tilde{\boldsymbol{q}}_{1E} = \tilde{\boldsymbol{\nabla}}_2 \tilde{n}_{1E}, \tag{4.8}$$

where $\tilde{\boldsymbol{\nabla}}_2$ is the two dimensional gradient operator on the surface Σ. Thus, by (4.4), $\tilde{n}_{1E}$ satisfies the two dimensional Laplace equation

$$\tilde{\boldsymbol{\nabla}}_2^2 \tilde{n}_{1E} = 0 \tag{4.9}$$

on the surface Σ. By multiplying (4.9) by $\tilde{n}_{1E}$ and integrating over that part Σ^* of the surface Σ bounded externally by a closed line L^* drawn on Σ (see figure 4), we obtain, using the divergence theorem,

$$\int_{L^*} \tilde{n}_{1E}\, \tilde{\boldsymbol{\nabla}}_2 \tilde{n}_{1E} \cdot \boldsymbol{n}^* \mathrm{d}\tilde{l} = \int_{\Sigma^*} |\tilde{\boldsymbol{\nabla}}_2 \tilde{n}_{1E}|^2\, \mathrm{d}\tilde{S}, \tag{4.10}$$

where $\mathrm{d}\tilde{S}$ is an element of area of Σ^*, $\mathrm{d}\tilde{l}$ an element of length of L^* and $\boldsymbol{n}^*$ a unit vector in the plane of Σ^* normal to L^*. If the equipotential surface Σ is closed (so that L^* can be shrunk to a point as $\Sigma^* \to \Sigma$) or if Σ is unbounded with $\tilde{n}_{1E}$ on Σ tending to a constant value sufficiently rapidly at infinity, we see that the integral on the left-hand side of (4.10) tends to zero giving

$$\int_{\Sigma} |\tilde{\boldsymbol{\nabla}}_2 \tilde{n}_{1E}|^2 \, d\tilde{S} = 0. \tag{4.11}$$

Since the integrand in (4.11) is strictly non-negative it follows that

$$\tilde{\boldsymbol{\nabla}}_2 \tilde{n}_{1E} = \mathbf{0} \tag{4.12}$$

so that $\tilde{n}_{1E}$ is constant on an equipotential surface Σ. Thus the ion flux $\tilde{\boldsymbol{q}}_{1E}$ (and by a similar argument the ion flux $\tilde{\boldsymbol{q}}_{2E}$) is zero everywhere. Thus equations (4.1 *a*) and (4.1 *b*) may be replaced by

$$\tilde{\boldsymbol{\nabla}} \tilde{n}_{1E} + \tilde{n}_{1E} \tilde{\boldsymbol{\nabla}} \tilde{\psi}_E = 0, \quad \tilde{\boldsymbol{\nabla}} \tilde{n}_{2E} - \tilde{n}_{2E} \tilde{\boldsymbol{\nabla}} \tilde{\psi}_E = 0, \tag{4.13 a, b}$$

the boundary conditions (4.2 *c*, *d*) then being automatically satisfied. The unique solution of (4.13) which satisfies the boundary conditions (4.2 *a*, *b*) is

$$\tilde{n}_{1E} = e^{-\tilde{\psi}_E}, \quad \tilde{n}_{2E} = e^{+\tilde{\psi}_E}. \tag{4.14}$$

Equations (4.1 *d*, *e*) then give

$$\tilde{\rho}_E = -\sinh \tilde{\psi}_E, \tag{4.15}$$

$$\tilde{p}_E = \lambda(\cosh \tilde{\psi}_E - 1), \tag{4.16}$$

where it has been assumed, without loss of generality, that $\tilde{p}_E \to 0$ as $|\tilde{\boldsymbol{r}}| \to \infty$. It should be noted that since $\tilde{\rho}_E$ is a function of $\tilde{\psi}_E$, the electrical body force $\lambda \tilde{\rho}_E \tilde{\boldsymbol{\nabla}} \tilde{\psi}_E$ acting on the liquid (see (4.1 *e*)) is conservative so that no fluid flow is produced. With $\tilde{n}_{1E}, \tilde{n}_{2E}$ given by (4.14) the remaining equation (4.1 *c*) with boundary conditions (4.2 *b*, *e*, *f*) give $\tilde{\psi}$ as being determined by

$$\epsilon^2 \tilde{\nabla}^2 \tilde{\psi}_E = \sinh \psi_E, \tag{4.17}$$

with

$$\tilde{\psi}_E \to 0 \quad \text{as} \quad |\tilde{\boldsymbol{r}}| \to \infty, \tag{4.18 a}$$

$$\tilde{\psi}_E = \tilde{\psi}_p \quad \text{on} \quad S_p, \tag{4.18 b}$$

$$\tilde{\psi}_E = \tilde{\psi}_w \quad \text{on} \quad S_2. \tag{4.18 c}$$

Although the solution (4.14)–(4.18) to the electrical problem considered here is valid if ϵ is large, we will want this solution in the limit $\epsilon \to 0$ in the inner and outer regions of expansion (see §3).

In the outer region where the above (tilde) variables are used we solve (4.17) with the boundary condition (4.18 *a*) at infinity by expanding $\tilde{\psi}_E$ in powers of ϵ^2 and substituting into (4.17) to obtain exactly

$$\tilde{\psi}_E = 0, \tag{4.19 a}$$

correct to all orders in ϵ. Equation (4.19 *a*) is inconsistent with the outer expansion derived by Chew & Sen (1982) for a sphere, who obtained a non-zero outer solution. Substituting (4.19 *a*) into (4.14)–(4.16) we have

$$\tilde{n}_{1E} = 1, \quad \tilde{n}_{2E} = 1, \tag{4.19 b}$$

$$\tilde{\rho}_E = 0, \quad \tilde{p}_E = 0 \tag{4.19 c, d}$$

everywhere in the outer region (correct to all orders in ϵ).

In the inner region (using barred variables) at a point Q on the particle surface S_p we see, from (4.17) and (4.18*a*), that $\tilde{\psi}_E$ satisfies on the $\bar{z}$-axis (i.e. where $\bar{x}=\bar{y}=0$)

$$\frac{\partial^2\bar{\psi}_E}{\partial\bar{z}^2}+\epsilon\left(\frac{\partial^2\bar{\psi}_E}{\partial\bar{x}^2}+\frac{\partial^2\bar{\psi}_E}{\partial\bar{y}^2}\right)=\sinh\bar{\psi}_E \tag{4.20}$$

with
$$\bar{\psi}_E=\tilde{\psi}_p \quad \text{at} \quad \bar{z}=0, \tag{4.21}$$

whilst matching onto the outer solution (4.19) requires

$$\bar{\psi}_E\rightarrow 0 \quad \text{as} \quad \bar{z}\rightarrow\infty. \tag{4.22}$$

Thus if we expand $\tilde{\psi}_E$ for small ϵ as

$$\bar{\psi}_E=\bar{\psi}_{E0}+\epsilon\bar{\psi}_{E1}+\dots \tag{4.23}$$

we see on substitution into (4.20)–(4.22) that, by equating like powers in ϵ, $\bar{\psi}_{E0}$ satisfies

$$\frac{\partial^2\bar{\psi}_{E0}}{\partial\bar{z}^2}=\sinh\bar{\psi}_{E0}, \tag{4.24a}$$

with
$$\bar{\psi}_{E0}=\tilde{\psi}_p \quad \text{at} \quad \bar{z}=0, \qquad \psi_{E0}\rightarrow 0 \quad \text{as} \quad \bar{z}\rightarrow\infty, \tag{4.24b, c}$$

and $\bar{\psi}_{E1}$ satisfies

$$\frac{\partial^2\bar{\psi}_{E1}}{\partial\bar{z}^2}-(\cosh\bar{\psi}_{E0})\,\bar{\psi}_{E1}=-\left(\frac{\partial^2\bar{\psi}_{E0}}{\partial\bar{x}^2}+\frac{\partial^2\bar{\psi}_{E0}}{\partial\bar{y}^2}\right), \tag{4.25a}$$

with
$$\bar{\psi}_{E1}=0 \quad \text{at} \quad \bar{z}=0, \quad \bar{\psi}_{E1}\rightarrow 0 \quad \text{as} \quad \bar{z}\rightarrow\infty. \tag{4.25b, c}$$

Equations (4.24) may be readily solved to give the value of $\bar{\psi}_{E0}$ as

$$\bar{\psi}_{E0}=2\ln\left\{\frac{1+A_p\,\mathrm{e}^{-\bar{z}}}{1-A_p\,\mathrm{e}^{-\bar{z}}}\right\}, \tag{4.26a}$$

where A_p is the constant

$$A_p=\tanh(\tilde{\psi}_p/4).$$

Equation (4.26*a*) is the well-known result of the Gouy–Chapman theory for the potential distribution at a flat plate.

By making use of the results (3.7) and (3.8), we obtain the $\bar{x}$- and $\bar{y}$-derivatives of $\bar{\psi}_{E0}$ (i.e. at order ϵ^0) on the $\bar{z}$-axis as

$$\frac{\partial\bar{\psi}_{E0}}{\partial\bar{x}}=0, \quad \frac{\partial\bar{\psi}_{E0}}{\partial\bar{y}}=0, \tag{4.26b}$$

$$\left(\frac{\partial^2}{\partial\bar{x}^2}+\frac{\partial^2}{\partial\bar{y}^2}\right)\bar{\psi}_{E0}=-\alpha_p\frac{\partial\bar{\psi}_{E0}}{\partial\bar{z}}=\alpha_p\frac{4A_p\,\mathrm{e}^{-\bar{z}}}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})}, \tag{4.26c}$$

where α_p is the value of α, the dimensionless sum of the principal curvatures, for the particle surface S_p at the point Q. Substituting (4.26*c*) into (4.25*a*) and solving along the $\bar{z}$-axis ($\bar{x}=\bar{y}=0$) with boundary conditions (4.25*b*, *c*) we obtain $\bar{\psi}_{E1}$ as

$$\bar{\psi}_{E1}=\frac{\alpha_p\,A_p\,\mathrm{e}^{-\bar{z}}\{2\bar{z}+A_p^2(\mathrm{e}^{-2\bar{z}}-1)\}}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})}. \tag{4.27}$$

This result agrees with that of Chew & Sen (1982) for the special case of a spherical particle for which $\alpha_p=-2$.

If the quantities $\bar{n}_{1E}$, $\bar{n}_{2E}$, $\bar{\rho}_E$ and $\bar{p}_E$ in the inner region are expanded in the same manner (4.23) as ψ_E so that

$$\left.\begin{aligned}\bar{n}_{1E} &= \bar{n}_{1E0}+\epsilon\bar{n}_{1E1}+\ldots, \quad \bar{n}_{2E} = \bar{n}_{2E0}+\epsilon\bar{n}_{2E1}+\ldots,\\ \bar{\rho}_E &= \bar{\rho}_{E0}+\epsilon\bar{\rho}_{E1}+\ldots, \quad \bar{p}_E = \bar{p}_{E0}+\epsilon\bar{p}_{E1}+\ldots,\end{aligned}\right\} \tag{4.28}$$

we see that if these expansions are substituted into equations (4.1 *a–e*) and boundary conditions (4.2 *c–e*) expressed in inner variables, then at lowest order in ϵ (i.e. at order ϵ^0)

$$\frac{\partial}{\partial\bar{z}}\left\{\frac{\partial\bar{n}_{1E0}}{\partial\bar{z}}+\bar{n}_{1E0}\frac{\partial\bar{\psi}_{E0}}{\partial\bar{z}}\right\} = 0, \quad \frac{\partial}{\partial\bar{z}}\left\{\frac{\partial\bar{n}_{2E0}}{\partial\bar{z}}-\bar{n}_{2E0}\frac{\partial\bar{\psi}_{E0}}{\partial\bar{z}}\right\} = 0, \tag{4.29 a, b}$$

$$\frac{\partial^2\bar{\psi}_{E0}}{\partial\bar{z}^2} = -\bar{\rho}_{E0}, \quad \bar{\rho}_{E0} = \tfrac{1}{2}(\bar{n}_{1E0}-\bar{n}_{2E0}), \quad \frac{\partial\bar{p}_{E0}}{\partial\bar{z}} = -\lambda\bar{\rho}_{E0}\frac{\partial\bar{\psi}_{E0}}{\partial\bar{z}}, \tag{4.29 c–e}$$

$$\frac{\partial p_{E0}}{\partial\bar{x}} = -\lambda\bar{\rho}_{E0}\frac{\partial\bar{\psi}_{E0}}{\partial\bar{x}} = 0, \quad \frac{\partial\bar{p}_{E0}}{\partial\bar{y}} = -\lambda\bar{\rho}_{E0}\frac{\partial\bar{\psi}_{E0}}{\partial\bar{y}} = 0, \tag{4.29 f}$$

with

$$\frac{\partial\bar{n}_{1E0}}{\partial\bar{z}}+\bar{n}_{1E0}\frac{\partial\bar{\psi}_{E0}}{\partial\bar{z}} = 0 \quad \text{at} \quad \bar{z} = 0, \tag{4.30 a}$$

$$\frac{\partial\bar{n}_{2E0}}{\partial\bar{z}}-\bar{n}_{2E0}\frac{\partial\bar{\psi}_{E0}}{\partial\bar{z}} = 0 \quad \text{at} \quad \bar{z} = 0, \tag{4.30 b}$$

$$\bar{\psi}_{E0} = \tilde{\psi}_p \quad \text{at} \quad \bar{z} = 0, \tag{4.30 c}$$

whilst matching onto the outer region gives

$$\bar{n}_{1E0}\to 1, \quad \bar{n}_{2E0}\to 1, \quad \bar{\psi}_{E0}\to 0 \quad \text{as} \quad \bar{z}\to\infty. \tag{4.31}$$

Integrating (4.29 *a*) and (4.29 *b*) with respect to $\bar{z}$ and making use of (4.30 *a*) and (4.30 *b*), we obtain

$$\frac{\partial\bar{n}_{1E0}}{\partial\bar{z}}+\bar{n}_{1E0}\frac{\partial\bar{\psi}_{E0}}{\partial\bar{z}} = 0, \quad \frac{\partial\bar{n}_{2E0}}{\partial\bar{z}}-\bar{n}_{2E0}\frac{\partial\bar{\psi}_{E0}}{\partial\bar{z}} = 0 \tag{4.32 a, b}$$

everywhere. Equations and boundary conditions for $\bar{n}_{1E1}, \bar{n}_{2E1}, \bar{\rho}_{E1}\ldots$ may be obtained by equating terms of order ϵ^{+1} in (4.1 *a–e*) and in (4.2 *c–e*) expressed in inner variables. Rather than solve for $\bar{n}_{1E0}, \bar{n}_{2E0}, \bar{\rho}_{E0}$ and for $\bar{n}_{1E1}, \bar{n}_{2E1}, \bar{\rho}_{E1}\ldots$ from the partial differential equations, it is easier to note that (4.14)–(4.16) are valid everywhere, including the inner region, so that we may substitute the expansions (4.23) and (4.28) directly into (4.14)–(4.16) with the known values of $\bar{\psi}_{E0}$ (given by (4.26 *a*)) and $\bar{\psi}_{E1}$ (given by (4.27)) and so obtain $\bar{n}_{1E0}, \bar{n}_{2E0}, \bar{\rho}_{E0}\ldots$ and $\bar{n}_{1E1}, \bar{n}_{2E1}, \bar{\rho}_{E1}\ldots$ on the $\bar{z}$-axis by equating like powers of ϵ. Also $\bar{x}$- and $\bar{y}$-derivatives of these quantities on the $\bar{z}$-axis may be obtained using (3.7) and (3.8). These values are all listed in Appendix A.

For an inner region of expansion at a point Q on the wall surface S_w the results (4.26), (4.27), (A 1)–(A 4) (in Appendix A) are valid if α_p is replaced by α_w (the value of α for the point Q on S_w) and A_p (given by (4.27)) is replaced by A_w, where

$$A_w = \tanh(\tfrac{1}{4}\tilde{\psi}_w). \tag{4.33}$$

5. Solution to the hydrodynamic problem

We consider now another special case of the problem discussed in §2 in which we have a purely hydrodynamic problem in which the liquid is flowing as a result only of the motion of the particle P and the wall W and of the prescribed flow at infinity. The ion concentrations are taken to be zero with no electric field present. The surface electrical potentials are set equal to zero so the ion concentrations are everywhere equal and hence $\rho = 0$ everywhere; thus there is no electrical force on the fluid. We use a subscript H to denote variables for this case (i.e. we use $\tilde{\boldsymbol{v}}_H, \tilde{p}_H$), the equations (2.9*a*, *b*) then becoming

$$\tilde{\nabla}^2 \tilde{\boldsymbol{v}}_H - \tilde{\boldsymbol{\nabla}} \tilde{p}_H = \boldsymbol{0}, \quad \tilde{\boldsymbol{\nabla}} \cdot \tilde{\boldsymbol{v}}_H = 0 \tag{5.1 a, b}$$

and boundary conditions (2.11*c*, *d*) becoming (with (2.11*a*, *b*), (2.13) automatically satisfied)

$$\tilde{\boldsymbol{v}}_H \sim \text{(given flow at infinity)} \quad \text{at} \quad |\tilde{\boldsymbol{r}}| \to \infty, \tag{5.2 a}$$

$$\tilde{\boldsymbol{v}}_H = \tilde{\boldsymbol{U}}_p \quad \text{on} \quad S_p, \quad \tilde{\boldsymbol{v}}_H = \tilde{\boldsymbol{U}}_w \quad \text{on} \quad S_w \tag{5.2 b}$$

Thus the flow field $\tilde{\boldsymbol{v}}_{H,\,\tilde{p}_H}$ is the creeping flow solution to the problem and in the outer region of expansion does not depend on the parameter ϵ.

