

The viscous flow of charged particles through a charged cylindrical tube

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(Received 2 November 1993 and in revised form 30 March 1994)

An analysis is given for the electro-kinetic transport properties in a system consisting of a line of identical spheres placed equidistantly with their centres on the axis of a cylindrical tube containing a viscous fluid. Both the spheres and the wall of the tube are charged and a two-species symmetrical electrolyte with valence Z is present in the system. As a result of the charges on the surface of the spheres and on the surface of the tube electrical double layers will develop. When an electrical field is applied to the system an electrokinetic motion is induced. We will use the thin double layer theory (Dukhin & Derjaguin 1974; O'Brien 1983), valid for sufficiently high electrolyte concentration and where the polarization of the electrical double layer is included. Using a multipole expansion an infinite set of linear equations for the multipoles will be derived from which the electro-kinetic transport coefficients may be determined. These coefficients depend on the system parameters, such as the radius of the tube R , the radius of the sphere a , the separation between the spheres d , the Debye radius κ^{-1} , the zeta-potentials of the spheres ζ_p and of the wall of the tube ζ_w and the valency Z of the electrolyte. From these coefficients a relation is found between the pressure drop Δp per unit length and the drag force D on the spheres on one side and with the velocity U of the spheres, the total discharge Q and the applied electrical field E_0 on the other side. For some values for the system parameters we have numerically solved the infinite set of linear equations by truncation and calculated the transport coefficients. We have also calculated the streamlines for some situations. The plots of these streamlines show that depending on the conditions on the system vortices may appear.

1. Introduction

This study is a theoretical examination of the steady axisymmetric creeping motion of fluid through a cylindrical tube containing a line of identical spheres placed equally spaced on the axis of the tube. Both the surfaces of the spheres as well as the surface of the tube possess a surface charge characterized by the zeta-potentials ζ_p and ζ_w respectively. As a result of electrolyte present in the system the surfaces are surrounded by an electrical double layer with a thickness given by the Debye radius κ^{-1} , depending on the ionic strength of the electrolyte. We assume that we are in the limit of thin double layers, so that both the conditions $\kappa a \gg 1$ and $\kappa R \gg 1$ are fulfilled, with a the radius of the spheres and R the radius of the tube. When an electrical field E_0 is applied to the system, the fluid will be set into motion. This motion is induced by the electrical double layers of the spheres and the wall where the charge density is non-zero. When the spheres flow force free through the tube they will attain a terminal velocity, i.e. the

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electrophoretic velocity. For a single charged sphere in an external electrical field E_0 in an unbounded fluid the electrophoretic velocity U is given by the Smoluchowski formula (Smoluchowski 1921) in SI units:

$$U = \frac{\epsilon_0 \epsilon_r \zeta_p}{\eta} E_0. \quad (1.1)$$

Here, η is the fluid viscosity, ζ_p the zeta-potential of the particle surface, $\epsilon_0 \epsilon_r$ the permittivity. This formula is derived under the condition of a thin double layer ($\kappa a \gg 1$), a uniform zeta-potential and an undisturbed ion distribution when the electrical field is applied. This last condition implies that the double layer will not become polarized when an electrical field is applied. Comparison of analytical expressions (e.g. O'Brien & Hunter 1981; O'Brien 1983) for the electrophoretic mobility of a sphere for finite κa with exact numerical calculations (O'Brien & White 1978) shows that the polarization of the double layer may be neglected when the following condition is fulfilled:

$$\frac{\exp(e |z_i \zeta_p| / 2kT)}{\kappa a} \ll 1, \quad (1.2)$$

with z_i the valency of the highest charged counterion, k the Boltzmann constant, T the absolute temperature and e the elementary charge. Relation (1.2) places a restriction on the value of the zeta-potential ζ_p . In the thin double layer theory (Dukhin & Derjaguin 1974; O'Brien 1983), where the polarization of the double layer is taken into account, this restriction on the zeta potential is overcome.

The electrophoretic motion of a charged sphere in the neighbourhood of a boundary or of an assembly of charged spheres has also been studied intensively. Keh & Anderson (1985) studied the motion of a single charged sphere in the neighbourhood of a single flat wall, two parallel walls and a long circular tube. Using a method of reflections the velocity of the sphere is determined in powers of λ up to $O(\lambda^6)$, where λ is the ratio of particle radius to distance from the boundary. Keh & Chen studied the electrophoretic motion of two charged spheres moving normal (1989*a*) and along (1989*b*) their lines of centres. Here the problem was solved exactly by using a spherical bipolar coordinate system. Employing the same method the motion of a charged sphere parallel to a dielectric plane was also studied (Keh & Chen 1988). All these studies, however, assume infinitely thin double layers where the double-layer polarization may be ignored. Dukhin & Derjaguin (1974) developed a theory where they do take into account the polarization effect for a charged sphere with a thin but still finite electrical double layer in a symmetrical electrolyte. This treatment was simplified and extended by O'Brien (1983) to include general electrolytes. Using this theory several electrokinetic transport properties, such as the conductivity (O'Brien 1981; O'Brien & Perrins 1983) and electro-osmotic transport properties (O'Brien 1985) were calculated for concentrated suspensions of charged spheres. The electrophoresis of a spheroid with a thin double layer was also studied (O'Brien & Ward 1988). A comparison of the results for the electrophoretic mobility of a single sphere in an unbounded fluid obtained by using the thin double layer theory including polarization (Chen & Keh 1992) with numerical solutions (O'Brien & White 1978) of the linearized electrokinetic equations valid for an arbitrary double layer thickness shows an accurate agreement for values of $\kappa a > 30$ and arbitrary zeta potentials. This result is in accord with the property of the thin double layer theory that produces results that are accurate for arbitrary zeta-potentials up to $O(1/\kappa a)$.

Chen & Keh (1992) employed a collocation technique to study the axisymmetric

electrophoretic motion of an assembly of charged spheres taking into account the polarization effect. Mobilities are calculated for clusters of spheres consisting of up to three spheres and apply for double layers with a small but still finite Debye radius κ^{-1} compared to the radius of the particles. None of the above-mentioned work focuses on the combined effect of multiple sphere interaction and a bounding surface at the same time. The main reason for studying this situation in this paper is the existence of a variety of practical applications associated with the motion of a charged emulsion or suspension through a porous medium under the action of an electrical field. As a result of the presence of surface charges on the spheres as well as on the wall of the porous medium the spheres will exhibit an electrophoretic motion that is disturbed by the electro-osmotic flow induced by the charged wall of the porous medium. In many cases (Tikhomolova 1993) there is no single view even as regards the direction of action on the suspended particles (acceleration or retardation compared to electrophoresis in an infinite medium) in these electro-kinetic flows. For describing this situation it is necessary to study the interaction between multiple spheres that are charged and a charged bounding surface. As a first practical example one may think of secondary oil recovery in the petroleum producing industry by the application of an electrical field (Tikhomolova 1993). A maximum of 40% of the oil in a header can generally be produced by primary methods. The next step is the employment of secondary methods, like the displacement of oil by pumping aqueous solutions under pressure (flooding) into the rock formation, which makes it possible to increase the oil yield by a maximum of 20%. In order to obtain a higher oil yield an electrical field near a well bottom may be applied, because when flooding becomes ineffective as a result of a high hydrodynamic friction in the porous body the electro-kinetic motion is still active. A second example may be found in the field of capillary electrophoresis, especially in micellar electro-kinetic capillary chromatography. Here a micellar solution together with a sample of uncharged compounds that have to be separated is injected into a capillary. Because the micelles are charged they will be set into motion when an electrical field is applied. This motion will be influenced by the electro-osmotic flow induced by the electrical double layer at the wall of the tube. Depending on the affinity for the micelles of the different compounds of the sample to be separated each of the compounds will spend a characteristic time inside the micelles. Because the micelles are moving at a speed that differs from the surrounding flow field the compounds of the sample will be separated. In order to increase the efficiency of this separation a better understanding of the details of the electro-kinetic flow is desirable.