In order to obtain an expansion in ϵ for this flow field in the inner region at a point Q (on either the surface of the particle S_p or of the wall S_w) we expand $\tilde{\boldsymbol{v}}_H, \tilde{p}_H$ as a Taylor series about Q in the $\tilde{x}, \tilde{y}, \tilde{z}$ coordinates. If the inner-region hydrodynamic variables $\tilde{\boldsymbol{v}}_H, \bar{p}_H$ are defined as in (3.2), i.e. as

$$\tilde{\boldsymbol{v}}_H = \tilde{\boldsymbol{U}} + \tilde{\boldsymbol{\Omega}} \times \tilde{\boldsymbol{r}} + \bar{\boldsymbol{v}}_H, \quad \tilde{p}_H = \bar{p}_H, \tag{5.3}$$

then we obtain

$$\left.\begin{aligned}
\bar{v}_{Hx} &= \left.\frac{\partial \tilde{v}_{Hx}}{\partial \tilde{x}}\right|_Q \tilde{x} + \left(\left.\frac{\partial \tilde{v}_{Hx}}{\partial \tilde{y}}\right|_Q + \tilde{\Omega}_z\right)\tilde{y} + \left(\left.\frac{\partial \tilde{v}_{Hx}}{\partial \tilde{z}}\right|_Q - \tilde{\Omega}_y\right)\tilde{z} + \frac{1}{2}\left.\frac{\partial^2 \tilde{v}_{Hx}}{\partial \tilde{x}^2}\right|_Q \tilde{x}^2 + \dots, \\
\bar{v}_{Hy} &= \left(\left.\frac{\partial \tilde{v}_{Hy}}{\partial \tilde{x}}\right|_Q - \tilde{\Omega}_z\right)\tilde{x} + \left.\frac{\partial \tilde{v}_{Hy}}{\partial \tilde{y}}\right|_Q \tilde{y} + \left(\left.\frac{\partial \tilde{v}_{Hy}}{\partial \tilde{z}}\right|_Q + \tilde{\Omega}_x\right)\tilde{z} + \frac{1}{2}\left.\frac{\partial^2 \tilde{v}_{Hy}}{\partial \tilde{x}^2}\right|_Q \tilde{x}^2 + \dots, \\
\bar{v}_{Hz} &= \left(\left.\frac{\partial \tilde{v}_{Hz}}{\partial \tilde{x}}\right|_Q + \tilde{\Omega}_y\right)\tilde{x} + \left(\left.\frac{\partial \tilde{v}_{Hz}}{\partial \tilde{y}}\right|_Q - \tilde{\Omega}_x\right)\tilde{y} + \left.\frac{\partial \tilde{v}_{Hz}}{\partial \tilde{z}}\right|_Q \tilde{z} + \frac{1}{2}\left.\frac{\partial^2 \tilde{v}_{Hz}}{\partial \tilde{x}^2}\right|_Q \tilde{x}^2 + \dots,
\end{aligned}\right\} \tag{5.4 a}$$

$$\bar{p}_H = \tilde{p}_H|_Q + \left.\frac{\partial \tilde{p}_H}{\partial \tilde{x}}\right|_Q \tilde{x} + \left.\frac{\partial \tilde{p}_H}{\partial \tilde{y}}\right|_Q \tilde{y} + \left.\frac{\partial \tilde{p}_H}{\partial \tilde{z}}\right|_Q \tilde{z} + \frac{1}{2}\left.\frac{\partial^2 \tilde{p}_H}{\partial \tilde{x}^2}\right|_Q \tilde{x}^2 + \dots, \tag{5.4 b}$$

where $|_Q$ denotes value at the point Q. From the no-slip boundary conditions on the solid surface and from the definition of $\bar{\boldsymbol{v}}$ in (3.2), it follows that

$$\bar{\boldsymbol{v}}_H = 0 \quad \text{on} \quad \tilde{z} = a_{11}\tilde{x}^2 + 2a_{12}\tilde{x}\tilde{y} + a_{22}\tilde{y}^2 + \dots \tag{5.5}$$

for all $\tilde{x}, \tilde{y}$. This, when substituted into (5.4*a*), gives restrictions on the values of the derivatives of $\tilde{\boldsymbol{v}}_H$ at Q. In addition, further restrictions are obtained from (5.4*a*) and (5.4*b*) and from their derivatives with respect to $\tilde{x}$, $\tilde{y}$ and $\tilde{z}$ by evaluating them at Q. If we then write (5.4*a*, *b*) in terms of the inner variables $\bar{x}$, $\bar{y}$ and $\bar{z}$ defined in (3.1) and make use of the above restrictions on the derivatives of $\tilde{\boldsymbol{v}}_H$ at Q, we may obtain the values of $\bar{\boldsymbol{v}}_H$ and $\bar{p}_H$ and their $\bar{x}$- and $\bar{y}$-derivatives evaluated on the $\bar{z}$-axis (where $\bar{x} = \bar{y} = 0$) as expansions in ϵ. These are listed in Appendix B.†

6. Electrohydrodynamic equations

We write the solution of the general electrohydrodynamic problem (considered in §2) determined by system (2.3), (2.5), (2.8), (2.9) and boundary conditions (2.11), (2.13), (2.14) as the sum of the solution of the purely electrical problem (considered in

† Appendix B is available from the Journal of Fluid Mechanics Editorial Office.

§4) with dependent variables $\tilde{n}_{1E}$, $\tilde{n}_{2E}$, $\tilde{\psi}_E$, $\tilde{\rho}_E$ and $\tilde{p}_E$, the solution of the purely hydrodynamic problem (considered in §5) with dependent variable $\tilde{\boldsymbol{v}}_H, \tilde{p}_H$ and a new set of electrohydrodynamic dependent variables denoted by an asterik. Thus

$$\left.\begin{aligned} \tilde{\boldsymbol{v}} = \tilde{\boldsymbol{v}}_H + \tilde{\boldsymbol{v}}^*, \quad \tilde{p} = \tilde{p}_H + \tilde{p}_E + \tilde{p}^*, \\ \tilde{n}_1 = \tilde{n}_{1E} + \tilde{n}_1^*, \quad \tilde{n}_2 = \tilde{n}_{2E} + \tilde{n}_2^*, \\ \tilde{\psi} = \tilde{\psi}_E + \tilde{\psi}^*, \quad \tilde{\rho} = \tilde{\rho}_E + \tilde{\rho}^*. \end{aligned}\right\} \tag{6.1}$$

Since $\tilde{\boldsymbol{v}}, \tilde{p}, \tilde{n}_1 \ldots$ satisfy system (2.5), (2.8), (2.9) with boundary conditions (2.11), (2.13), (2.14), $\tilde{n}_{1E}, \tilde{n}_{2E}, \tilde{\psi}_E, \ldots$ satisfy (4.1) with boundary conditions (4.2) and $\tilde{\boldsymbol{v}}_H, \tilde{p}_H$ satisfy (5.1) with boundary conditions (5.2), we see that the electrohydrodynamic variables $\tilde{\boldsymbol{v}}^*, \tilde{p}^*, \tilde{n}_1^* \ldots$ satisfy

$$\tilde{\nabla}^2 \tilde{n}_1^* + \tilde{\boldsymbol{\nabla}} \cdot (\tilde{n}_{1E} \tilde{\boldsymbol{\nabla}} \tilde{\psi}^* + \tilde{n}_1^* \tilde{\boldsymbol{\nabla}} \tilde{\psi}_E + \tilde{n}_1^* \tilde{\boldsymbol{\nabla}} \tilde{\psi}^*) \\ - Pe(\tilde{\boldsymbol{v}}_H \cdot \tilde{\boldsymbol{\nabla}} \tilde{n}_{1E} + \tilde{\boldsymbol{v}}_H \cdot \tilde{\boldsymbol{\nabla}} \tilde{n}_1^* + \tilde{\boldsymbol{v}}^* \cdot \tilde{\boldsymbol{\nabla}} \tilde{n}_{1E} + \tilde{\boldsymbol{v}}^* \cdot \tilde{\boldsymbol{\nabla}} \tilde{n}_1^*) - Pe\left(\frac{\partial \tilde{n}_{1E}}{\partial \tilde{t}} + \frac{\partial \tilde{n}_1^*}{\partial \tilde{t}}\right) = 0, \tag{6.2a}$$

$$\tilde{\nabla}^2 \tilde{n}_2^* - \tilde{\boldsymbol{\nabla}} \cdot (\tilde{n}_{2E} \tilde{\boldsymbol{\nabla}} \tilde{\psi}^* + \tilde{n}_2^* \tilde{\boldsymbol{\nabla}} \tilde{\psi}_E + \tilde{n}_2^* \tilde{\boldsymbol{\nabla}} \tilde{\psi}^*) \\ - Pe\left(\frac{D_1}{D_2}\right)(\tilde{\boldsymbol{v}}_H \cdot \tilde{\boldsymbol{\nabla}} \tilde{n}_{2E} + \tilde{\boldsymbol{v}}_H \cdot \tilde{\boldsymbol{\nabla}} \tilde{n}_2^* + \tilde{\boldsymbol{v}}^* \cdot \tilde{\boldsymbol{\nabla}} \tilde{n}_{2E} + \tilde{\boldsymbol{v}}^* \cdot \tilde{\boldsymbol{\nabla}} \tilde{n}_2^*) - Pe\left(\frac{D_1}{D_2}\right)\left(\frac{\partial \tilde{n}_{2E}}{\partial \tilde{t}} + \frac{\partial \tilde{n}_2^*}{\partial \tilde{t}}\right) = 0, \tag{6.2b}$$

$$\epsilon^2 \tilde{\nabla}^2 \tilde{\psi}^* = -\tilde{\rho}^*, \quad \tilde{\rho}^* = \tfrac{1}{2}(\tilde{n}_1^* - \tilde{n}_2^*), \tag{6.2c, d}$$

$$\tilde{\nabla}^2 \tilde{\boldsymbol{v}}^* - \tilde{\boldsymbol{\nabla}} \tilde{p}^* = \lambda(\tilde{\rho}^* \tilde{\boldsymbol{\nabla}} \tilde{\psi}_E + \tilde{\rho}_E \tilde{\boldsymbol{\nabla}} \tilde{\psi}^* + \tilde{\rho}^* \tilde{\boldsymbol{\nabla}} \tilde{\psi}^*), \quad \tilde{\boldsymbol{\nabla}} \cdot \tilde{\boldsymbol{v}}^* = 0, \tag{6.2e, f}$$

with boundary conditions

$$\tilde{n}_1^* \to 0, \tilde{n}_2^* \to 0; \quad \tilde{\psi}^* \to 0; \quad \tilde{\boldsymbol{v}}^* \to \boldsymbol{0} \tag{6.3a–c}$$

as $|\tilde{\boldsymbol{r}}| \to \infty$ and

$$\tilde{\boldsymbol{v}}^* = \boldsymbol{0}, \tag{6.3d}$$

$$\boldsymbol{n} \cdot \{\tilde{\boldsymbol{\nabla}} \tilde{n}_1^* + \tilde{n}_{1E} \tilde{\boldsymbol{\nabla}} \tilde{\psi}^* + \tilde{n}_1^* \boldsymbol{\nabla} \tilde{\psi}_E + \tilde{n}_1^* \tilde{\boldsymbol{\nabla}} \tilde{\psi}^*\} = 0, \tag{6.3e}$$

$$\boldsymbol{n} \cdot \{\tilde{\boldsymbol{\nabla}} \tilde{n}_2^* - \tilde{n}_{1E} \tilde{\boldsymbol{\nabla}} \tilde{\psi}^* - \tilde{n}_2^* \boldsymbol{\nabla} \tilde{\psi} E - \tilde{n}_2^* \tilde{\boldsymbol{\nabla}} \tilde{\psi}^*\} = 0, \tag{6.3f}$$

$$\tilde{\psi}^* = 0, \tag{6.3g}$$

on S_p and on S_w.

In the outer region of the expansion (where the tilde variables are used), since the solution of the purely electrical problem is given by (4.19) and since we apply boundary conditions only at infinity (and match onto the inner-region expansions as the surfaces S_p or S_w are approached), we see that in this outer region, the electrohydrodynamic variables $\tilde{\boldsymbol{v}}^*, \tilde{p}^*, \tilde{n}_1^* \ldots$ satisfy

$$\tilde{\nabla}^2 \tilde{n}_1^* + \tilde{\nabla}^2 \tilde{\psi}^* + \tilde{\boldsymbol{\nabla}} \cdot (\tilde{n}_1^* \tilde{\boldsymbol{\nabla}} \tilde{\psi}^*) - Pe(\tilde{\boldsymbol{v}}_H \cdot \tilde{\boldsymbol{\nabla}} \tilde{n}_1^* + \tilde{\boldsymbol{v}}^* \cdot \tilde{\boldsymbol{\nabla}} \tilde{n}_1^*) - Pe \frac{\partial \tilde{n}_1^*}{\partial \tilde{t}} = 0, \tag{6.4a}$$

$$\tilde{\nabla}^2 \tilde{n}_2^* - \tilde{\nabla}^2 \tilde{\psi}^* - \tilde{\boldsymbol{\nabla}} \cdot (\tilde{n}_2^* \tilde{\boldsymbol{\nabla}} \tilde{\psi}^*) - Pe\left(\frac{D_1}{D_2}\right)(\tilde{\boldsymbol{v}}_H \cdot \tilde{\boldsymbol{\nabla}} \tilde{n}_2^* + \tilde{\boldsymbol{v}}^* \cdot \tilde{\boldsymbol{\nabla}} \tilde{n}_2^*) - Pe\left(\frac{D_1}{D_2}\right)\frac{\partial \tilde{n}_2^*}{\partial \tilde{t}} = 0, \tag{6.4b}$$

$$\epsilon^2 \tilde{\nabla}^2 \tilde{\psi}^* = -\tilde{\rho}^*, \quad \tilde{\rho}^* = \tfrac{1}{2}(\tilde{n}_1^* - \tilde{n}_2^*), \tag{6.4c, d}$$

$$\tilde{\nabla}^2 \tilde{\boldsymbol{v}}^* - \tilde{\boldsymbol{\nabla}} \tilde{p}^* = \lambda \tilde{\rho}^* \tilde{\boldsymbol{\nabla}} \tilde{\psi}^*, \quad \tilde{\boldsymbol{\nabla}} \cdot \tilde{\boldsymbol{v}}^* = 0, \tag{6.4e, f}$$

with boundary conditions

$$\tilde{n}_1^* \to 0, \tilde{n}_2^* \to 0; \quad \tilde{\psi}^* \to 0; \tilde{\boldsymbol{v}}^* \to \boldsymbol{0} \tag{6.5a–c}$$

as $|\tilde{\boldsymbol{r}}| \to \infty$. In deriving (6.2*a*, *b*) it should be noted that, in general, $\partial \tilde{n}_{1E}/\partial \tilde{t}$ and $\partial \tilde{n}_{2E}/\partial \tilde{t}$ are non-zero and must be included since the boundaries S_p and S_w move and thus the time-independent solutions for $\tilde{n}_{1E}$ and $\tilde{n}_{2E}$ as calculated in §4 must be considered as functions of $\tilde{t}$.

In the inner region of expansion (where barred variables are used) at a point Q (on either surface S_p or S_w) we obtain the equations and boundary conditions for $\bar{\boldsymbol{v}}^*, \bar{p}^*, \bar{n}_1^*, \ldots$ valid on the $\bar{z}$-axis (i.e. on $\bar{x} = \bar{y} = 0$) by writing (6.2) and (6.3) in terms of the inner variables using (3.1)–(3.3) (noting that, by (5.3) $\bar{\boldsymbol{v}}^* = \tilde{\boldsymbol{v}}^*, \bar{p}^* = \tilde{p}^*$) and then substituting the known expansions (see (4.23), (4.26), (4.27), (4.28) (A 1)–(A 4)) for the electrical problem variables (and their $\bar{x}$- and $\bar{y}$-derivatives) and the expansions (given in Appendix B) from the purely hydrodynamic problem variables (and their $\bar{x}$- and $\bar{y}$-derivatives). In doing this it should be noted that, since the $\bar{x}, \bar{y}, \bar{z}$ coordinates translate and rotate with the solid surface, if we define $\partial/\partial \bar{t}$ as a derivative with respect to dimensionless time at fixed $\bar{x}, \bar{y}, \bar{z}$ so that

$$\frac{\partial}{\partial \bar{t}} = \frac{\partial}{\partial \tilde{t}} + (\tilde{\boldsymbol{U}} + \tilde{\boldsymbol{\Omega}} \times \tilde{\boldsymbol{r}}) \cdot \tilde{\boldsymbol{\nabla}}$$

then

$$\frac{\partial \bar{n}_{1E}}{\partial \bar{t}} = \frac{\partial \bar{n}_{2E}}{\partial \bar{t}} = 0.$$

Boundary conditions are applied in the inner region only at the solid boundary (i.e. at $\bar{z} = 0$) and match onto the outer region (at Q) as $\bar{z} \to \infty$. The equations and boundary conditions for $\bar{\boldsymbol{v}}^*, \bar{p}^*, \bar{n}_1^* \ldots$ so obtained are listed in Appendix C.