In this study the assumption is made that the spheres move along the axis of the tube. This assumption is not necessarily unrealistic, especially when the radius of the tube is not much larger than the particle radius and because when the particles are deformable they tend to migrate towards the axis of the tube. This behaviour was observed first by Fåhræus (1928) and extensively studied by Goldsmith & Mason (1962). It is responsible for the Fåhræus-Lindqvist effect (1931), which refers to the observation that the effective viscosity of blood is less in capillaries than in vessels. In the system we study two additional effects occur in comparison with the electrophoretic motion of an isolated sphere in an infinite medium. On the one hand, when the spheres flow force free through an uncharged tube they will attain an electrophoretic velocity that depends on the interaction with the other spheres and the wall of the tube. When on the other hand the tube has a surface charge an electro-osmotic flow will also develop in the tube. This has a strong influence on the resulting flow field within the tube and on the velocity of the spheres. In this respect it is important to distinguish between two situations. In the first place we may consider a closed system, where the total discharge

of fluid and particles relative to the tube equals zero. To accomplish this an additional counter-pressure is built up in the system which induces a counterflow establishing a zero discharge. In the second place we may consider an open system where we have a non-zero discharge. Another situation of interest that will be addressed is a purely electro-osmotic flow, a situation which will occur when the spheres are held fixed at their positions relative to the tube. The electro-osmotic flow through a cylindrical tube in the absence of spheres has been treated by Rice & Whitehead (1965). Their treatment uses the Debye–Hückel approximation and is therefore only valid for low zeta potentials. The way we formulate the problem makes it possible to study not only the purely electrophoretic motion of the spheres or the purely electro-osmotic flow properties, but also all intermediate situations. Owing to the periodicity of the system we study it is possible by using a multipole expansion method to obtain results for the transport properties. The multipole moments are obtained numerically by truncating an infinite set of linear equations. By taking into account more and more multipole moments it is possible to obtain results with the desired accuracy.

The outline of the paper is as follows. In §2 the basic equations for the thin double layer theory are formulated as derived by O'Brien (1983). In §3 we specify the system and in §4 the equation and the boundary conditions for the ionic function in this geometry are formulated and a solution is constructed in terms of a multipole expansion. In §5 the equation and boundary conditions for the velocity field of the fluid are formulated for this system in terms of the Stokes stream function. Again, a multipole expansion is used to construct a solution. In §6 the transport properties in the system are expressed in terms of the multipole moments. A linear relation between the pressure drop per unit length and the drag exerted on a sphere on the one side and the velocity of the spheres, discharge and the electrical field on the other is given. The coefficients in these relations are the electro-kinetic coefficients and are expressed in terms of the multipole moments. For some system parameters these electro-kinetic coefficients are tabulated. In §7 some modes of electro-kinetic transport depending on the conditions placed on the system, e.g. a closed or open system, are discussed. In §8 some plots of the streamlines are given to illustrate the possibility of the occurrence of vortices.

2. Basic electro-kinetic equations and boundary conditions

In the absence of any chemical reaction in the electrolyte and in a stationary situation, we may apply the ion conservation law:

$$\nabla \cdot \mathbf{j}_i = 0, \quad (2.1)$$

with \mathbf{j}_i the flux density of ions of type i . In the double layer theory this flux is assumed to be given by

$$\mathbf{j}_i = -D_i \left[\nabla n_i + \frac{z_i e}{kT} n_i \nabla \Psi \right] + n_i \mathbf{v}, \quad (2.2)$$

where n_i , D_i and $z_i e$ are the number density, diffusivity and the charge of the ion of type i , Ψ is the electrostatical potential and \mathbf{v} the fluid velocity. The terms in \mathbf{j}_i denote the contribution due to diffusion, conduction and convection, respectively. The ion density n_i and the electrostatical potential Ψ are related to each other by the Poisson equation

$$\Delta \Psi = - \sum_{i=1}^N \frac{z_i e}{\epsilon_0 \epsilon_r} n_i, \quad (2.3)$$

where $\epsilon_0 \epsilon_r$ is the permittivity of the electrolyte and Δ the Laplace operator. The fluid motion is described by the equations

$$\rho \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla p + \eta \Delta \mathbf{v} - \sum_{i=1}^N n_i z_i e \nabla \Psi, \quad (2.4)$$

$$\nabla \cdot \mathbf{v} = 0. \quad (2.5)$$

Here η is the viscosity and p the hydrostatical pressure. The last term in (2.4) represents the electrical force per unit volume of the fluid. In order to determine the dimensionless quantities in the problem we scale (Saville 1977) all distances by a characteristic length L , the potential Ψ by e/kT and the fluid velocity \mathbf{v} by $\epsilon_0 \epsilon_r (kT/e)^2 / (1/\eta L)$. The diffusivities of the ions are scaled by the diffusivity D_1 of one of the ions and the ion concentrations are scaled on $\sum_{i=1}^N z_i^2 n_i^\infty$. Substitution into (2.1) to (2.5) leads to the following set of equations with dimensionless (primed) variables:

$$Re \mathbf{v}' \cdot \nabla' \mathbf{v}' = -\nabla' p' + \Delta' \Psi' \nabla' \Psi' + \Delta' \mathbf{v}', \quad (2.6)$$

$$Pe \mathbf{v}' \cdot \nabla' n'_i = D'_i \nabla' \cdot (z_i n'_i \nabla' \Psi' + \nabla' n'_i), \quad (2.7)$$

$$\nabla' \cdot \mathbf{v}' = 0, \quad (2.8)$$

$$\Delta' \Psi' = -(\kappa L)^2 \Psi'. \quad (2.9)$$

This identifies the following dimensionless groups: Reynolds number $Re = \epsilon_0 \epsilon_r (kT)^2 \rho / (\eta e)^2$, the Péclet number $Pe = \epsilon_0 \epsilon_r (kT/e)^2 / \eta D_1$ and $\kappa L = (e^2 \sum_{i=1}^N z_i^2 n_i^\infty L^2 / \epsilon_0 \epsilon_r)^{1/2}$ as a measure for thickness of the electrical double layer. The electrical field is \mathbf{E}_0 scaled as $Le \mathbf{E}_0 / kT$ and the zeta potential ζ as $e\zeta / kT$. For typical values of the parameters Re is small and we are allowed to ignore inertial term in (2.4), but we have to take into account convective effects because $Pe = O(1)$. We will use the thin double layer theory and we therefore require $\kappa L \gg 1$, but there is no restriction on the zeta potentials. We assume that an external electrical field is applied that is so small that $\mathbf{E}'_0 \ll 1$ and we only consider disturbances linear in the electrical field. This enables us to expand the electrokinetic equations (2.1)–(2.5) in δn_i and $\delta \Psi$, which are the linear deviations from equilibrium values as a result of the applied electrical field, as

$$n_i = n_i^0 + \delta n_i \quad \text{and} \quad \Psi = \Psi^0 + \delta \Psi. \quad (2.10)$$

Here n_i^0 and Ψ^0 denote the equilibrium values for the ion densities and electrostatical potential. From (2.1)–(2.3) it follows that Ψ^0 fulfils the Poisson–Boltzmann equation and n_i^0 a Boltzmann distribution (Appendix A). It is convenient to define the ionic function μ_i for ion species i as (O'Brien 1981)

$$n_i(\mathbf{r}) = n_i^\infty \exp\left(\frac{\mu_i(\mathbf{r}) - ez_i \Psi(\mathbf{r})}{kT}\right). \quad (2.11)$$

For a dilute electrolyte μ_i differs from the electrochemical potential by a constant depending on temperature and pressure. Linearizing this expression, by substituting (2.10) and ignoring small terms of $O(\delta^2)$ gives

$$\mu_i(\mathbf{r}) = kT \frac{\delta n_i(\mathbf{r})}{n_i^\infty} + ez_i \delta \Psi. \quad (2.12)$$

After linearizing the electrokinetic equations (2.2) and (2.4), using (2.10) and substituting

the expression for δn_i obtained from (2.12) we find the following equations for μ_i and v (O'Brien & White 1978):

$$n_i^0 \Delta \mu_i + \nabla n_i^0 \cdot \nabla \mu_i = \frac{kT}{D_i} \nabla n_i^0 \cdot v, \quad (2.13)$$

$$\eta \Delta (\nabla \times v) = \sum_{i=1}^N \nabla n_i^0 \times \nabla \mu_i, \quad (2.14)$$

$$\nabla \cdot v = 0. \quad (2.15)$$

The hydrostatical pressure p has been eliminated by taking the curl of (2.4). Beyond the double layers the ionic gradients are absent to $\nabla n_i^0 = 0$ and the equations simplify to

$$\Delta \mu_i = 0, \quad (2.16)$$

$$\eta \Delta (\nabla \times v) = 0, \quad (2.17)$$

$$\nabla \cdot v = 0. \quad (2.18)$$

The thin double layer theory now uses the fact that the Debye radius κ^{-1} is much smaller than the particle radius a . From (2.18) it now follows that the ratio of tangential to normal fluid velocity is of $O(\kappa a)$, so the fluid velocity is mainly tangential to the surface of the particle. Furthermore, from a local solution of the electro-kinetic equations it can be shown (O'Brien 1983) that the ionic potential is approximately constant in the direction normal to the surface of the particle. By integrating (2.14) over the double layer the tangential fluid velocity relative to the particle surface at the outer edge of the double layer can be derived (O'Brien 1983) as

$$v_s = -\frac{1}{\eta} \sum_{i=1}^N \nabla_s \mu_i \int_0^\infty y (n_i^0 - n_i^\infty) dy, \quad (2.19)$$

where

$$v_s = v \cdot (1 - nn) \quad \text{and} \quad \nabla_s = \nabla \cdot (1 - nn), \quad (2.20)$$

with n the unit vector pointing normal to the particle surface and y the distance as measured normal from the surface. Since we are dealing with thin double layers the particle density n_i^0 is supposed to fulfil the flat-plate solution of the Poisson–Boltzmann equation. When we are in the limit of thin double layers (2.19) reduces to the Helmholtz expression for electro-osmotic flow, i.e. $v_s = -(\zeta_p \epsilon_0 \epsilon_r / \eta) \nabla \psi$. For the ionic function μ_i it can be shown that, by equating the net tangential flux of ions entering a portion of the double layer to the flux leaving to the bulk electrolyte (O'Brien 1983), on the outer edge of the double layer the following boundary conditions apply:

$$\frac{\partial \mu_i}{\partial n} = -\beta_i a \Delta_s \mu_i, \quad (2.21)$$

with the surface Laplacian $\Delta_s = (1 - nn) : \nabla \nabla$ and β_i given by

$$\beta_i = \left(\frac{2}{n_i'} \right)^{1/2} \frac{1}{|z_i| \kappa a} \left(1 + \frac{3m_i}{z_i^2} \right) (\exp(e|z_i \xi|/2kT) - 1) \quad (2.22)$$

for the highest charged counter-ion and $\beta_i = 0$ for all other ions. Here it is assumed that there is only one kind of counter-ion with the largest valence present and that the tangential fluxes of the remaining ions are negligible. Furthermore

$$n_i' = \frac{n_i^\infty}{\sum_{j=1}^N z_j^2 n_j^\infty}; \quad m_i = \frac{2\epsilon_r \epsilon_0 (kT)^2}{3\eta e^2 D_i}; \quad \kappa = \left(\frac{2e^2}{\epsilon_0 \epsilon_r kT} n^\infty Z^2 \right)^{1/2}, \quad (2.23)$$

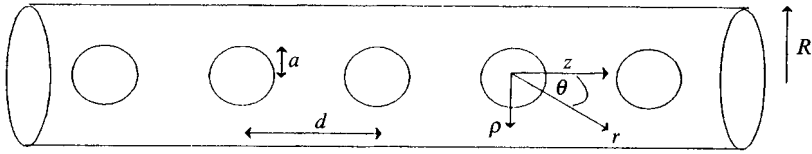


FIGURE 1. Geometry of the system.

where m_i is the non-dimensional ionic drag coefficient in SI units, n_j^∞ is the bulk number density of the ions of type j and Z is the absolute valence of the electrolyte. The expressions (2.19)–(2.23) for μ_i and v valid at the outer edge of the double layer will be used as boundary conditions for the solution outside these double layers. Because the double layers are thin, these boundary conditions will be applied at the surface of the particles instead of on the outer edge of the double layer, introducing an error of $O(1/\kappa a)$. For simplicity, it is assumed that we have to deal with one symmetrical electrolyte with a valence Z and we only consider the flux of the counter-ion. Chen & Keh (1992) tested this approximation for the electrophoretic motion of one sphere in a symmetrical electrolyte and found very good agreement with calculation where the contribution of all ions to the flux was taken into account. Apart from the boundary conditions at infinity (2.16)–(2.23) form the basic set of equations of the thin double layer theory that we will use for analysing the electro-kinetic effects occurring when an electrical field is applied to a line of charged particles placed regularly on the axis of a charged cylindrical tube.