7. Inner-region solution for $\bar{n}_1^*, \bar{n}_2^*, \bar{\psi}^*$ at order ϵ^2

In equations (C 1) and boundary conditions (C 2) (in Appendix C) for the inner region, it is observed that the lowest-order terms in ϵ in which the electrohydrodynamic (starred) variables do not appear (i.e. the lowest-order non-homogeneous terms) are of order ϵ^3 and occur in equations (C 1*a*, *b*). This suggests that $\bar{n}_1^*$ and $\bar{n}_2^*$ and hence also $\bar{\rho}^*$ and $\bar{\psi}^*$ (see (C 1*c*, *d*)) are all of order ϵ^3. However, as will be observed later (see (8.5)), such terms behave like $\bar{z}^{+1}$ as $\bar{z} \to \infty$. A term like $\epsilon^3 \bar{z} = \epsilon^2 \tilde{z}$ would match onto a term of order ϵ^2 in the outer region so that $\tilde{n}_1^*, \tilde{n}_2^*, \tilde{\rho}^*$ and $\tilde{\psi}^*$ would be of order ϵ^2. Such outer-region terms, as will be shown later (see (9.9)), tend to constants (containing terms like $\epsilon^2 \tilde{z}^0$) as the solid boundaries are approached. A term like $\epsilon^2 \tilde{z}^0 = \epsilon^2 \bar{z}^0$ would match to a term of order ϵ^2 in the inner region so that $\bar{n}_1^*, \bar{n}_2^*, \bar{\rho}^*$ and $\bar{\psi}^*$ contain terms of order ϵ^2 as well as those of order ϵ^3 and hence we write

$$\left.\begin{aligned} &\bar{n}_i^* = \bar{n}_{i2}^* \epsilon^2 + \bar{n}_{i3}^* \epsilon^3 + \ldots \quad (i = 1, 2), \quad \bar{\rho}^* = \bar{\rho}_2^* \epsilon^2 + \bar{\rho}_3^* \epsilon^3 + \ldots, \\ &\bar{\psi}^* = \bar{\psi}_2^* \epsilon^2 + \bar{\psi}_3^* \epsilon^3 + \ldots, \quad \bar{p}^* = \bar{p}_2^* \epsilon^2 + \bar{p}_3^* \epsilon^3 + \ldots. \end{aligned}\right\} \tag{7.1}$$

Substituting these expansions into (C 1*a*–*d*, *g*) and boundary conditions (C 2*b*–*d*) we obtain, by equating terms of order ϵ^2,

$$\frac{\partial^2 \bar{n}_{12}^*}{\partial \bar{z}^2} + \frac{\partial}{\partial \bar{z}}\left(\bar{n}_{1E0} \frac{\partial \bar{\psi}_2^*}{\partial \bar{z}}\right) + \frac{\partial}{\partial \bar{z}}\left(\bar{n}_{12}^* \frac{\partial \bar{\psi}_{E0}}{\partial \bar{z}}\right) = 0, \tag{7.2a}$$

$$\frac{\partial \bar{n}_{22}^*}{\partial \bar{z}^2} - \frac{\partial}{\partial \bar{z}}\left(\bar{n}_{2E0} \frac{\partial \bar{\psi}_2^*}{\partial \bar{z}}\right) - \frac{\partial}{\partial \bar{z}}\left(\bar{n}_{22}^* \frac{\partial \bar{\psi}_{E0}}{\partial \bar{z}}\right) = 0, \tag{7.2b}$$

$$\frac{\partial^2 \bar{\psi}^{*2}}{\partial \bar{z}^2} = -\bar{\rho}_2^*, \quad \bar{\rho}_2^* = \tfrac{1}{2}(\bar{n}_{12}^* - \bar{n}_{22}^*), \tag{7.2c, d}$$

$$\frac{\partial \bar{p}_2^*}{\partial \bar{z}} = -\lambda \left\{ \bar{\rho}_2^* \frac{\partial \bar{\psi}_{E0}}{\partial \bar{z}} + \bar{\rho}_{E0} \frac{\partial \bar{\psi}_2^*}{\partial \bar{z}} \right\}, \tag{7.2e}$$

with

$$\frac{\partial \bar{n}_{12}^*}{\partial \bar{z}} + \bar{n}_{1E0} \frac{\partial \bar{\psi}_2^*}{\partial \bar{z}} + \bar{n}_{12}^* \frac{\partial \bar{\psi}_{E0}}{\partial \bar{z}} = 0, \tag{7.3a}$$

$$\frac{\partial \bar{n}_{22}^*}{\partial \bar{z}} - \bar{n}_{2E0} \frac{\partial \bar{\psi}_2^*}{\partial \bar{z}} - \bar{n}_{22}^* \frac{\partial \bar{\psi}_{E0}}{\partial \bar{z}} = 0, \quad \bar{\psi}_2^* = 0 \tag{7.3b, c}$$

on $\bar{z} = 0$. By integrating (7.2a, b) with respect to $\bar{z}$ and making use of (7.3a, b), we see that

$$\frac{\partial \bar{n}_{12}^*}{\partial \bar{z}} + \bar{n}_{1E0} \frac{\partial \bar{\psi}_2^*}{\partial \bar{z}} + \bar{n}_{12}^* \frac{\partial \bar{\psi}_{E0}}{\partial \bar{z}} = 0, \quad \frac{\partial \bar{n}_{22}^*}{\partial \bar{z}} - \bar{n}_{1E0} \frac{\partial \bar{\psi}_2^*}{\partial \bar{z}} - \bar{n}_{22}^* \frac{\partial \bar{\psi}_{E0}}{\partial \bar{z}} = 0 \tag{7.4a, b}$$

for all $\bar{z}$.

As already mentioned, we assume that $\bar{n}_{12}^*$, $\bar{n}_{22}^*$, $\bar{\rho}_2^*$ and $\bar{\psi}_2^*$ tend to constants as $\bar{z} \to \infty$, with the constants being determined by matching onto the order-ϵ^2 terms in the outer region. Thus we take

$$\bar{n}_{12}^* \to \beta_1, \quad \bar{n}_{22}^* \to \beta_3, \quad \bar{\rho}_2^* \to \beta_4, \quad \bar{\psi}_2^* \to \beta_2 \tag{7.5}$$

and, since (7.2c, d) are to be satisfied,

$$\beta_3 = \beta_1, \quad \beta_4 = 0. \tag{7.6}$$

If we define $\hat{n}_1$, $\hat{n}_2$, $\hat{\rho}$, $\hat{\psi}$ and $\hat{p}$ as

$$\left.\begin{aligned} \hat{n}_1 &= \bar{n}_{1E0} + \epsilon^2 \bar{n}_{12}^*, \quad \hat{n}_2 = \bar{n}_{2E0} + \epsilon^2 \bar{n}_{22}^*, \\ \hat{\rho} &= \rho_{E0} + \epsilon^2 \bar{\rho}_2^*, \quad \hat{\psi} = \bar{\psi}_{E0} + \epsilon^2 \bar{\psi}_2^*, \\ \hat{p} &= \bar{p}_{E0} + \epsilon^2 \bar{p}_2^*, \end{aligned}\right\} \tag{7.7}$$

it is seen, by adding ϵ^2 times (7.2a–e) (and boundary conditions (7.3a–c)) to (4.29a–e) (and boundary conditions (4.30a–c)), that $\hat{n}_1, \hat{n}_2, \hat{\rho} \ldots$ satisfy the same equations (4.29a–e) and boundary conditions (4.30a–c) as $\bar{n}_{1E0}, \bar{n}_{2E0}, \bar{\rho}_{E0} \ldots$. However the boundary conditions for $\bar{n}_{1E0}, \bar{n}_{2E0}, \bar{\rho}_{E0} \ldots$ as $\bar{z} \to \infty$, namely

$$\bar{n}_{1E0} \to 1, \quad \bar{n}_{2E0} \to 1, \quad \bar{\psi}_{E0} \to 0, \tag{7.8}$$

must be replaced by

$$\hat{n}_1 \to 1 + \epsilon^2 \beta_1, \quad \hat{n}_2 \to 1 + \epsilon^2 \beta_1, \quad \hat{\psi} \to \epsilon^2 \beta_2 \tag{7.9}$$

as $\bar{z} \to \infty$. Solving for $\hat{\psi}$, $\hat{n}_1$, $\hat{n}_2$, $\hat{\rho}$ and $\hat{p}$ in a manner similar to that for $\tilde{\psi}_E$, $\tilde{n}_{1E}$, $\tilde{n}_{2E}$, $\tilde{\rho}_E$ and $\tilde{p}_E$ (see (4.14)–(4.18)) we may obtain on the $\bar{z}$-axis (for Q on the particle surface S_p)

$$\hat{\psi} = \epsilon^2 \beta_2 + 2 \ln \left\{ \frac{1 + \tanh[\frac{1}{4}(\tilde{\psi}_p - \epsilon^2 \beta_2)] \exp[-(1+\epsilon^2\beta_1)^{1/2} \bar{z}]}{1 - \tanh[\frac{1}{4}(\tilde{\psi}_p - \epsilon^2 \beta_2)] \exp[-(1+\epsilon^2\beta_1)^{1/2} \bar{z}]} \right\}, \tag{7.10a}$$

$$\hat{n}_1 = (1+\epsilon^2\beta_1) \left\{ \frac{1 - \tanh[\frac{1}{4}(\tilde{\psi}_p - \epsilon^2 \beta_2)] \exp[-(1+\epsilon^2\beta_1)^{1/2} \bar{z}]}{1 + \tanh[\frac{1}{4}(\tilde{\psi}_p - \epsilon^2 \beta_2)] \exp[-(1+\epsilon^2\beta_1)^{1/2} \bar{z}]} \right\}^2, \tag{7.10b}$$

$$\hat{n}_2 = (1+\epsilon^2\beta_1) \left\{ \frac{1 + \tanh[\frac{1}{4}(\tilde{\psi}_p - \epsilon^2 \beta_2)] \exp[-(1+\epsilon^2\beta_1)^{1/2} \bar{z}]}{1 - \tanh[\frac{1}{4}(\tilde{\psi}_p - \epsilon^2 \beta_2)] \exp[-(1+\epsilon^2\beta_1)^{1/2} \bar{z}]} \right\}^2, \tag{7.10c}$$

with

$$\hat{\rho} = \tfrac{1}{2}(\hat{n}_1 - \hat{n}_2), \quad \hat{p} = \lambda\{\tfrac{1}{2}(\hat{n}_1 + \hat{n}_2) - (1+\epsilon^2\beta_1)\}. \tag{7.10d, e}$$

Expanding these results as a power series in ϵ^2 and comparing with (7.7), the values of $\bar{\psi}_2^*$, $\bar{n}_1^*$, $\bar{n}_2^*$, $\bar{\rho}_2^*$ and $\bar{p}_2^*$ on the $\bar{z}$-axis are obtained as

$$\bar{\psi}_2^* = \beta_2 - \frac{\mathrm{e}^{-\bar{z}}\{2\beta_1 A_p \bar{z} + \beta_2(1-A_p^2)\}}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})}, \tag{7.11a}$$

$$\bar{n}_{12}^* = \left(\frac{1-A_p\,\mathrm{e}^{-\bar{z}}}{1+A_p\,\mathrm{e}^{-\bar{z}}}\right)^2 \left\{\beta_1 + \frac{\mathrm{e}^{-\bar{z}}\{2\beta_1 A_p \bar{z} + \beta_2(1-A_p^2)\}}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})}\right\}, \tag{7.11b}$$

$$\bar{n}_{22}^* = \left(\frac{1+A_p\,\mathrm{e}^{-\bar{z}}}{1-A_p\,\mathrm{e}^{-\bar{z}}}\right)^2 \left\{\beta_1 - \frac{\mathrm{e}^{-\bar{z}}\{2\beta_1 A_p \bar{z} + \beta_2(1-A_p^2)\}}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})}\right\}, \tag{7.11c}$$

$$\begin{aligned}\bar{\rho}_2^* = &-\frac{4\beta_1 A_p\,\mathrm{e}^{-\bar{z}}(1+A_p^2\,\mathrm{e}^{-2\bar{z}})}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})^2} \\ &+\frac{\mathrm{e}^{-\bar{z}}(2\beta_1 A_p \bar{z} + \beta_2(1-A_p^2))\,(1+6A_p^2\,\mathrm{e}^{-2\bar{z}} + A_p^4\,\mathrm{e}^{-4\bar{z}})}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})^3},\end{aligned} \tag{7.11d}$$

$$\begin{aligned}\bar{p}_2^* = &-\frac{4\lambda A_p\,\mathrm{e}^{-2\bar{z}}}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})^3}\{2\beta_1 A_p(\bar{z}-1+A_p^2\,\bar{z}\,\mathrm{e}^{-2\bar{z}} + A_p^2\,\mathrm{e}^{-2\bar{z}}) \\ &+\beta_2(1-A_p^2)\,(1+A_p^2\,\mathrm{e}^{-2\bar{z}})\},\end{aligned} \tag{7.11e}$$

where (see (4.16)) it has been assumed, without loss of generality, that $\bar{p}_2^* \to 0$ as $\bar{z} \to \infty$. The constants β_1 and β_2 will later be obtained by matching onto the outer-region expansion and will be found to have values which in general depend on position on the surface S_p in the outer variables. Thus by making use of (3.8) and (3.9) we obtain on the $\bar{z}$-axis

$$\begin{aligned}\frac{\partial \bar{p}_2^*}{\partial \bar{x}} = &-\epsilon^{1/2}\frac{4\lambda A_p\,\mathrm{e}^{-2\bar{z}}}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})^3}\left\{2\frac{\partial \beta_1}{\partial \tilde{x}} A_p(\bar{z}-1+A_p^2\,\bar{z}\,\mathrm{e}^{-2\bar{z}} + A_p^2\,\mathrm{e}^{-2\bar{z}})\right. \\ &\left.+\frac{\partial \beta_2}{\partial \tilde{x}}(1-A_p^2)\,(1+A_p^2\,\mathrm{e}^{-2\bar{z}})\right\},\end{aligned} \tag{7.12a}$$

$$\begin{aligned}\frac{\partial \bar{p}_2^*}{\partial \bar{y}} = &-\epsilon^{1/2}\frac{4\lambda A_p\,\mathrm{e}^{-2\bar{z}}}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})^3}\left\{2\frac{\partial \beta_1}{\partial \tilde{y}} A_p(\bar{z}-1+A_p^2\,\bar{z}\,\mathrm{e}^{-2\bar{z}} + A_p^2\,\mathrm{e}^{-2\bar{z}})\right. \\ &\left.+\frac{\partial \beta_2}{\partial \tilde{y}}(1-A_p^2)\,(1+A_p^2\,\mathrm{e}^{-2\bar{z}})\right\},\end{aligned} \tag{7.12b}$$

$$\frac{\partial \bar{\psi}_2^*}{\partial \bar{x}} = \epsilon^{1/2}\left[\frac{\partial \beta_1}{\partial \tilde{x}}\left\{-\frac{2A_p\,\bar{z}\,\mathrm{e}^{-\bar{z}}}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})}\right\} + \frac{\partial \beta_2}{\partial \tilde{x}}\left\{1-\frac{(1-A_p^2)\,\mathrm{e}^{-\bar{z}}}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})}\right\}\right], \tag{7.13a}$$

$$\frac{\partial \bar{\psi}_2^*}{\partial \bar{y}} = \epsilon^{1/2}\left[\frac{\partial \beta_1}{\partial \tilde{y}}\left\{-\frac{2A_p\,\bar{z}\,\mathrm{e}^{-\bar{z}}}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})}\right\} + \frac{\partial \beta_2}{\partial \tilde{y}}\left\{1-\frac{(1-A_p^2)\,\mathrm{e}^{-\bar{z}}}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})}\right\}\right], \tag{7.13b}$$

and also

$$\left(\frac{\partial^2}{\partial \bar{x}^2} + \frac{\partial^2}{\partial \bar{y}^2}\right)\bar{\psi}_2^* = -\alpha_p\frac{\partial \bar{\psi}_2^*}{\partial \bar{z}} + O(\epsilon), \tag{7.14a}$$

$$\left(\frac{\partial^2}{\partial \bar{x}^2} + \frac{\partial^2}{\partial \bar{y}^2}\right)\bar{n}_{12}^* = -\alpha_p\frac{\partial \bar{n}_{12}^*}{\partial \bar{z}} + O(\epsilon), \tag{7.14b}$$

$$\left(\frac{\partial^2}{\partial \bar{x}^2} + \frac{\partial^2}{\partial \bar{y}^2}\right)\bar{n}_{22}^* = -\alpha_p\frac{\partial \bar{n}_{22}^*}{\partial \bar{z}} + O(\epsilon), \tag{7.14c}$$

where $\bar{\psi}_2^*$, $\bar{n}_{12}^*$ and $\bar{n}_{22}^*$ on the right-hand sides of these equations are given by (7.11 *a–c*). For Q on the surface S_w, we obtain similarly in the inner region the same results (7.11)–(7.14) with A_p and α_p replaced by A_w and α_{w}.