3. The motion of a line of charged spheres placed regularly on the axis of a charged tube

We consider a line of charged identical hard spheres placed at equidistant positions from each other with their centres on the axis of a cylindrical tube. The spheres are all identical and are characterized by a radius a and a zeta potential ζ_p . The spacing between the spheres is d . The cylindrical tube has a radius R and a zeta potential ζ_w . As shown in figure 1 an external electrical field is applied directed along the axis of the tube in the positive z -direction. The origin of the coordinate system is at the centre of one of the spheres. For simplicity we assume that we have an one-species symmetrical electrolyte with an absolute valency Z . Our aim is to find the solution for the ionic function μ_i , with $i = 1, 2$ labelling the positive and negative ions of the electrolyte respectively, and for the velocity field v when an electrical field E_0 is applied. In view of (2.19) the boundary condition for the velocity field contains the ionic function μ_i , so one first has to find a solution for the ionic function μ_i before a solution for the velocity field v may be found.

4. Governing equations and solution for the ionic function

4.1. Governing equations for the ionic function

The ionic function μ_i for ion type i has to satisfy the Laplace equation, cf. (2.16):

$$\Delta\mu_i = 0. \quad (4.1)$$

Because the system consists of a cylindrical tube containing spheres we will employ both cylindrical and spherical coordinates as shown in figure 1, denoted by (ρ', z') and (r', θ) , respectively. The distances in the problem are non-dimensionalised by the radius

R of the tube, and we furthermore define the following dimensionless (unprimed) variables:

$$\lambda = \frac{a}{R}, \quad \kappa^* = \kappa R, \quad \beta = \frac{d}{R}, \quad \rho = \frac{\rho'}{R}, \quad z = \frac{z'}{R}, \quad r = \frac{r'}{R}, \quad E_0 = \frac{eE'_0 R}{kT}, \quad \mu_i = \frac{\mu'_i}{kT}. \quad (4.2)$$

As follows from §2, (4.1) is supplemented by the following boundary conditions:

(i) at the wall of the tube

$$\left. \frac{\partial \mu_i}{\partial \rho} \right|_{\rho=1} = -\beta_i \frac{\partial^2 \mu_i}{\partial z^2} \Big|_{\rho=1}, \quad (4.3a)$$

$$\text{with } \beta_i = \frac{1}{Z^2 \kappa^*} \left(1 + \frac{3m_i}{Z^2} \right) (\exp(eZ|\zeta_w|/2kT) - 1) \quad \text{for the counter-ions,} \quad (4.3b)$$

$$\beta_i = 0 \quad \text{for the co-ions;} \quad (4.3c)$$

(ii) at the surface of the spheres

$$\left. \frac{\partial \mu_i}{\partial r} \right|_{r=\lambda} = -\frac{\beta_i^*}{\lambda} \Delta'_s \mu_i \Big|_{r=\lambda}, \quad (4.4a)$$

with Δ'_s the surface Laplacian on the unit sphere and

$$\beta_i^* = \frac{1}{Z^2 \kappa^* \lambda} \left(1 + \frac{3m_i}{Z^2} \right) (\exp(eZ|\zeta_p|/2kT) - 1) \quad \text{for the counter-ions,} \quad (4.4b)$$

$$\beta_i^* = 0 \quad \text{for the co-ions.} \quad (4.4c)$$

The $\mu_{i,0}$ represents the electrostatical potential Ψ of the undisturbed external electrical field E_0 pointing in the positive z -direction with $E = -\nabla\Psi$ and is given by

$$\mu_{i,0} = -z_i E_0 z. \quad (4.5)$$

We assume that there are no macroscopic gradients in the electrolyte concentration.

4.2. Solution for the ionic function

Noting that we have to deal with a linear problem we may write the solution as a superposition of three fields:

$$\mu_i = \mu_{i,\text{sph}}^* + \mu_{i,\text{cyl}} + \mu_{i,0}. \quad (4.6)$$

Here $\mu_{i,0}$ is given by (4.5) and $\mu_{i,\text{sph}}^*$ represents the influence of the spheres on the ionic function and may be written in terms of decaying solid spherical harmonics as

$$\mu_{i,\text{sph}}^* = \sum_{n=-\infty}^{\infty} \sum_{l=1}^{\infty} p_l^i \frac{P_l(\mu_n)}{r_n^{l+1}}, \quad (4.7)$$

with $\mu_n = \cos(\theta_n)$, $\mathbf{r}_n = \mathbf{r} - \mathbf{R}_n$ and \mathbf{R}_n pointing to the centre of sphere n , θ_n the angle that \mathbf{r}_n makes with the z -axis and $P_l(\mu_n)$ denoting Legendre polynomials of the l th degree (Hobson 1955). The as yet unknown coefficients p_l^i are spherical multipole coefficients and are independent of n because all spheres are identical to each other. The summation in (4.7) starts at $l = 1$ because the system contains no spheres having a net charge and therefore the $l = 0$ term is not present. Furthermore only terms with l odd will contribute because the external field $\mu_{i,0}$ is a field odd in z . The $\mu_{i,\text{cyl}}$ is the field resulting from the tube and is written as in cylindrical coordinates as

$$\mu_{i,\text{cyl}} = \sum_{m=1}^{\infty} q_m^i I_0(mk\rho) \sin(mkz) \quad \text{with } k = \frac{2\pi}{\beta}. \quad (4.8)$$

This is the solution of the Laplace equation in cylindrical coordinates that is uneven and periodic in z and has a finite value when $\rho = 0$. Here I_0 is a modified Bessel function (Watson 1944) of the first kind and q_m^i are the as yet undetermined coefficients. We will now construct a solution that fulfils the Laplace equation (4.1) and the boundary conditions (4.3) and (4.4). In order to construct this solution we will use a two-step procedure. In the first step we only take into account the dipole moment of (4.7) and the full solution in cylindrical coordinates. At this point we emphasize the fact that all higher-order spherical multipole moments will be included into the calculation in the second step. The multipole coefficients q_m^i are determined in the first step by the boundary condition on the wall of the tube and will be referred to as cylindrical multipole moments. So we have

$$\mu_i = \mu_{i, \text{sph}} + \mu_{i, \text{cyl}} + \mu_{i, 0}, \quad (4.9)$$

$$\mu_{i, \text{sph}} = \sum_{n=-\infty}^{\infty} p_1^i \frac{P_1(\mu_n)}{r_n^2}. \quad (4.10)$$

Transforming the first term on the right-hand side into cylindrical coordinates, we have

$$\mu_i = \sum_{n=-\infty}^{\infty} p_1^i \frac{(z-n\beta)}{((\rho^2 + (z-n\beta)^2)^{3/2})} + \mu_{i, \text{cyl}} + \mu_{i, 0}. \quad (4.11)$$

Applying boundary condition (4.3) we obtain

$$\begin{aligned} & -3 \sum_{n=-\infty}^{\infty} p_1^i \frac{(z-n\beta)}{((1+(z-n\beta)^2)^{5/2})} + \sum_{m=1}^{\infty} q_m^i mk I_1(mk) \sin(mkz) \\ & = -\beta_i \left\{ \sum_{n=-\infty}^{\infty} p_1^i \frac{\partial^2}{\partial z^2} \left(\frac{(z-n\beta)}{((1+(z-n\beta)^2)^{3/2})} \right) - \sum_{m=1}^{\infty} q_m^i (mk)^2 I_0(mk) \sin(mkz) \right\}. \end{aligned} \quad (4.12)$$

Note that $\mu_{i, 0}$ drops out of the equation. To solve for q_m^i from (4.11) we use the orthogonality of the sin-series and multiply (4.12) by $\sin(mkz)$ and integrate over one period to find (Appendix B)

$$q_m^i = \frac{2(mk) K_1(mk) - 2\beta_i (mk)^2 K_0(mk)}{\frac{1}{2}\beta_i \{I_1(mk) + \beta_i (mk) I_0(mk)\}} p_1^i \quad \text{for } m = 1, 2, 3, 4, \dots \quad (4.13)$$

Here K_0 is a modified Bessel function (Watson 1944) of the second kind. Note that not only does $(\mu_{i, \text{sph}} + \mu_{i, \text{cyl}})$ with q_m^i given by (4.13) satisfy the Laplace equation and boundary condition (4.3) at the wall of the tube, but also all derivatives of μ_i of arbitrary order with respect to z will. In order to fulfil boundary condition (4.4) at the spheres we now write as a second step the solution as

$$\mu_i = \sum_{s=1}^{\infty} G_{2s}^i \frac{\partial^{2s-2}}{\partial z^{2s-2}} \{\mu_{i, \text{sph}} + \mu_{i, \text{cyl}}\} + \mu_{i, 0}. \quad (4.14)$$