8. Inner-region solution for $\bar{n}_1^*, \bar{n}_2^*, \bar{\psi}^*$ at order ϵ^3

Substituting the expansions (7.1) into (C 1 *a–d*) and boundary conditions (C 2 *b–d*) we obtain, by equating terms of order ϵ^3, the equations for $\bar{n}_{13}^*$, $\bar{n}_{23}^*$, $\bar{\rho}_3^*$ and $\bar{\psi}_3^*$ as

$$\begin{aligned}\frac{\partial^2 \bar{n}_{13}^*}{\partial \bar{z}^2} &+ \left(\frac{\partial^2}{\partial \bar{x}^2} + \frac{\partial^2}{\partial \bar{y}^2}\right)\bar{n}_{12}^* + \frac{\partial}{\partial \bar{z}}\left(\bar{n}_{1E0}\frac{\partial \bar{\psi}_3^*}{\partial \bar{z}}\right) + \frac{\partial}{\partial \bar{z}}\left(\bar{n}_{1E1}\frac{\partial \bar{\psi}_2^*}{\partial \bar{z}}\right) \\ &+ \frac{\partial}{\partial \bar{z}}\left(\bar{n}_{13}^*\frac{\partial \bar{\psi}_{E0}}{\partial \bar{z}}\right) + \frac{\partial}{\partial \bar{z}}\left(\bar{n}_{12}^*\frac{\partial \bar{\psi}_{E1}}{\partial \bar{z}}\right) + \bar{n}_{1E0}\left(\frac{\partial^2}{\partial \bar{x}^2} + \frac{\partial^2}{\partial \bar{y}^2}\right)\bar{\psi}_2^* \\ &+ \bar{n}_{12}^*\left(\frac{\partial^2}{\partial \bar{x}^2} + \frac{\partial^2}{\partial \bar{y}^2}\right)\bar{\psi}_{E0} - \tfrac{1}{2}Pe\left.\frac{\partial^2 \tilde{v}_{Hz}}{\partial \tilde{z}^2}\right|_Q \bar{z}^2\frac{\partial \bar{n}_{1E0}}{\partial \bar{z}} = 0, \qquad (8.1\,a)\end{aligned}$$

$$\begin{aligned}\frac{\partial^2 \bar{n}_{23}^*}{\partial \bar{z}^2} &+ \left(\frac{\partial^2}{\partial \bar{x}^2} + \frac{\partial^2}{\partial \bar{y}^2}\right)\bar{n}_{22}^* - \frac{\partial}{\partial \bar{z}}\left(\bar{n}_{1E0}\frac{\partial \bar{\psi}_3^*}{\partial \bar{z}}\right) - \frac{\partial}{\partial \bar{z}}\left(\bar{n}_{2E1}\frac{\partial \bar{\psi}_2^*}{\partial \bar{z}}\right) \\ &- \frac{\partial}{\partial \bar{z}}\left(\bar{n}_{23}^*\frac{\partial \bar{\psi}_{E0}}{\partial \bar{z}}\right) - \frac{\partial}{\partial \bar{z}}\left(\bar{n}_{22}^*\frac{\partial \bar{\psi}_{E1}}{\partial \bar{z}}\right) - \bar{n}_{2E0}\left(\frac{\partial^2}{\partial \bar{x}^2} + \frac{\partial^2}{\partial \bar{y}^2}\right)\bar{\psi}_2^* \\ &- \bar{n}_{22}^*\left(\frac{\partial^2}{\partial \bar{x}^2} + \frac{\partial^2}{\partial \bar{y}^2}\right)\bar{\psi}_{E0} - \tfrac{1}{2}Pe\left(\frac{D_1}{D_2}\right)\left.\frac{\partial^2 \tilde{v}_{Hz}}{\partial \tilde{z}^2}\right|_Q \bar{z}^2\frac{\partial \bar{n}_{2E0}}{\partial \bar{z}} = 0, \qquad (8.1\,b)\end{aligned}$$

$$\frac{\partial^2 \bar{\psi}_3^*}{\partial \bar{z}^2} + \left(\frac{\partial^2}{\partial \bar{x}^2} + \frac{\partial^2}{\partial \bar{y}^2}\right)\bar{\psi}_2^* = -\bar{\rho}_3^*, \quad \rho_3^* = \tfrac{1}{2}(\bar{n}_{13}^* - \bar{n}_{23}^*), \qquad (8.1\,c,\,d)$$

and the boundary conditions as

$$\frac{\partial \bar{n}_{13}^*}{\partial \bar{z}} + \bar{n}_{1E0}\frac{\partial \bar{\psi}_3^*}{\partial \bar{z}} + \bar{n}_{1E1}\frac{\partial \bar{\psi}_2^*}{\partial \bar{z}} + \bar{n}_{13}^*\frac{\partial \bar{\psi}_{E0}}{\partial \bar{z}} + \bar{n}_{12}^*\frac{\partial \bar{\psi}_{E1}}{\partial \bar{z}} = 0, \qquad (8.2\,a)$$

$$\frac{\partial \bar{n}_{23}^*}{\partial \bar{z}} - \bar{n}_{2E0}\frac{\partial \bar{\psi}_3^*}{\partial \bar{z}} - \bar{n}_{2E1}\frac{\partial \bar{\psi}_2^*}{\partial \bar{z}} - \bar{n}_{23}^*\frac{\partial \bar{\psi}_{E0}}{\partial \bar{z}} - \bar{n}_{22}^*\frac{\partial \bar{\psi}_{E1}}{\partial \bar{z}} = 0, \qquad (8.2\,b)$$

$$\bar{\psi}_3^* = 0 \qquad (8.2\,c)$$

on $\bar{z} = 0$. In deriving (8.1 *a*, *b*) it is assumed, as will be shown later (see (11.1)), that $\bar{v}_x^*$ and $\bar{v}_y^*$ are of order ϵ^4 and $\bar{v}_z^*$ of order ϵ^5.

By making use of (7.14 *a–c*), (4.26 *c*) and (7.4 *a*, *b*) it is seen that (8.1 *a*, *b*) may be simplified to give

$$\frac{\partial}{\partial \bar{z}}\left\{\frac{\partial \bar{n}_{13}^*}{\partial \bar{z}} + \bar{n}_{1E0}\frac{\partial \bar{\psi}_3^*}{\partial \bar{z}} + \bar{n}_{1E1}\frac{\partial \bar{\psi}_2^*}{\partial \bar{z}} + \bar{n}_{13}^*\frac{\partial \bar{\psi}_{E0}}{\partial \bar{z}} + \bar{n}_{12}^*\frac{\partial \bar{\psi}_{E1}}{\partial \bar{z}}\right\} = \tfrac{1}{2}Pe\left.\frac{\partial^2 \tilde{v}_{Hz}}{\partial \tilde{z}^2}\right|_Q \bar{z}^2\frac{\partial \bar{n}_{1E0}}{\partial \bar{z}}, \qquad (8.3\,a)$$

$$\frac{\partial}{\partial \bar{z}}\left\{\frac{\partial \bar{n}_{23}^*}{\partial \bar{z}} - \bar{n}_{2E0}\frac{\partial \bar{\psi}_3^*}{\partial \bar{z}} - \bar{n}_{2E1}\frac{\partial \bar{\psi}_2^*}{\partial \bar{z}} - \bar{n}_{23}^*\frac{\partial \bar{\psi}_{E0}}{\partial \bar{z}} - \bar{n}_{22}^*\frac{\partial \bar{\psi}_{E1}}{\partial \bar{z}}\right\} = \tfrac{1}{2}Pe\left(\frac{D_1}{D_2}\right)\left.\frac{\partial^2 \tilde{v}_{Hz}}{\partial \tilde{z}^2}\right|_Q \bar{z}^2\frac{\partial \bar{n}_{2E0}}{\partial \bar{z}}, \qquad (8.3\,b)$$

which when integrated with respect to $\bar{z}$, with use being made of (8.2 *a*, *b*), gives

$$\lim_{\bar{z}\to\infty}\left\{\frac{\partial \bar{n}^*_{13}}{\partial \bar{z}}+\bar{n}_{1E0}\frac{\partial \bar{\psi}^*_3}{\partial \bar{z}}+\bar{n}_{1E1}\frac{\partial \bar{\psi}^*_2}{\partial \bar{z}}+\bar{n}^*_{13}\frac{\partial \bar{\psi}_{E0}}{\partial \bar{z}}+\bar{n}^*_{12}\frac{\partial \psi_{E1}}{\partial \bar{z}}\right\} = \tfrac{1}{2}Pe\left.\frac{\partial^2\tilde{v}_{Hz}}{\partial \tilde{z}^2}\right|_Q\int_0^\infty \bar{z}^2\frac{\partial \bar{n}_{1E0}}{\partial \bar{z}}\,\mathrm{d}\bar{z}, \quad (8.4\,a)$$

$$\lim_{\bar{z}\to\infty}\left\{\frac{\partial \bar{n}^*_{23}}{\partial \bar{z}}-\bar{n}_{2E0}\frac{\partial \bar{\psi}^*_3}{\partial \bar{z}}-\bar{n}_{2E1}\frac{\partial \bar{\psi}^*_2}{\partial \bar{z}}-\bar{n}^*_{23}\frac{\partial \bar{\psi}_{E0}}{\partial \bar{z}}-\bar{n}^*_{22}\frac{\partial \psi_{E1}}{\partial \bar{z}}\right\} = \tfrac{1}{2}Pe\left(\frac{D_1}{D_2}\right)\left.\frac{\partial^2\tilde{v}_{Hz}}{\partial \tilde{z}^2}\right|_Q\int_0^\infty \bar{z}^2\frac{\partial \bar{n}_{2E0}}{\partial \bar{z}}\,\mathrm{d}\bar{z}, \quad (8.4\,b)$$

where, by the values of $\bar{n}_{1E0}$ and $\bar{n}_{2E0}$ (given by (A 1*a*) and (A 2*a*)), it is readily observed that the integrals on the right-hand sides are convergent. By making use of (7.14*a*), we may write (8.1 *c*, *d*) as

$$\frac{\partial^2\bar{\psi}^*_3}{\partial \bar{z}^2}-\alpha\frac{\partial \bar{\psi}^*_2}{\partial \bar{z}} = -\bar{\rho}^*_3, \quad \bar{\rho}^*_3 = \tfrac{1}{2}(\bar{n}^*_{13}-\bar{n}^*_{23}). \quad (8.4\,c,\,d)$$

Since the right hand sides of (8.4 *a*, *b*) are constants independent of $\bar{z}$, it would appear that the solution of (8.4 *a*–*d*) for $\bar{n}^*_{13}$, $\bar{n}^*_{23}$, $\bar{\rho}^*_3$ and $\bar{\psi}^*_3$ in the limit of $\bar{z}\to\infty$ must give values increasing with $\bar{z}$ like $\bar{z}^{+1}$. Thus we take

$$\bar{n}^*_{13}\sim\alpha_1\bar{z}, \quad \bar{n}^*_{23}\sim\alpha_3\bar{z}, \quad \bar{\rho}^*_3\sim\alpha_4\bar{z}, \quad \bar{\psi}^*_3\sim\alpha_2\bar{z} \quad (8.5)$$

as $\bar{z}\to\infty$. Since we know the asymptotic forms for $\bar{z}\to\infty$ of $\bar{n}_{1E0}$, $\bar{n}_{2E0}$ and $\bar{\psi}_{E0}$ (obtained from (4.26*a*), (A 1*a*) (A 2*a*)), of $\bar{n}_{1E1}$, $\bar{n}_{2E1}$ and $\bar{\psi}_{E1}$ (obtained from (4.27), (A 1*b*), (A 2*b*)) and of $\bar{n}^*_{12}$, $\bar{n}^*_{22}$ and $\bar{\psi}^*_2$ (given by (7.5), (7.6)), we see that (8.4 *a*–*d*) in the limit of $\bar{z}\to\infty$ give four linear algebraic equations for α_1, α_2, α_3 and α_4. These may be solved to give

$$\alpha_1 = \alpha_3 = \tfrac{1}{4}Pe\left.\frac{\partial^2\tilde{v}_{Hz}}{\partial \tilde{z}^2}\right|_Q\left\{\int_0^\infty \bar{z}^2\frac{\partial \bar{n}_{1E0}}{\partial \bar{z}}\,\mathrm{d}\bar{z}+\frac{D_1}{D_2}\int_0^\infty \bar{z}^2\frac{\partial \bar{n}_{2E0}}{\partial \bar{z}}\,\mathrm{d}\bar{z}\right\}, \quad (8.6\,a)$$

$$\alpha_2 = \tfrac{1}{4}Pe\left.\frac{\partial^2\tilde{v}_{Hz}}{\partial \tilde{z}^2}\right|_Q\left\{\int_0^\infty \bar{z}^2\frac{\partial \bar{n}_{1E0}}{\partial \bar{z}}\,\mathrm{d}\bar{z}-\frac{D_1}{D_2}\int_0^\infty \bar{z}^2\frac{\partial \bar{n}_{2E0}}{\partial \bar{z}}\,\mathrm{d}\bar{z}\right\}, \quad (8.6\,b)$$

$$\alpha_4 = 0. \quad (8.6\,c)$$

By substituting into these integrals the known values of $\bar{n}_{1E0}$ and $\bar{n}_{2E0}$ given by (A 1*a*) and (A 2*a*) we obtain

$$\alpha_1 = \alpha_3 = \frac{1}{2D_2}Pe\left.\frac{\partial^2\tilde{v}_{Hz}}{\partial \tilde{z}^2}\right|_Q\{(D_2-D_1)\,\tilde{\psi}_p-4(D_1+D_2)\ln[\cosh(\tfrac{1}{4}\tilde{\psi}_p)]\}, \quad (8.7\,a)$$

$$\alpha_2 = \frac{1}{2D_2}Pe\left.\frac{\partial^2\tilde{v}_{Hz}}{\partial \tilde{z}^2}\right|_Q\{(D_1+D_2)\,\tilde{\psi}_p-4(D_2-D_1)\ln[\cosh(\tfrac{1}{4}\tilde{\psi}_p)]\}, \quad (8.7\,b)$$

$$\alpha_4 = 0. \quad (8.7\,c)$$

As $\bar{z}\to\infty$, the asymptotic forms of $\bar{n}^*_1$, $\bar{n}^*_2$, $\bar{\rho}^*$ and $\bar{\psi}^*$ may be determined from (7.1), (7.5) and (8.5) as

$$\bar{n}^*_1 = \epsilon^2(\beta_1+\dots)+\epsilon^3(\alpha_1\bar{z}+\dots)+\dots, \quad \bar{n}^*_2 = \epsilon^2(\beta_1+\dots)+\epsilon^3(\alpha_1\bar{z}+\dots)+\dots, \quad (8.8\,a,\,b)$$

$$\bar{\rho}^* = \epsilon^2(0+\dots)+\epsilon^3(0\bar{z}+\dots)+\dots, \quad \bar{\psi}^* = \epsilon^2(\beta_2+\dots)+\epsilon^3(\alpha_2\bar{z}+\dots)+\dots, \tag{8.8c, d}$$

where use has been made of the results (7.6) and (8.6). Here α_1 and α_2 are given by (8.7), but β_1 and β_2 are as yet undetermined. By matching onto the outer region of expansion (noting from the equations in Appendix C that any term of order ϵ^4 in (8.8) will be no larger than order $\bar{z}^{+1}$ as $\bar{z}\to\infty$) we see that at a general point Q on a solid boundary we require that

$$\tilde{n}_1^* = \epsilon^2(\beta_1+\alpha_1\tilde{z})+\dots, \quad \tilde{n}_2^* = \epsilon^2(\beta_1+\alpha_1\tilde{z})+\dots, \tag{8.9a, b}$$

$$\tilde{\rho}^* = \epsilon^2(0+0\tilde{z})+\dots, \quad \tilde{\psi}^* = \epsilon^2(\beta_2+\alpha_2\tilde{z})+\dots \tag{8.9c, d}$$

as $\tilde{z}\to 0$ with α_1 and α_2 given by (8.7) if Q is on the particle surface S_p but by (8.7) with $\bar{\psi}_w$ replacing $\bar{\psi}_p$ if Q is on the wall surface S_w.

9. Outer-region solution for $\tilde{n}_1^*, \tilde{n}_2^*, \tilde{\psi}^*$ at order ϵ^2

The matching conditions (8.9) indicate that in the outer region of expansion $\tilde{n}_1^*$, $\tilde{n}_2^*$, $\tilde{\rho}^*$ and $\tilde{\psi}^*$ are of order ϵ^2. Thus we write

$$\tilde{n}_i^* = \epsilon^2\tilde{n}_{i2}^*+\dots \quad (i=1,2), \quad \tilde{\rho}^* = \epsilon^2\tilde{\rho}_2^*+\dots, \quad \tilde{\psi}^* = \epsilon^2\tilde{\psi}_2^*+\dots, \tag{9.1}$$

which when substituted into (6.4e, f) shows that $\tilde{\boldsymbol{v}}^*$ and $\tilde{p}^*$ are zero at this order in ϵ. Also substitution into (6.4c, d) gives

$$\tilde{\rho}_2^* = 0, \quad \tilde{n}_{12}^* = \tilde{n}_{22}^*. \tag{9.2}$$

The remaining equations (6.4a, b) and boundary conditions (6.5a, b) then give

$$\tilde{\nabla}^2\tilde{n}_{12}^*+\tilde{\nabla}^2\tilde{\psi}_2^*-Pe\,\tilde{\boldsymbol{v}}_H\cdot\tilde{\boldsymbol{\nabla}}\tilde{n}_{12}^*-Pe\frac{\partial\tilde{n}_{12}^*}{\partial\tilde{t}} = 0, \tag{9.3a}$$

$$\tilde{\nabla}^2\tilde{n}_{22}^*-\tilde{\nabla}^2\tilde{\psi}_2^*-Pe\left(\frac{D_1}{D_2}\right)\tilde{\boldsymbol{v}}_H\cdot\tilde{\boldsymbol{\nabla}}\tilde{n}_{22}^*-Pe\left(\frac{D_1}{D_2}\right)\frac{\partial\tilde{n}_{22}^*}{\partial\tilde{t}} = 0, \tag{9.3b}$$

with

$$\tilde{n}_{12}^*\to 0, \quad \tilde{n}_{22}^*\to 0, \tag{9.4a}$$

$$\tilde{\nabla}^2\tilde{n}_{22}^*-\tilde{\nabla}^2\tilde{\psi}_2^*-Pe\left(\frac{D_1}{D_2}\right)\tilde{\boldsymbol{v}}_H\cdot\tilde{\boldsymbol{\nabla}}\tilde{n}_{22}^*-Pe\left(\frac{D_1}{D_2}\right)\frac{\partial\tilde{n}_{22}^*}{\partial\tilde{t}} = 0 \tag{9.4b}$$

as $|\tilde{\boldsymbol{r}}|\to\infty$. Also for matching (see (8.9)) we require that on the surfaces S_p and S_w

$$\boldsymbol{n}\cdot\tilde{\boldsymbol{\nabla}}\tilde{n}_{12}^* = \alpha_1, \quad \boldsymbol{n}\cdot\tilde{\boldsymbol{\nabla}}\tilde{n}_{22}^* = \alpha_1, \quad \boldsymbol{n}\cdot\boldsymbol{\nabla}\tilde{\rho}_2^* = 0, \quad \boldsymbol{n}\cdot\boldsymbol{\nabla}\tilde{\psi}_2^* = \alpha_2. \tag{9.5}$$

Thus, by making use of (9.2), it is seen that $\tilde{n}_{12}^* = \tilde{n}_{22}^*$ satisfies the convective-diffusion equation

$$\tilde{\nabla}^2\tilde{n}_{12}^* = Pe\left(\frac{D_1+D_2}{2D_2}\right)\left(\tilde{\boldsymbol{v}}_H\cdot\tilde{\boldsymbol{\nabla}}\tilde{n}_{12}^*+\frac{\partial\tilde{n}_{12}^*}{\partial\tilde{t}}\right), \tag{9.6a}$$

with

$$\tilde{n}_{12}^*\to 0 \quad \text{as} \quad |\tilde{\boldsymbol{r}}|\to\infty \tag{9.6b}$$

and

$$\boldsymbol{n}\cdot\tilde{\boldsymbol{\nabla}}\tilde{n}_{12}^* = \alpha_1 \quad \text{on} \quad S_p \text{ and } S_w, \tag{9.6c}$$

which, since the value of α_1 is known from (8.7a), may be written as

$$\boldsymbol{n}\cdot\tilde{\boldsymbol{\nabla}}\tilde{n}_{12}^* = \frac{1}{2D_2}Pe\{(D_2-D_1)\,\bar{\psi}_p-4(D_2+D_1)\ln[\cosh(\tfrac{1}{4}\bar{\psi}_p)]\}$$
$$\times(\boldsymbol{n}\cdot\tilde{\boldsymbol{\nabla}})(\boldsymbol{n}\cdot\tilde{\boldsymbol{\nabla}})(\boldsymbol{n}\cdot\tilde{\boldsymbol{v}}_H) \quad \text{on} \quad S_p, \tag{9.6d}$$

$$\boldsymbol{n}\cdot\tilde{\boldsymbol{\nabla}}\tilde{n}_{12}^* = \frac{1}{2D_2}Pe\{(D_2-D_1)\,\bar{\psi}_w-4(D_2+D_1)\ln[\cosh(\tfrac{1}{4}\bar{\psi}_w)]\}$$
$$\times(\boldsymbol{n}\cdot\tilde{\boldsymbol{\nabla}})(\boldsymbol{n}\cdot\tilde{\boldsymbol{\nabla}})(\boldsymbol{n}\cdot\tilde{\boldsymbol{v}}_H) \quad \text{on} \quad S_w. \tag{9.6e}$$

The value of $\tilde{\psi}_2^*$ is then

$$\tilde{\psi}_2^* = \left(\frac{D_2-D_1}{D_2+D_1}\right)\tilde{n}_{12}^* + \tilde{\phi}, \tag{9.7}$$

where $\tilde{\phi}$ satisfies Laplace's equation

$$\tilde{\nabla}^2\tilde{\phi} = 0 \tag{9.8a}$$

with

$$\tilde{\phi} \to 0 \quad \text{as} \quad |\tilde{\boldsymbol{r}}| \to \infty \tag{9.8b}$$

and

$$\boldsymbol{n}\cdot\tilde{\boldsymbol{\nabla}}\tilde{\phi} = \alpha_2 - \left(\frac{D_2-D_1}{D_2+D_1}\right)\alpha_1 \quad \text{on} \quad S_p \text{ and } S_w. \tag{9.8c}$$

This last boundary condition may, by (8.7a), be written in the form

$$\boldsymbol{n}\cdot\tilde{\boldsymbol{\nabla}}\tilde{\phi} = Pe\left(\frac{2D_1}{D_1+D_2}\right)\tilde{\psi}_p(\boldsymbol{n}\cdot\tilde{\boldsymbol{\nabla}})(\boldsymbol{n}\cdot\tilde{\boldsymbol{\nabla}})(\boldsymbol{n}\cdot\tilde{\boldsymbol{v}}_H) \quad \text{on} \quad S_p, \tag{9.8d}$$

$$\boldsymbol{n}\cdot\tilde{\boldsymbol{\nabla}}\tilde{\phi} = Pe\left(\frac{2D_1}{D_1+D_2}\right)\tilde{\psi}_w(\boldsymbol{n}\cdot\tilde{\boldsymbol{\nabla}})(\boldsymbol{n}\cdot\tilde{\boldsymbol{\nabla}})(\boldsymbol{n}\cdot\tilde{\boldsymbol{v}}_H) \quad \text{on} \quad S_w. \tag{9.8e}$$

Once $\tilde{n}_{12}^*$ has been determined from (9.6) and $\tilde{\psi}_2^*$ determined from (9.7) and (9.8), we see that by matching (see (8.9)), β_1 and β_2 are now determined with

$$\beta_1 = \tilde{n}_{12}^* \quad \text{on} \quad S_p \text{ and } S_w, \tag{9.9a}$$

$$\beta_2 = \tilde{\psi}_2^* \quad \text{on} \quad S_p \text{ and } S_w. \tag{9.9b}$$

Note that β_1 and β_2 will thus be functions of position (in the outer variables) on the surfaces S_p and S_w. Since β_1 and β_2 are now known, the inner-region variables at order ϵ^2 (see §7), which involve β_1 and β_2, are determined.

Since $\tilde{\rho}_2^* = 0$ everywhere (see (9.2)) it is observed from (6.2c) that $\tilde{\rho}^*$ is of order ϵ^4. Thus in our outer region the charge density $\tilde{\rho}^*$ is

$$\tilde{\rho}^* = \epsilon^4\tilde{\rho}_4^* + \dots \tag{9.10}$$

where

$$\tilde{\rho}_4^* = -\tilde{\nabla}^2\tilde{\psi}_2^*. \tag{9.11}$$

This, by (9.6a), (9.7) and (9.8a), reduces to

$$\tilde{\rho}_4^* = Pe\left(\frac{D_1-D_2}{2D_2}\right)\left(\tilde{\boldsymbol{v}}_H\cdot\tilde{\boldsymbol{\nabla}}\tilde{n}_{12}^* + \frac{\partial\tilde{n}_{12}^*}{\partial\tilde{t}}\right), \tag{9.12}$$

where $\tilde{n}_{12}^*$ is determined by (9.6a) and boundary conditions (9.6b, d).

10. Inner-region flow at order ϵ^4

By substituting the expansion (7.1) for $\bar{n}_1^*$, $\bar{n}_2^*$, $\bar{\rho}^*$ and $\bar{\psi}^*$ into the inner-region equations (C 1e, f, h) it is observed that $\bar{v}_x^*$ and $\bar{v}_y^*$ must be order ϵ^4 and $\bar{v}_z^*$ of order ϵ^5. Thus we write

$$\bar{v}_x^* = \epsilon^4\bar{v}_{4x}^* + \dots, \quad \bar{v}_y^* = \epsilon^4\bar{v}_{4y}^* + \dots, \quad \bar{v}_z^* = \epsilon^5\bar{v}_{5z}^* + \dots, \tag{10.1}$$

which when substituted into (C 1e, f, h) and (C 2a) with the expansions (7.1) give equations and boundary conditions for $\bar{v}_{4x}^*$, $\bar{v}_{4y}^*$, and $\bar{v}_{5z}^*$ as

$$\frac{\partial^2\bar{v}_{4x}^*}{\partial\bar{z}^2} = \left(\epsilon^{-1/2}\frac{\partial\bar{p}_2^*}{\partial\bar{x}}\right) + \lambda\bar{\rho}_{E0}\left(\epsilon^{-1/2}\frac{\partial\bar{\psi}_2^*}{\partial\bar{x}}\right), \tag{10.2a}$$

$$\frac{\partial^2\bar{v}_{4y}^*}{\partial\bar{z}^2} = \left(\epsilon^{-1/2}\frac{\partial\bar{p}_2^*}{\partial\bar{y}}\right) + \lambda\bar{\rho}_{E0}\left(\epsilon^{-1/2}\frac{\partial\bar{\psi}_2^*}{\partial\bar{y}}\right), \tag{10.2b}$$

$$\frac{\partial^2\bar{v}_{5z}^*}{\partial\bar{z}} + \left(\epsilon^{-1/2}\frac{\partial\bar{v}_{4x}^*}{\partial\bar{x}}\right) + \left(\epsilon^{-1/2}\frac{\partial\bar{v}_{4y}^*}{\partial\bar{y}}\right) = 0, \tag{10.2c}$$

with
$$\bar{v}^*_{4x} = \bar{v}^*_{4y} = 0, \quad \bar{v}^*_{5z} = 0 \tag{10.3 a, b}$$
on $\bar{z} = 0$. In writing (10.2) it is noted that, by (3.7), the $\bar{x}$- and $\bar{y}$-derivatives are of order $\epsilon^{1/2}$.

Since, from the values of $\bar{\rho}_{E0}$, $\partial\bar{p}^*_2/\partial\bar{x}$ and $\partial\bar{\psi}^*_2/\partial\bar{x}$ given respectively by (A 3 *a*) (7.12) and (7.13), the right-hand side of (10.2 *a*) is exponentially small, it follows that as $\bar{z} \to \infty, \bar{v}^*_{4x}$ must be of the form
$$\bar{v}^*_{4x} \sim A_x \bar{z} + B_x. \tag{10.4}$$
However, an asymptotic term like $A_x \bar{z}$ in $\bar{v}^*_{4x}$ (i.e. a term like $\epsilon^4 A_x \bar{z}$ in the inner region) would match onto a velocity field of order ϵ^3 in the outer expansion. This would give velocities of order $\epsilon^3\bar{z}^0$ on the boundaries which would then match back onto a term of order $\epsilon^3\bar{z}^0$ in the inner-region expansion for $\bar{v}^*_x$. Such a term was assumed in (10.1) not to exist (or even if it were to be included, it may, upon writing down its equations and boundary conditions, be readily shown to be zero). Thus we must have $A_x = 0$ so that, as $\bar{z} \to \infty$,
$$\bar{v}^*_{4x} < B_x. \tag{10.5 a}$$
Integrating (10.2 *a*) twice with respect to $\bar{z}$ using (10.3 *a*) and (10.5 *a*), the value of B_x may be obtained as
$$B_x = \int_0^\infty \left[\int_\infty^{\bar{z}} \left\{ \left(\epsilon^{-1/2} \frac{\partial \bar{p}^*_2}{\partial \bar{x}} \right) + \lambda \bar{\rho}_{E0} \left(\epsilon^{-1/2} \frac{\partial \bar{\psi}^*_2}{\partial \bar{x}} \right) \right\} \mathrm{d}\bar{z} \right] \mathrm{d}\bar{z}. \tag{10.5 b}$$
Also in a similar manner we see that
$$\bar{v}^*_{4y} \to B_y \tag{10.6 a}$$
as $\bar{z} < \infty$ where
$$B_y = \int_0^\infty \left[\int_\infty^{\bar{z}} \left\{ \left(\epsilon^{-1/2} \frac{\partial \bar{p}^*_2}{\partial \bar{y}} \right) + \lambda \bar{\rho}_{E0} \left(\epsilon^{-1/2} \frac{\partial \bar{\psi}^*_2}{\partial \bar{y}} \right) \right\} \mathrm{d}\bar{z} \right] \mathrm{d}\bar{z}. \tag{10.6 b}$$
By substituting the values of $\partial\bar{p}^*_2/\partial\bar{x}$ and $\partial\bar{p}^*_2/\partial\bar{y}$ given by (7.12), of $\partial\bar{\psi}^*_2/\partial\bar{x}$ and $\partial\bar{\psi}^*_2/\partial\bar{y}$ given by (7.13) and of $\bar{\rho}_{E0}$ given by (A 3 *a*) into (10.5 *b*), (10.6 *b*) and evaluating the resulting integrals, the values of B_x and B_y may be obtained as
$$B_x = \lambda \left\{ -4 \ln [\cosh (\tfrac{1}{4} \tilde{\psi}_p)] \frac{\partial \beta_1}{\partial \tilde{x}} + \tilde{\psi}_p \frac{\partial \beta_2}{\partial \tilde{x}} \right\}, \tag{10.7 a}$$
$$B_y = \lambda \left\{ -4 \ln [\cosh (\tfrac{1}{4} \tilde{\psi}_p)] \frac{\partial \beta_1}{\partial \tilde{y}} + \tilde{\psi}_p \frac{\partial \beta_2}{\partial \tilde{y}} \right\} \tag{10.7 b}$$
for an inner expansion at a point Q on the particle surface S_p. Likewise for an inner region at a point Q on the wall surface S_w equations (10.7) are still valid if $\tilde{\psi}_p$ is replaced by $\tilde{\psi}_w$.

11. Outer-region flow at order ϵ^4

Since in the inner region we have velocities $\epsilon^4\bar{v}^*_{4x}, \epsilon^4\bar{v}^*_{4y}$, where $\bar{v}^*_{4x} \to B_x$ and $\bar{v}^*_{4y} \to B_y$ as $\bar{z} \to \infty$ with B_x and B_y given by (10.7), it follows by matching that in the outer region the velocity $\tilde{\boldsymbol{v}}^*$ and pressure $\tilde{p}^*$ must be of order ϵ^4. Thus we write
$$\tilde{\boldsymbol{v}}^* = \epsilon^4 \tilde{\boldsymbol{v}}^*_4 + \dots, \quad \tilde{p}^* = \epsilon^4 \tilde{p}^*_4 + \dots. \tag{11.1}$$

This when substituted into (6.4e, f) and (6.5c) (noting that $\tilde{\psi}^*$ is of order ϵ^2, see (9.1), and $\tilde{\rho}^*$ is of order ϵ^4, see (9.10)), shows that $\tilde{\boldsymbol{v}}_4^*, \tilde{p}_4$ satisfies the creeping flow equations

$$\tilde{\nabla}^2 \tilde{\boldsymbol{v}}_4^* - \tilde{\boldsymbol{\nabla}} \tilde{p}_4^* = \mathbf{0}, \quad \boldsymbol{\nabla} \cdot \tilde{\boldsymbol{v}}_4^* = 0, \tag{11.2a, b}$$

where

$$\tilde{\boldsymbol{v}}_4^* \to 0 \tag{11.2c}$$

as $|\tilde{\boldsymbol{r}}| \to \infty$. Also on the solid surfaces S_p and S_w we require, by matching onto the inner region, that

$$\tilde{v}_{4x}^* = B_x, \quad \tilde{v}_{4y}^* = B_y,$$

with B_x and B_y given by (10.7). If on the solid surface the normal component $\tilde{v}_{4z}^*$ of $\tilde{\boldsymbol{v}}_4^*$ were to have a value B_z this would match onto a term of order ϵ^4 in the inner-region expansion of $\bar{v}_{4z}^*$. However no such term exists since, by (10.1), $\bar{v}_{4z}^*$ is of order ϵ^5. Thus $B_z = 0$ and so the boundary condition for $\tilde{\boldsymbol{v}}_4^*$ on the solid surfaces S_p and S_w is

$$\tilde{\boldsymbol{v}}_4^* = B_x \boldsymbol{c}_x + B_y \boldsymbol{c}_y, \tag{11.2d}$$

where $\boldsymbol{c}_x$ and $\boldsymbol{c}_y$ are unit vectors in the x- and y-directions in the tangent plane to the surface.

12. Force and torque on a particle

The dimensionless force $\tilde{\boldsymbol{F}}$ (defined by (2.19)) and moment of force $\tilde{\boldsymbol{G}}$ (defined by (2.21)) on the particle P have been shown (in §2) to be given by the integrals (2.20) and (2.22) taken over any chosen surface S completely enclosing the particle. It is simplest to take this surface S to be the particle surface S_p in the outer region (i.e. it is taken to be just outside the double layer surrounding the particle) so that in the integrands of (2.20) and (2.22) we use the stress tensor $\tilde{\sigma}_{ij}$ given in terms of outer variables (as in (2.1)). In the outer region we have shown (see (6.1), (9.1) and (11.1)) that $\tilde{\boldsymbol{v}}$, $\tilde{p}$ and $\tilde{\psi}$ have expansions in ϵ of the form

$$\tilde{\boldsymbol{v}} = \tilde{\boldsymbol{v}}_H + \epsilon^4 \tilde{\boldsymbol{v}}_4^* + \ldots, \quad \tilde{p} = \tilde{p}_H + \epsilon^4 \tilde{p}_4^* + \ldots, \quad \tilde{\psi} = \epsilon^2 \tilde{\psi}_2^* + \ldots, \tag{12.1a–c}$$

where we have used the results (4.19a, d) that $\tilde{\psi}_E = 0$ and $\tilde{p}_E = 0$ throughout the outer region. By substituting the expansions (12.1) into the stress tensor (2.17), the dimensionless force on the particle $\tilde{\boldsymbol{F}}$ may be obtained as

$$\tilde{\boldsymbol{F}} = \tilde{\boldsymbol{F}}_H + \epsilon^4 \tilde{\boldsymbol{F}}_4^* + \ldots, \tag{12.2}$$

where

$$\tilde{F}_{Hi} = \int_{S_p} \left\{ -\tilde{p}_4 \, \delta_{ij} + \frac{\partial \tilde{v}_{Hi}^*}{\partial \tilde{r}_j} + \frac{\partial \tilde{v}_{Hj}}{\partial \tilde{r}_i} \right\} n_j \, \mathrm{d}\tilde{S} \tag{12.3}$$

is the dimensionless force on the particle due to the purely hydrodynamic problem (discussed in §5) and

$$\tilde{F}_{4i}^* = \int_{S_p} \left\{ -\tilde{p}_4^* \, \delta_{ij} + \frac{\partial \tilde{v}_{4i}^*}{\partial \tilde{r}_j} + \frac{\partial \tilde{v}_{4j}^*}{\partial \tilde{r}_i} \right\} n_j \, \mathrm{d}\tilde{S} \tag{12.4}$$

is the lowest-order correction due to electrohydrodynamic effects and is in fact the drag force due to the creeping flow $\tilde{\boldsymbol{v}}^*, \tilde{p}^*$ resulting from the apparent slip at the boundaries S_p and S_w (see (11.2d)). Note that the contribution to the force on the particle from the electrical Maxwell stress due to the electric field resulting from $\tilde{\psi}_2^*$, is of order ϵ^6 and is therefore negligible compared to the lowest-order electrohydrodynamic contribution $\epsilon^4 \tilde{\boldsymbol{F}}_4^*$.

The hydrodynamic force $\tilde{\boldsymbol{F}}_H$ is obtained by solving the creeping flow equations (5.1 a, b) for $\tilde{\boldsymbol{v}}_H, \tilde{p}_H$ with the boundary conditions (5.2a, b) and then substituting the solution into (12.3). Also likewise the electroviscous force $\tilde{\boldsymbol{F}}_4^*$ is obtained by solving the creeping flow equations (11.2a, b) for $\tilde{\boldsymbol{v}}_4^*, \tilde{p}_4^*$ with the boundary conditions (11.2c, d) (using the known values of B_x and B_y given by (10.7)) and then substituting that solution into (12.4).

However, an easier method to obtain the electroviscous force $\tilde{\boldsymbol{F}}_4^*$ is to make use of the Lorentz reciprocal theorem (see Happel & Brenner 1965, p. 85). Other details can be found in Teubner (1982) and Fair & Anderson (1989). Thus we define a velocity with the ith component $\tilde{v}_{Tik}$ and pressure $\tilde{p}_{Tk}$ satisfying the creeping flow equations

$$\frac{\partial^2 \tilde{v}_{Tik}}{\partial \tilde{r}_j \partial \tilde{r}_j} - \frac{\partial \tilde{p}_{Tk}}{\partial \tilde{r}_i} = 0, \quad \frac{\partial \tilde{v}_{Tik}}{\partial \tilde{r}_i} = 0 \tag{12.5a, b}$$

due to the particle translating without rotation with unit velocity in the k-direction with the wall W at rest and the flow tending to zero at infinity so that

$$\tilde{v}_{Tik} = \delta_{ik} \quad \text{on} \quad S_p, \tag{12.5c}$$

$$\tilde{v}_{Tik} = 0 \quad \text{on} \quad S_w, \tag{12.5d}$$

$$\tilde{v}_{Tik} \rightarrow 0 \quad \text{as} \quad |\tilde{\boldsymbol{r}}| \rightarrow \infty. \tag{12.5e}$$

Then by applying the reciprocal theorem to the two flows $\tilde{v}_{Tik}, \tilde{p}_{Tk}$ and $\tilde{v}_{4i}^*, \tilde{p}_4^*$ over the fluid volume bounded by S_p, S_w and a large sphere S_R of radius R (where we let $R \rightarrow \infty$), we obtain $\tilde{\boldsymbol{F}}_4^*$ as

$$\tilde{F}_{4i}^* = \int_{S_p} B_j^* \, \tilde{\sigma}_{Tjki} \, n_k \, \mathrm{d}\tilde{S} + \int_{S_w} B_j^* \, \tilde{\sigma}_{Tjki} \, n_k \, \mathrm{d}\tilde{S}, \tag{12.6}$$

where $\tilde{\sigma}_{Tjki}$ is the stress tensor corresponding to the flow $\tilde{v}_{Tji}, \tilde{p}_{Ti}$, i.e.

$$\tilde{\sigma}_{Tjki} = -\tilde{p}_{Ti} \, \delta_{jk} + \frac{\partial \tilde{v}_{Tji}}{\partial \tilde{r}_k} + \frac{\partial \tilde{v}_{Tki}}{\partial \tilde{r}_j} \tag{12.7}$$

and $$\boldsymbol{B}^* = B_x \, \boldsymbol{i}_x + B_y \, \boldsymbol{i}_y$$

so that by (10.7)

$$\boldsymbol{B}^* = \lambda \langle \{-4 \ln [\cosh (\tfrac{1}{4} \tilde{\psi}_p)]\} \{ \tilde{\boldsymbol{\nabla}} \beta_1 - \boldsymbol{n} \cdot \tilde{\boldsymbol{\nabla}} \beta_1 \, \boldsymbol{n} \} + \tilde{\psi}_p \{ \tilde{\boldsymbol{\nabla}} \beta_2 - \boldsymbol{n} \cdot \tilde{\boldsymbol{\nabla}} \beta_2 \, \boldsymbol{n} \} \rangle \tag{12.8a}$$

on the surface S_p and

$$\boldsymbol{B}^* = \lambda \langle \{-4 \ln [\cosh (\tfrac{1}{4} \tilde{\psi}_w)]\} \{ \tilde{\boldsymbol{\nabla}} \beta_1 - \boldsymbol{n} \cdot \tilde{\boldsymbol{\nabla}} \beta_1 \, \boldsymbol{n} \} + \tilde{\psi}_w \{ \tilde{\boldsymbol{\nabla}} \beta_2 - \boldsymbol{n} \cdot \tilde{\boldsymbol{\nabla}} \beta_2 \, \boldsymbol{n} \}] \tag{12.8b}$$

on the surface S_w.

In a manner similar to that shown above, the dimensionless moment of force $\tilde{\boldsymbol{G}}$ on the particle about some chosen reference point O, may be shown to be

$$\tilde{\boldsymbol{G}} = \tilde{\boldsymbol{G}}_H + \epsilon^4 \tilde{\boldsymbol{G}}_4^* + \dots, \tag{12.9}$$

where $$\tilde{G}_{Hi} = \int_{S_p} \epsilon_{ijk} \, \tilde{r}_j \left\{ -\tilde{p}_4 \, \delta_{kl} + \frac{\partial \tilde{v}_{Hk}}{\partial \tilde{r}_l} + \frac{\partial \tilde{v}_{Hl}}{\partial \tilde{r}_k} \right\} n_l \, \mathrm{d}\tilde{S} \tag{12.10}$$

is the dimensionless hydrodynamic moment of force with $\tilde{\boldsymbol{v}}_4, \tilde{p}_4$ satisfying (5.1 a, b) and

(5.2a, b) and $\tilde{\boldsymbol{v}}$ being the position vector of a surface element relative to the reference point O. Here also the electrohydrodynamic moment of force $\tilde{\boldsymbol{G}}_4^*$ may be most easily calculated using the Lorentz reciprocal theorem as

$$\tilde{G}_{4i} = \int_{S_p} B_j^* \, \tilde{\sigma}_{Rjki} \, n_k \, \mathrm{d}\tilde{S} + \int_{S_w} B_j^* \, \tilde{\sigma}_{Rjki} \, n_k \, \mathrm{d}\tilde{S}, \tag{12.11}$$

where $\boldsymbol{B}^*$ is given by (12.8). Here $\tilde{\sigma}_{Rjki}$ is the stress tensor corresponding to a flow $\tilde{v}_{Rik}, \tilde{p}_{Rk}$ so that

$$\tilde{\sigma}_{Rjki} = -\tilde{p}_{Ri}\,\delta_{jk} + \frac{\partial \tilde{v}_{Rji}}{\partial \tilde{r}_k} + \frac{\partial \tilde{v}_{Rki}}{\partial \tilde{r}_j}, \tag{12.12}$$

where $\tilde{v}_{Rik}, \tilde{p}_{Rk}$ is defined as satisfying the creeping flow equations

$$\frac{\partial^2 \tilde{v}_{Rik}}{\partial \tilde{r}_j \, \partial \tilde{r}_j} - \frac{\partial \tilde{p}_{Rk}}{\partial \tilde{r}_i} = 0, \quad \frac{\partial \tilde{v}_{Rik}}{\partial \tilde{r}_i} = 0 \tag{12.13a, b}$$

due to the particle rotating about a fixed point at O with unit angular velocity about an axis in the k-direction with the wall W at rest and the flow tending to zero at infinity so that

$$\boldsymbol{v}_{Rik} = \epsilon_{ikj}\,\tilde{r}_j \quad \text{on} \quad S_p, \tag{12.13c}$$

$$\boldsymbol{v}_{Rik} = 0 \quad \text{on} \quad S_w, \tag{12.13d}$$

$$\boldsymbol{v}_{Rik} \to 0 \quad \text{as} \quad |\tilde{\boldsymbol{r}}| \to \infty, \tag{12.13e}$$

where $\tilde{\boldsymbol{r}}$ is again position relative to the reference point O.

13. Solution procedure

In this section we lay out the recipe, determined in the previous sections, by which the force $\boldsymbol{F}$ and moment of force $\boldsymbol{G}$ (about a reference point O) on the particle P may be determined. Thus one proceeds as follows:

(*a*) Calculate the purely hydrodynamic flow $\tilde{\boldsymbol{v}}_H, \tilde{p}_H$ in the outer region by solving the creeping flow equations (5.1a, b) with boundary conditions (5.2a, b).

(*b*) Calculate the dimensionless force $\tilde{\boldsymbol{F}}_H$ and moment of force $\tilde{\boldsymbol{G}}$ (about O) on the particle due to the flow field $\tilde{\boldsymbol{v}}_H, \tilde{p}_H$ using (12.3) and (12.10).

(*c*) Calculate the ion concentrations $\tilde{n}_{12}^*$ $(= \tilde{n}_{22}^*)$ in the outer region by solving the convective diffusive equation (9.6a) with boundary conditions (9.6b, d).

(*d*) Calculate the quantity $\tilde{\phi}$ in the outer regions satisfying Laplace's equation (9.8a) with boundary conditions (9.8b, d, e), from which the electric potential $\tilde{\psi}_2^*$ in the outer region is calculated using (9.7).

(*e*) On S_p and on S_w calculate from the results of (*c*) and (*d*) the values of β_1 and β_2 defined by (9.9a, b).

(*f*) Calculate the value of $\boldsymbol{B}^*$ on the surfaces (given by (12.8a) for S_p and (12.8b) for S_w).

(*g*) Calculate the stress tensor $\tilde{\sigma}_{Tjki}$ in the outer region (given by (12.7)) from the flow field $\tilde{v}_{Tik}$, $\tilde{p}_{Tk}$ satisfying the creeping flow equations (12.5a, b) with boundary conditions (12.5c–e).

(*h*) Calculate the stress tensor $\tilde{\sigma}_{Rjki}$ in the outer region (given by (12.12)) from the flow field $\tilde{v}_{Rik}, \tilde{p}_{Rk}$ satisfying the creeping flow equations (12.13a, b) with boundary conditions (12.13c–e).

(*i*) Calculate the electrohydrodynamic force $\tilde{\boldsymbol{F}}_4^*$ and moment of force $\tilde{\boldsymbol{G}}_4^*$ (about O) acting on the particle using, respectively, (12.6) and (12.11).

(*j*) Calculate the total dimensionless force $\tilde{\boldsymbol{F}}$ and moment of force $\tilde{\boldsymbol{G}}$ (about O) using, respectively (12.2) and (12.9).

(*k*) Calculate the dimensional force $\boldsymbol{F}$ and moment of force $\boldsymbol{G}$ (about O) acting on the particle using (2.19) and (2.21).

14. Drag on a sedimenting charged sphere

As an example of the solution procedure given in the previous section, we consider a solid charged sphere of radius a and surface potential ψ_p translating without rotation through an unbounded liquid with a constant speed (with no wall W present). Thus in the previous analysis we take the lengthscale L to be the sphere radius a and the velocity scale V as the sphere's speed. For simplicity we will consider here only the limit where the ion Péclet number Pe is very small, i.e.

$$aV/D_1 \ll 1 \quad \text{and} \quad aV/D_2 \ll 1. \tag{14.1}$$

We take in the outer-region spherical polar coordinates $(\tilde{r}, \theta, \phi)$ with origin at the sphere centre and the polar axis ($\theta = 0$) in the direction of the sphere's motion. These axes are taken to be translating with the sphere so that we have a steady situation in which the sphere is at rest with the flow at infinity past the sphere in the $\theta = \pi$ direction as shown in figure 5. Then (§ 13, step *a*) the purely hydrodynamic flow $\bar{\boldsymbol{v}}_H, \bar{p}_H$ is the well-known creeping flow past a sphere (see Happel & Brenner 1965, p. 124) from which the dimensionless hydrodynamic drag in the $\theta = 0$ direction is found (step *b*) to be (Stokes (1851))

$$\tilde{F}_H = -6\pi. \tag{14.2}$$

Then (step *c*) $\tilde{n}_{12}^*$ satisfies (9.6*a*) which in our limit of $Pe \to 0$ reduces to Laplace's equation. This, with the boundary conditions (9.6*b*, *d*) possesses the solution

$$\tilde{n}_{12}^* = \frac{3}{4D_2} Pe\{(D_2 - D_1)\tilde{\psi}_p - 4(D_2 + D_1)\ln[\cosh(\tfrac{1}{4}\tilde{\psi}_p)]\}\,\tilde{r}^{-2}\cos\theta$$

which may be written in the form

$$\tilde{n}_{12}^* = -\frac{3}{D_2} Pe\{D_2 G + D_1 H\}\,\tilde{r}^{-2}\cos\theta, \tag{14.3a}$$

where G and H are defined as

$$G = \ln\tfrac{1}{2}(1 + \exp(-\tfrac{1}{2}\tilde{\psi}_p)), \quad H = \ln\tfrac{1}{2}(1 + \exp(+\tfrac{1}{2}\tilde{\psi}_p)). \tag{14.3b}$$

From (14.3*a*) it is seen that the actual dimensional concentration of ions in the outer region is

$$n_1 = n_2 = n_\infty - \frac{3}{2}\frac{(\epsilon_r\epsilon_0)(kT)V}{(z_1 e)^2 (D_1 D_2)^{1/2} a}\left\{\left(\frac{D_2}{D_1}\right)^{1/2} G + \left(\frac{D_1}{D_2}\right)^{1/2} H\right\}\left(\frac{a}{r}\right)^2 \cos\theta \tag{14.4a}$$

G and H can also be expressed in dimensional form as

$$G = \ln\left\{\frac{1}{2}\left[1 + \exp\left(-\frac{z_1 e\psi_p}{2kT}\right)\right]\right\}, \quad H = \ln\left\{\frac{1}{2}\left[1 + \exp\left(+\frac{z_1 e\psi_p}{2kT}\right)\right]\right\}. \tag{14.4b}$$

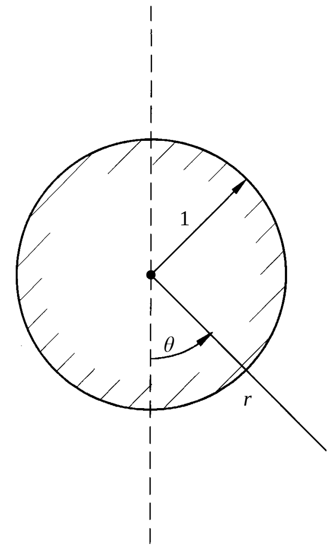

FIGURE 5. Flow in the direction $\theta = \pi$ past a solid sphere ($\tilde{r}, \theta$ are spherical polar coordinates in the outer region).

The value of $\tilde{\psi}_2^*$ is then found (step d) to be

$$\tilde{\psi}_2^* = -\frac{3}{D_2} Pe\{D_2 G - D_1 H\} \tilde{r}^{-2} \cos\theta, \tag{14.5a}$$

which in dimensional form gives the electric potential in the outer region as

$$\psi = -\frac{3}{2} \frac{(\epsilon_r \epsilon_0)(kT)^2 V}{(z_1 e)^3 (D_1 D_2)^{1/2} n_\infty a} \left\{ \left(\frac{D_2}{D_1}\right)^{1/2} G - \left(\frac{D_1}{D_2}\right)^{1/2} H \right\} \left(\frac{a}{r}\right)^2 \cos\theta. \tag{14.5b}$$

From (14.3a) and (14.5a) we obtain on the sphere surface (step e)

$$\beta_1 = -\frac{3}{D_2} Pe(D_2 G + D_1 H) \cos\theta, \quad \beta_2 = -\frac{3}{D_2} Pe(D_2 G - D_1 H) \cos\theta, \tag{14.6}$$

from which it is seen that the vector $\boldsymbol{B}^*$ is in the θ-direction and has the value (step f)

$$B_\theta^* = -\frac{12\lambda Pe}{D_2} (D_2 G^2 + D_1 H^2) \sin\theta. \tag{14.7}$$

The electroviscous drag force $\tilde{\boldsymbol{F}}_4^*$ may then be calculated (steps g and i) to obtain its component in the $\theta = 0$ direction as

$$\tilde{F}_4^* = -48\pi\lambda\, Pe\, D_2^{-1} (D_2 G^2 + D_1 H^2) \tag{14.8}$$

to give the total dimensionless force on the sphere in the direction of the polar axis ($\theta = 0$) as (step j)

$$\tilde{F} = -6\pi - 48\pi\lambda\epsilon^4\, Pe\, D_1 (D_1^{-1} G^2 + D_2^{-1} H^2). \tag{14.9}$$

Notice that the final result depends on the product of the dimensionless parameters λ and Pe. If we define $\Lambda = \lambda Pe = 12\pi n_\infty b_1 L^2$, we see that the result depends not on the

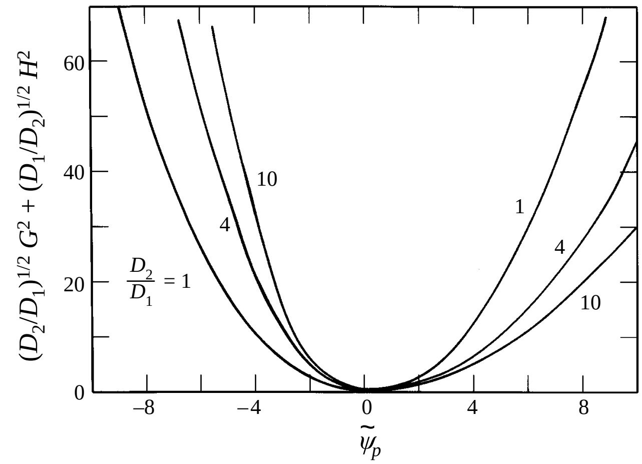

FIGURE 6. Dimensionless electroviscous drag $(D_2/D_1)^{1/2}\,G^2+(D_1/D_2)\,H^2$ plotted as a function of dimensionless surface potention $\tilde{\psi}_p$ for various values of the ion diffusivity ratio D_2/D_1.

fluid velocity but on the bulk ion concentration, particle size (L), and the Stokes–Einstein radius of ion 1 ($b_1 = kT/6\pi\eta D_1$).

In terms of dimensional quantities, the dimensional drag force F in the polar direction is thus (step k)

$$F = -6\pi\eta a V - 24\pi\frac{(\epsilon_r\,\epsilon_0)^2\,(kT)^3\,V}{(z_1\,e)^4\,(D_1\,D_2)^{1/2}\,n_\infty\,a}\left\{\left(\frac{D_2}{D_1}\right)^{1/2} G^2 + \left(\frac{D_1}{D_2}\right)^{1/2} H^2\right\}. \tag{14.10}$$

Ohshima *et al.* (1984) examined theoretically the sedimentation of a charged sphere in an unbounded liquid for general values of $\tilde{\psi}_p$ and κa and obtained an expression for the drag force F which for the limit $\epsilon \equiv (\kappa a)^{-1} \rightarrow 0$ has a value (see their equation (78)) which agrees exactly with that given above by (14.10) (when terms smaller than ϵ^4 are omitted). While it does not seem to be explicitly stated in Ohshima *et al.* that they assumed that $Pe \ll 1$, they must have done so since, as is seen above, the result (14.10) does require $Pe \ll 1$ and is not valid for Pe of order unity.

It is observed from (14.10) that the effect of the electrohydrodynamic (or electroviscous) force is always to increase the drag on the sphere since

$$(D_2/D_1)^{1/2}\,G^2 + (D_1/D_2)^{1/2}\,H^2$$

is strictly positive. This quantity representing the dimensionless increase in drag has been plotted as a function of $\tilde{\psi}_p$ for various values of D_2/D_1 in figure 6.

The electric field in the outer region (outside the double layer) is exactly that of an electric dipole at the sphere centre (see (14.5b)) and thus dies away like r^{-3} as $r \rightarrow \infty$. The strength of this dipole in the direction of the sphere's motion is proportional to the dimensionless quantity

$$-(D_2/D_1)^{1/2}\,G + (D_1/D_2)^{1/2}\,H$$

and is thus directed with the sphere's motion for $\tilde{\psi}_p > 0$ and against the sphere's motion for $\tilde{\psi}_p < 0$. This dimensionless dipole strength has been plotted as a function of $\tilde{\psi}_p$ for various values of D_2/D_1 in figure 7.

The excess ion concentration over and above that at infinity dies away like $\tilde{r}^{-2}$ as

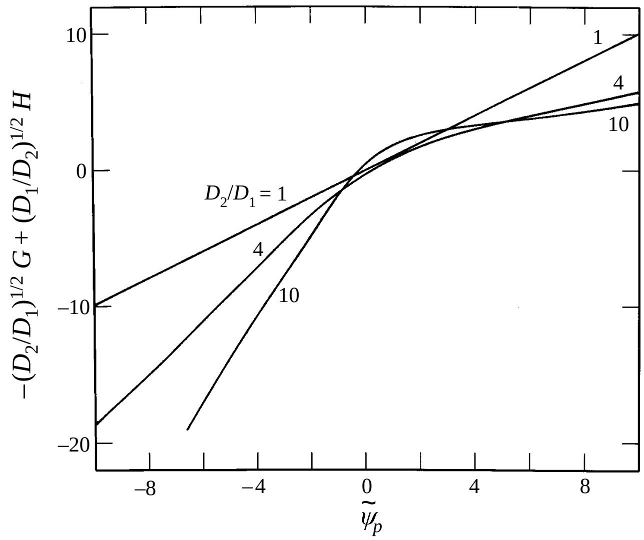

FIGURE 7. Dimensionless dipole strength $-(D_2/D_1)^{1/2}\,G+(D_1/D_2)^{1/2}\,H$ in the direction of the sphere's translation plotted as a function of dimensionless surface potential $\tilde{\psi}_p$ for various values of the ion diffusivity ratio D_2/D_1.

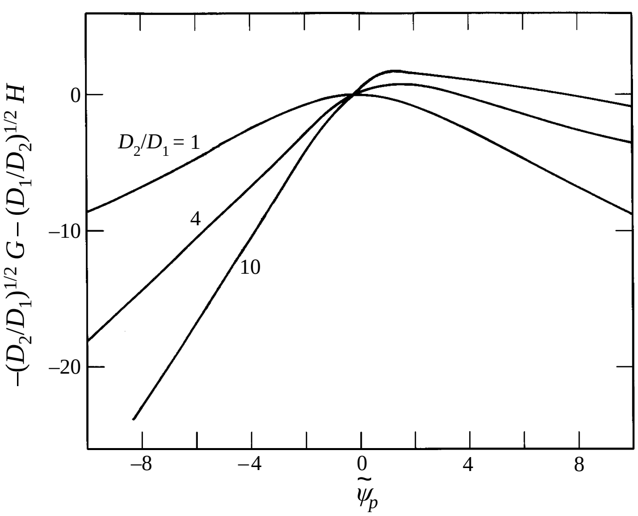

FIGURE 8. Dimensionless excess in concentration $-(D_2/D_1)^{1/2}\,G-(D_1/D_2)^{1/2}\,H$ ahead of the sphere plotted as a function of dimensionless surface potential $\tilde{\psi}_p$ for various values of the ion diffusivity ratio D_2/D_1.

$\tilde{r}\to\infty$ in the outer region (see (14.4*a*)) with the total ion concentration being greatest ahead of the sphere and lowest behind the sphere if the quantity

$$-(D_2/D_1)^{1/2}\,G-(D_1/D_2)^{1/2}\,H$$

is positive and the converse if it is negative. This quantity, a measure of the strength of the dimensionless excess ion concentration, has been plotted in figure 8 as a function of $\tilde{\psi}_p$ for various values of D_2/D_1 from which it is observed that for $D_2/D_1 = 1$, the ion concentration is least ahead of the sphere, but for $D_2/D_1 > 1$ there is a range of positive $\tilde{\psi}_p$ for which the ion concentration is greatest ahead of the sphere with the ion concentration otherwise being least ahead of the sphere.

15. Conclusions

In the present paper we have determined the force (and moment of force) exerted on a charged particle moving in a polar liquid (such as an aqueous electrolyte solution) in the presence of a charged solid boundary (or boundaries). This was done for the situation in which the double-layer thickness κ^{-1} is very much smaller than the size L of the particle so that a singular perturbation expansion could be made in terms of the small parameter $\epsilon \equiv (\kappa L)^{-1}$ while keeping all other parameters (namely the ion Péclet number Pe, the ion diffusivity ratio D_1/D_2, the parameter λ and the dimensionless surface potentials of particle $\tilde{\psi}_p$ and wall $\tilde{\psi}_w$) fixed and of order unity.

The actual matching procedure given for this problem has been presented in simplified form in table 1. Thus the purely hydrodynamic flow of order ϵ^0 with velocity $\tilde{\boldsymbol{v}}_H$ and pressure $\tilde{p}_H$ in the outer region satisfying the creeping flow equations (and giving rise to the hydrodynamic force $\tilde{F}$ of order ϵ^0) is matched onto shear flows $(\bar{v}_{Hx}, \bar{v}_{Hy})$ of order ϵ^{+1} and a normal flow $\bar{v}_{Hz}$ of order ϵ^2 in the inner region. Also in the inner double-layer region there is at order ϵ^0 the equilibrium double-layer values of $\bar{\psi}_{E0}$, $\bar{n}_{1E0}$, $\bar{n}_{2E0}$ and $\bar{\rho}^*_{E01}$ and at order ϵ^{+1} values of $\bar{\psi}_{E1}$, $\bar{n}_{1E1}$, $\bar{n}_{2E1}$ and $\bar{\rho}_{E1}$ which would occur in the absence of any flow. This double layer is then distorted by the flow $(\bar{v}_{Hx}, \bar{v}_{Hy}, \bar{v}_{Hz})$, the distortion being of order ϵ^3 and described by $\bar{\psi}^*_3$, $\bar{n}^*_{13}$, $\bar{n}^*_{23}$ and $\bar{\rho}^*_3$. This then matches onto the outer region, producing there a normal flux of ions and a normal electric field at boundaries which gives rise to an electric field (with potential $\tilde{\psi}^*_2$) and an ion concentration variation $\tilde{n}^*_{12} = \tilde{n}^*_{22}$ of order ϵ^2 (with no net charge density at this order). This potential $\tilde{\psi}^*_2$, often known as the streaming potential, gives a variation of potential along the outside of the double layer causing a further distortion of the double layer, this time of order ϵ^2 (and described by $\bar{\psi}^*_2$, $\bar{n}^*_{12}$, $\bar{n}^*_{22}$ and $\bar{\rho}^*_2$) and inducing a static pressure variation $\bar{p}^*_2$ also of order ϵ^2. The gradient of $\tilde{\psi}^*_2$ tangential to the double layer together with the equilibrium charge density $\bar{\rho}_{E0}$ gives a tangential force on the liquid in the double layer. This together with the tangential gradient of pressure $\bar{p}_{E0}$ gives a tangential force on the liquid in the double layer of order ϵ^4 (with velocities $\bar{v}^*_{4x}, \bar{v}^*_{4y}$). This when matched onto the outer region gives rise to a creeping flow (with velocity $\tilde{\boldsymbol{v}}^*_4$ and pressure $\tilde{p}^*_4$) in the outer region with an apparent slip at the boundaries. It is the viscous and pressure drag due to this flow $(\tilde{\boldsymbol{v}}^*_4, \tilde{p}^*_4)$ given by $\tilde{F}^*_4$ which, of order ϵ^4 (or more precisely of order $\lambda Pe\epsilon^4$), gives rise to the largest contribution to the electroviscous force on the particle. The recipe for obtaining this force is given in §13.

When the theory described here was applied (in §14) to the problem of a sedimenting charged sphere, with no walls W being present, the drag force on the sphere from the limiting case of $Pe \rightarrow 0$ was, as already mentioned, in agreement with Ohshima *et al.* (1984). However in a number of papers, including those concerning the translation of a charged sphere near a plane wall (Bike & Prieve 1990; van de Ven *et al.* 1993*a*) and the approach of two spheres (van de Ven *et al.* 1993*b*), the force on the sphere was obtained as being of order $\lambda Pe^2\epsilon^6$ instead of the much larger force of order $\lambda Pe\epsilon^4$ (or order of $\lambda Pe^2\epsilon^4$ for the lift force on a sphere near a plane) predicted by the present theory. This is because the previous authors had assumed *a priori* that the dominant electroviscous force was that resulting from the Maxwell stress tensor due to the streaming potential $\tilde{\psi}^*_2$ (see §12 and table 1). Actually in addition to the possible contribution to the force at order ϵ^4 calculated here, there could be effects of order ϵ^5 and ϵ^6 which would be of the same order or larger than that due to the Maxwell stress arising from the streaming potential. The fact that experiments show the lift force on a charged sphere in a shear flow near a plane wall to be several orders of magnitude greater than the predictions based on the order-ϵ^6 theory derived solely from the

	Inner region						Outer region					
	$\bar{\psi}$	$\bar{n}_1$ (and $\bar{n}_2$)	$\bar{\rho}$	$\bar{p}$	$\bar{v}_x$ (and $\bar{v}_y$)	$\bar{v}_z$	$\tilde{\psi}$	$\tilde{n}_1$ (and $\tilde{n}_2$)	$\tilde{\rho}$	$\tilde{p}$	$\tilde{\mathbf{v}}$	Force
ϵ^0	$\bar{\psi}_{E0}$	$\bar{n}_{1E0}$	$\bar{\rho}_{E0}$	$\bar{p}_{E0}$ $\bar{p}_H$	0	0	0	$\tilde{n}_\infty$	0	$\bar{p}_H$	$\bar{v}_H$	$(\epsilon^0)\tilde{F}_H$
ϵ^1	$(\epsilon)\bar{\psi}_{E1}$	$(\epsilon)\bar{n}_{1E1}$	$(\epsilon)\bar{\rho}_{E1}$	$(\epsilon)\bar{p}_{E1}$	$(\epsilon)\bar{v}_{Hx}$	0	0	0	0	0		
ϵ^2	$(Pe\epsilon^2)\bar{\psi}_2^*$	$(Pe\epsilon^2)\bar{n}_{12}^*$	$(Pe\epsilon^2)\bar{\rho}_2^*$	$(\lambda Pe\epsilon^2)\bar{p}_2^*$		$(\epsilon^2)\bar{v}_{Hz}$	$(Pe\epsilon^2)\bar{\psi}_2^*$	$(Pe\epsilon^2)\tilde{n}_{12}^*$	0	0	0	$(\lambda Pe^2\epsilon^6)$
ϵ^3	$(Pe\epsilon^3)\bar{\psi}_3^*$	$(Pe\epsilon^3)\bar{n}_{13}^*$	$(Pe\epsilon^3)\bar{\rho}_3^*$						0	0	0	
ϵ^4					$(\lambda Pe\epsilon^4)\bar{v}_{4x}^*$				$(Pe\epsilon^4)\tilde{\rho}_4$	$(\lambda Pe\epsilon^4)\tilde{p}_4^*$	$(\lambda Pe\epsilon^4)\tilde{v}_4^*$	$(\lambda Pe\epsilon^4)\tilde{F}_4^*$
ϵ^5						$(\lambda Pe\epsilon^5)\bar{v}_{5z}^*$						

Table 1. Matching procedure described in §§2–12.

Maxwell tensor (Bike & Prieve 1995; Wu, Warszynski & van de Ven 1996) supports the assertion that the hydrodynamic effects derived here are indeed dominant. It would also seem that in addition two further papers by Warszynski & van de Ven (1990, 1991) might also be in error for this same reason.

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Appendix A

On the $\bar{z}$-axis ($\bar{x}=\bar{y}=0$) in the inner region, the values of $\bar{n}_{1E0}$, $\bar{n}_{2E0}$, $\bar{\rho}_{E0}$ and $\bar{p}_{E0}$ and their $\bar{x}$- and $\bar{y}$-derivatives and the values of $\bar{n}_{1E1}$, $\bar{n}_{2E1}$, $\bar{\rho}_{E1}$ and $\bar{p}_{E1}$ required for the expansion (4.28) of the solution to the electrical problem considered in §4, are obtained as

$$\bar{n}_{1E0}=\left(\frac{1-A_p\,\mathrm{e}^{-\bar{z}}}{1+A_p\,\mathrm{e}^{-\bar{z}}}\right)^2,\quad \bar{n}_{1E1}=-\frac{\alpha_p A_p\,\mathrm{e}^{-\bar{z}}\{2\bar{z}+A_p^2(\mathrm{e}^{-2\bar{z}}-1)\}(1-A_p\,\mathrm{e}^{-\bar{z}})}{(1+A_p\,\mathrm{e}^{-\bar{z}})^3}, \tag{A 1a, b}$$

$$\frac{\partial\bar{n}_{1E0}}{\partial\bar{x}}+\frac{\partial\bar{n}_{1E0}}{\partial\bar{y}}=0,\quad \left(\frac{\partial^2}{\partial\bar{x}^2}+\frac{\partial^2}{\partial\bar{y}^2}\right)\bar{n}_{1E0}=-\alpha_p\frac{4A_p\,\mathrm{e}^{-\bar{z}}(1-A_p\,\mathrm{e}^{-\bar{z}})}{(1+A_p\,\mathrm{e}^{-\bar{z}})^3}, \tag{A 1c, d}$$

$$\bar{n}_{2E0}=\left(\frac{1+A_p\,\mathrm{e}^{-\bar{z}}}{1-A_p\,\mathrm{e}^{-\bar{z}}}\right)^2,\quad \bar{n}_{2E1}=+\frac{\alpha_p A_p\,\mathrm{e}^{-\bar{z}}\{2\bar{z}+A_p^2(\mathrm{e}^{-2\bar{z}}-1)\}(1+A\,\mathrm{e}^{-\bar{z}})}{(1-A_p\,\mathrm{e}^{-\bar{z}})^3} \tag{A 2a, b}$$

$$\frac{\partial\bar{n}_{2E0}}{\partial\bar{x}}=\frac{\partial\bar{n}_{2E0}}{\partial\bar{y}}=0,\quad \left(\frac{\partial^2}{\partial\bar{x}^2}+\frac{\partial^2}{\partial\bar{y}^2}\right)\bar{n}_{2E0}=+\alpha_p\frac{4A_p\,\mathrm{e}^{-\bar{z}}(1+A_p\,\mathrm{e}^{-\bar{z}})}{(1-A_p\,\mathrm{e}^{-\bar{z}})^3}, \tag{A 2c, d}$$

$$\bar{\rho}_{E0}=-\frac{4A_p\,\mathrm{e}^{-\bar{z}}(1+A_p^2\,\mathrm{e}^{-2\bar{z}})}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})^2}, \tag{A 3a}$$

$$\bar{\rho}_{E1}=-\frac{\alpha_p A_p\,\mathrm{e}^{-\bar{z}}\{2\bar{z}+A_p^2(\mathrm{e}^{-2\bar{z}}-1)\}(1+6A_p^2\,\mathrm{e}^{-2\bar{z}}+A_p^4\,\mathrm{e}^{-4\bar{z}})}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})^3}, \tag{A 3b}$$

$$\frac{\partial\bar{\rho}_{E0}}{\partial\bar{x}}=\frac{\partial\bar{\rho}_{E0}}{\partial\bar{y}}=0,\quad \left(\frac{\partial^2}{\partial\bar{x}^2}+\frac{\partial^2}{\partial\bar{y}^2}\right)\bar{\rho}_{E0}=-\alpha_p\frac{4A_p\,\mathrm{e}^{-\bar{z}}(1+6A_p^2\,\mathrm{e}^{-2\bar{z}}+A_p^4\,\mathrm{e}^{-4\bar{z}})}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})^3} \tag{A 3c, d}$$

and

$$\bar{p}_{E0}=\frac{8\lambda A_p^2\,\mathrm{e}^{-2\bar{z}}}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})^2},\quad \bar{p}_{E1}=\frac{4\lambda\alpha_p A_p^2\,\mathrm{e}^{-2\bar{z}}\{2\bar{z}+A_p^2(\mathrm{e}^{-2\bar{z}}-1)\}(1+A_p^2\,\mathrm{e}^{-2\bar{z}})}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})^3}, \tag{A 4a, b}$$

$$\frac{\partial\bar{p}_{E0}}{\partial\bar{x}}=\frac{\partial\bar{p}_{E0}}{\partial\bar{y}}=0,\quad \left(\frac{\partial^2}{\partial\bar{x}^2}+\frac{\partial^2}{\partial\bar{y}^2}\right)\bar{p}_{E0}=+\alpha_p\frac{16\lambda A_p^2\,\mathrm{e}^{-2\bar{z}}(1+A_p^2\,\mathrm{e}^{-2\bar{z}})}{(1-A_p^2\,\mathrm{e}^{-2\bar{z}})^3}. \tag{A 4c, d}$$

Appendix B

Appendix B is not reproduced here, but can be obtained from the Journal of Fluid Mechanics Editorial Office.

Appendix C

The equations for $\bar{\boldsymbol{v}}^*, \bar{p}^*, \bar{n}^* \ldots$ valid on the $\bar{z}$-axis in the inner region at Q obtained in the manner described in §6 are

$$
\begin{aligned}
&\frac{\partial^2 \bar{n}_1^*}{\partial \bar{z}^2}+\epsilon\left(\frac{\partial^2 \bar{n}_1^*}{\partial \bar{x}^2}+\frac{\partial^2 \bar{n}_1^*}{\partial \bar{y}^2}\right)+\frac{\partial}{\partial \bar{z}}\left\{(\bar{n}_{1E0}+\epsilon \bar{n}_{1E1}+\ldots)\frac{\partial \bar{\psi}^*}{\partial \bar{z}}+\bar{n}_1^*\frac{\partial}{\partial \bar{z}}(\bar{\psi}_{E0}+\epsilon\bar{\psi}_{E1}+\ldots)\right. \\
&\quad\left.+\bar{n}_1^*\frac{\partial \bar{\psi}^*}{\partial \bar{z}}\right\}+\epsilon\left\{(\bar{n}_{1E0}+\ldots)\frac{\partial^2 \bar{\psi}^*}{\partial \bar{x}^2}+\frac{\partial \bar{\psi}^*}{\partial \bar{x}}((O(\epsilon))\right. \\
&\quad\left.+\bar{n}_1^*\frac{\partial^2}{\partial \bar{x}^2}(\bar{\psi}_{E0}+\ldots)+\frac{\partial \bar{n}_1^*}{\partial \bar{x}}(O(\epsilon))+\frac{\partial}{\partial \bar{x}}\left(\bar{n}_1^*\frac{\partial \bar{\psi}^*}{\partial \bar{x}}\right)\right\}+\epsilon\left\{(\bar{n}_{1E0}+\ldots)\frac{\partial^2 \bar{\psi}^*}{\partial \bar{y}^2}\right. \\
&\quad\left.+\frac{\partial \bar{\psi}^*}{\partial \bar{y}}(O(\epsilon))+\bar{n}_1^*\frac{\partial^2}{\partial \bar{y}^2}(\bar{\psi}_{E0}+\ldots)+\frac{\partial \bar{n}_1^*}{\partial \bar{y}}(O(\epsilon))+\frac{\partial}{\partial \bar{y}}\left(\bar{n}_1^*\frac{\partial \bar{\psi}^*}{\partial \bar{y}}\right)\right\} \\
&\quad-Pe\,\epsilon\left\{\left(\tfrac{1}{2}\epsilon^2\frac{\partial^2 \tilde{v}_{Hz}}{\partial \tilde{z}^2}\bigg|_Q\bar{z}^2+\ldots\right)\frac{\partial}{\partial \bar{z}}(\bar{n}_{1E0}+\ldots)+\left(\tfrac{1}{2}\epsilon^2\frac{\partial^2 \tilde{v}_{Hz}}{\partial \tilde{z}^2}\bigg|_Q\bar{z}^2+\ldots\right)\frac{\partial \bar{n}_1^*}{\partial \bar{z}}\right. \\
&\quad\left.+\bar{v}_z^*\frac{\partial}{\partial \bar{z}}(\bar{n}_{1E0}+\ldots)+\bar{v}_z^*\frac{\partial \bar{n}_1^*}{\partial \bar{z}}\right\}-Pe\,\epsilon^{3/2}\left\{\left[\epsilon\left(\frac{\partial \tilde{v}_{Hx}}{\partial \tilde{z}}\bigg|_Q-\tilde{\Omega}_y\right)\bar{z}+\ldots\right](O(\epsilon))\right. \\
&\quad\left.+\left[\epsilon\left(\frac{\partial \tilde{v}_{Hx}}{\partial \tilde{z}}\bigg|_Q-\tilde{\Omega}_y\right)\bar{z}+\ldots\right]\frac{\partial \bar{n}_1^*}{\partial \bar{x}}+\bar{v}_x^*(O(\epsilon))+\bar{v}_x^*\frac{\partial \bar{n}_1^*}{\partial \bar{x}}\right\} \\
&\quad-Pe\,\epsilon^{3/2}\left\{\left[\epsilon\left(\frac{\partial \tilde{v}_{Hy}}{\partial \tilde{z}}\bigg|_Q+\tilde{\Omega}_x\right)\bar{z}+\ldots\right](O(\epsilon))+\left[\epsilon\left(\frac{\partial \tilde{v}_{Hz}}{\partial \tilde{z}}\bigg|_Q+\tilde{\Omega}_x\right)\bar{z}+\ldots\right]\frac{\partial \bar{n}_1^*}{\partial \bar{y}}\right. \\
&\quad\left.+\bar{v}_y^*(O(\epsilon))+\bar{v}_y^*\frac{\partial \bar{n}_1^*}{\partial \bar{y}}\right\}-Pe\,\epsilon^2\frac{\partial \bar{n}_1^*}{\partial \bar{t}}=0, \qquad \text{(C 1}a\text{)}
\end{aligned}
$$

$$
\begin{aligned}
&\frac{\partial^2 \bar{n}_2^*}{\partial \bar{z}^2}+\epsilon\left(\frac{\partial^2 \bar{n}_2^*}{\partial \bar{x}^2}+\frac{\partial^2 \bar{n}_2^*}{\partial \bar{y}^2}\right)-\frac{\partial}{\partial \bar{z}}\left\{(\bar{n}_{2E0}+\epsilon \bar{n}_{2E1}+\ldots)\frac{\partial \bar{\psi}^*}{\partial \bar{z}}+\bar{n}_2^*\frac{\partial}{\partial \bar{z}}(\bar{\psi}_{E0}+\epsilon\bar{\psi}_{E1}+\ldots)\right. \\
&\quad\left.+\bar{n}_2^*\frac{\partial \bar{\psi}^*}{\partial \bar{z}}\right\}-\epsilon\left\{(\bar{n}_{2E0}+\ldots)\frac{\partial^2 \bar{\psi}^*}{\partial \bar{x}^2}+\frac{\partial \bar{\psi}^*}{\partial \bar{x}}((O(\epsilon))\right. \\
&\quad\left.+\bar{n}_2^*\frac{\partial^2}{\partial \bar{x}^2}(\bar{\psi}_{E0}+\ldots)+\frac{\partial \bar{n}_2^*}{\partial \bar{x}}(O(\epsilon))+\frac{\partial}{\partial \bar{x}}\left(\bar{n}_2^*\frac{\partial \bar{\psi}^*}{\partial \bar{x}}\right)\right\}-\epsilon\left\{(\bar{n}_{2E0}+\ldots)\frac{\partial^2 \bar{\psi}^*}{\partial \bar{y}^2}\right. \\
&\quad\left.+\frac{\partial \bar{\psi}^*}{\partial \bar{y}}(O(\epsilon))+\bar{n}_2^*\frac{\partial^2}{\partial \bar{y}^2}(\bar{\psi}_{E0}+\ldots)+\frac{\partial \bar{n}_2^*}{\partial \bar{y}}(O(\epsilon))+\frac{\partial}{\partial \bar{y}}\left(\bar{n}_2^*\frac{\partial \bar{\psi}^*}{\partial \bar{y}}\right)\right\} \\
&\quad-Pe\,\epsilon\left(\frac{D_1}{D_2}\right)\left\{\left(\tfrac{1}{2}\epsilon^2\frac{\partial^2 \tilde{v}_{Hz}}{\partial \tilde{z}^2}\bigg|_Q\bar{z}^2+\ldots\right)\frac{\partial}{\partial \bar{z}}(\bar{n}_{2E0}+\ldots)+\left(\tfrac{1}{2}\epsilon^2\frac{\partial^2 \tilde{v}_{Hz}}{\partial \tilde{z}^2}\bigg|_Q\bar{z}^2+\ldots\right)\frac{\partial \bar{n}_2^*}{\partial \bar{z}}\right. \\
&\quad\left.+\bar{v}_z^*\frac{\partial}{\partial \bar{z}}(\bar{n}_{2E0}+\ldots)+\bar{v}_z^*\frac{\partial \bar{n}_2^*}{\partial \bar{z}}\right\}-Pe^{\,3/2}\left(\frac{D_1}{D_2}\right)\left\{\left[\epsilon\left(\frac{\partial \tilde{v}_{Hx}}{\partial \bar{z}}\bigg|_Q-\tilde{\Omega}_y\right)\bar{z}+\ldots\right](O(\epsilon))\right. \\
&\quad\left.+\left[\epsilon\left(\frac{\partial \tilde{v}_{Hx}}{\partial \tilde{z}}\bigg|_Q-\tilde{\Omega}_y\right)\bar{z}+\ldots\right]\frac{\partial \bar{n}_2^*}{\partial \bar{x}}+\bar{v}_x^*(O(\epsilon))+\bar{v}_x^*\frac{\partial \bar{n}_2^*}{\partial \bar{x}}\right\}
\end{aligned}
$$

$$-Pe\,\epsilon^{3/2}\left(\frac{D_1}{D_2}\right)\left\{\left[\epsilon\left(\frac{\partial\tilde{v}_{Hy}}{\partial\tilde{z}}\bigg|_Q+\tilde{\Omega}_x\right)\bar{z}+\dots\right](O(\epsilon))+\left[\epsilon\left(\frac{\partial\tilde{v}_{Hz}}{\partial\tilde{z}}\bigg|_Q+\tilde{\Omega}_x\right)\bar{z}+\dots\right]\frac{\partial\bar{n}_2^*}{\partial\bar{y}}\right.$$

$$\left.+\bar{v}_y^*(O(\epsilon))+\bar{v}_y^*\frac{\partial\bar{n}_2^*}{\partial\bar{y}}\right\}-Pe\,\epsilon^2\left(\frac{D_1}{D_2}\right)\frac{\partial\bar{n}_1^*}{\partial\bar{t}}=0, \quad \text{(C 1}b\text{)}$$

$$\frac{\partial^2\bar{\psi}^*}{\partial\bar{z}^2}+\epsilon\left(\frac{\partial^2\bar{\psi}^*}{\partial\bar{x}^2}+\frac{\partial^2\bar{\psi}^*}{\partial\bar{y}^2}\right)=-\bar{\rho}^*, \quad \bar{\rho}^*=\tfrac{1}{2}(\bar{n}_1^*-\bar{n}_2^*), \quad \text{(C 1}c,d\text{)}$$

$$\frac{\partial^2\bar{v}_x^*}{\partial\bar{z}^2}+\epsilon\left(\frac{\partial^2\bar{v}_x^*}{\partial\bar{x}^2}+\frac{\partial^2\bar{v}_x^*}{\partial\bar{y}^2}\right)-\epsilon^{3/2}\frac{\partial\bar{p}^*}{\partial\bar{x}}=\lambda\epsilon^{3/2}\left\{\bar{\rho}^*(O(\epsilon))+(\bar{\rho}_{E0}+\dots)\frac{\partial\bar{\psi}^*}{\partial\bar{x}}+\bar{\rho}^*\frac{\partial\bar{\psi}^*}{\partial\bar{x}}\right\}, \quad \text{(C 1}e\text{)}$$

$$\frac{\partial^2\bar{v}_y^*}{\partial\bar{z}^2}+\epsilon\left(\frac{\partial^2\bar{v}_y^*}{\partial\bar{x}^2}+\frac{\partial^2\bar{v}_y^*}{\partial\bar{y}^2}\right)-\epsilon^{3/2}\frac{\partial\bar{p}^*}{\partial\bar{y}}=\lambda\epsilon^{3/2}\left\{\bar{\rho}^*(O(\epsilon))+(\bar{\rho}_{E0}+\dots)\frac{\partial\bar{\psi}^*}{\partial\bar{y}}+\bar{\rho}^*\frac{\partial\bar{\psi}^*}{\partial\bar{y}}\right\}, \quad \text{(C 1}f\text{)}$$

$$\frac{\partial^2\bar{v}_z^*}{\partial\bar{z}^2}+\epsilon\left(\frac{\partial^2\bar{v}_z^*}{\partial\bar{x}^2}+\frac{\partial^2\bar{v}_z^*}{\partial\bar{y}^2}\right)-\epsilon\frac{\partial\bar{p}^*}{\partial\bar{z}}=\lambda\epsilon\left\{\bar{\rho}^*\frac{\partial}{\partial\bar{z}}(\bar{\psi}_{E0}+\dots)+(\bar{\rho}_{E0}+\dots)\frac{\partial\bar{\psi}^*}{\partial\bar{z}}+\bar{\rho}^*\frac{\partial\bar{\psi}^*}{\partial\bar{z}}\right\}, \quad \text{(C 1}g\text{)}$$

$$\frac{\partial\bar{v}_z^*}{\partial\bar{z}}+\epsilon^{1/2}\left(\frac{\partial\bar{v}_x^*}{\partial\bar{x}}+\frac{\partial\bar{v}_y^*}{\partial\bar{y}}\right)=0, \quad \text{(C 1}h\text{)}$$

with the boundary conditions at $\bar{z}=0$ of

$$\bar{v}^*=0, \quad \text{(C 2}a\text{)}$$

$$\frac{\partial\bar{n}_1^*}{\partial\bar{z}}+(\bar{n}_{1E0}+\epsilon\bar{n}_{1E1}+\dots)\frac{\partial\bar{\psi}^*}{\partial\bar{z}}+\bar{n}_1^*\frac{\partial}{\partial\bar{z}}(\bar{\psi}_{E0}+\epsilon\bar{\psi}_{E1}+\dots)+\bar{n}_1^*\frac{\partial\bar{\psi}^*}{\partial\bar{z}}=0, \quad \text{(C 2}b\text{)}$$

$$\frac{\partial\bar{n}_2^*}{\partial\bar{z}}-(\bar{n}_{2E0}+\epsilon\bar{n}_{2E1}+\dots)\frac{\partial\bar{\psi}^*}{\partial\bar{z}}-\bar{n}_2^*\frac{\partial}{\partial\bar{z}}(\bar{\psi}_{E0}+\epsilon\bar{\psi}_{E1}+\dots)-\bar{n}_2^*\frac{\partial\bar{\psi}^*}{\partial\bar{z}}=0, \quad \text{(C 2}c\text{)}$$

$$\bar{\psi}^*=0. \quad \text{(C 2}d\text{)}$$

REFERENCES

Bike, S. G. & Prieve, D. C. 1990 *J. Colloid Interface Sci.* **136**, 95.

Bike, S. G. & Prieve, D. C. 1995 *J. Colloid Interface Sci.* **175**, 422.

Chew, W. C. & Sen, P. M. 1982 *J. Phys. Chem.* **77**, 2042.

Deryagin, B. V. & Landau, L. 1941 *Acta Phys. Chim., URSS* **14**, 633.

Everett, D. H. 1988 *Basic Principles of Colloid Science*. Royal Society of Chemistry, London.

Fair, M. C. & Anderson, J. L. 1989 *J. Colloid Interface Sci.* **127**, 388.

Happel, J. & Brenner, H. 1965 *Low Reynolds Number Hydrodynamics*. Prentice-Hall.

Ohshima, H., Healy, T. W., White, L. R. & O'Brien, R. W. 1984 *J. Chem. Soc., Faraday Trans.* II. **80**, 1299.

Shaw, D. J. 1986 *Introduction to Colloid and Surface Chemistry*. Butterworths.

Stokes, G. G. 1851 *Trans. Camb. Phil. Soc.* **9**, 8.

Teubner, M. 1982 *J. Phys. Chem.* **76**, 5564.

Ven, T. G. M. van de, Warszynski, P. & Dukhin, S. S. 1993*a* *J. Colloid Interface Sci.* **157**, 328.

Ven, T. G. M. van de, Warszynski, P. & Dukhin, S. S. 1993*b* *Colloids Surfaces* A **79**, 33.

Verwey, E. J. W. & Overbeek, J. Th. G. 1948 *Theory of the Stability of Lyophobic Colloids*. Elsevier.

Warszynski, P. & Ven, T. G. M. van de 1990 *Faraday Discuss. Chem. Soc.* **90**, 313.

Warszynski, P. & Ven, T. G. M. van de 1991 *Adv. Colloid Interface Sci.* **36**, 33.

Wu, X., Warszynski, P. & Ven, T. G. M. van de 1996 *J. Colloid Interface Sci.* **180**, 61.