Because p_1^i is a common factor of $\mu_{i, \text{sph}}$ and $\mu_{i, \text{cyl}}$, we have absorbed this coefficient, without loss of generality, in the as yet undetermined coefficients G_{2s}^i . It is important to realize that all higher-order spherical multipole terms in (4.7) are now generated by the higher-order derivatives with respect to z of dipole term $\mu_{i, \text{sph}}$ in (4.14) (Hobson 1955) and in this way all multipole terms occurring in (4.7) are included in the calculation. To secure that the solution is odd in z , only derivatives of even order in z are taken into account. The spherical multipole moments G_{2s}^i are to be determined from boundary condition (4.4) at the spheres. Because all spheres are identical to each

other, and so the coefficients G_{2s}^i are the same for each sphere, we only have to satisfy (4.4) at an arbitrary chosen reference sphere. We choose our reference sphere (labelled by $n = 0$) the one centred at origin of the coordinate system, so $\mathbf{R}_0 = \mathbf{0}$. Before we can apply boundary condition (4.4), (4.14) must be expressed in spherical coordinates and expanded around the origin. First we will express $\mu_{i, \text{sph}}$ in spherical coordinates by using (4.9) (Hobson 1955):

$$\frac{\partial^{2s-2}}{\partial z^{2s-2}} \{\mu_{i, \text{sph}}\} = (2s-1)! \sum_{n=-\infty}^{\infty} \frac{P_{2s-1}(\mu_n)}{r_n^{2s}}. \quad (4.15)$$

The next term in (4.14) may be expanded in spherical coordinates as

$$\frac{\partial^{2s-2}}{\partial z^{2s-2}} \{\mu_{i, \text{cyl}}\} = \sum_{m=1}^{\infty} q_m^i \sum_{n=0}^{\infty} \frac{(-1)^{n+s-1} (mk)^{2n+2s-1} r^{2n+1}}{(2n+1)!} P_{2n+1}(\mu_0), \quad (4.16)$$

with $\mu_0 = \cos(\theta_0)$, $\mathbf{r}_0 = \mathbf{r} - \mathbf{R}_0$ and θ_0 the angle that \mathbf{r}_0 makes with the z -axis. Result (4.16) may be obtained in two steps. First we use

$$I_0(mk\rho) \sin(mkz) = \sum_{n=0}^{\infty} \frac{(-1)^n (mk)^{2n+1} r^{2n+1}}{(2n+1)!} P_{2n+1}(\mu_0), \quad (4.17)$$

a relation which is derived in Appendix C. After substitution of this expression we take the derivatives with respect to z (Hobson 1955) to find (4.16). The cylindrical part of the solution (4.16) is now expanded around the reference sphere at $\mathbf{R}_0 = \mathbf{0}$. The spherical part (4.15) is, however, not yet expanded around this point. In order to accomplish this we proceed by writing (4.15) as

$$(2s-1)! \sum_{n=-\infty}^{\infty} \frac{P_{2s-1}(\mu_n)}{r_n^{2s}} = (2s-1)! \frac{P_{2s-1}(\mu_0)}{r_0^{2s}} + (2s-1)! \sum'_{n=-\infty} \frac{P_{2s-1}(\mu_n)}{r_n^{2s}}. \quad (4.18)$$

The prime on the summation sign indicates that the term $n = 0$ is excluded in the summation. The last term on the right-hand side is expanded around $\mathbf{R}_0 = \mathbf{0}$, by means of a generalized form of the addition theorem (see Appendix D). The result is

$$(2s-1)! \sum_{n=-\infty}^{\infty} \frac{P_{2s-1}(\mu_n)}{r_n^{2s}} = (2s-1)! \frac{P_{2s-1}(\mu_0)}{r_0^{2s}} + (2s-1)! \sum_{l_1=0}^{\infty} H(2l_1+1 | 2s-1) S_{l_1} r^{2l_1+1} P_{2l_1+1}(\mu_0), \quad (4.19)$$

an expansion valid for $r \leq \beta$, with $l = 2(l_1 + s)$, where matrix element $H(2l_1+2 | 2s-1)$ and the lattice sums S_{l_1} are given by

$$H(2l_1+1 | 2s-1) = -\frac{2(l_1+s)}{(2l_1+1)!(2s-1)!}, \quad S_{l_1} = \sum_{n=1}^{\infty} \frac{2}{(n\beta)^{l_1+1}}. \quad (4.20)$$

Taking all terms together we find the following expression for μ_i in spherical coordinates:

$$\begin{aligned} \mu_i = & \sum_{n=0}^{\infty} \left\{ \sum_{s=1}^{\infty} G_{2s}^i \sum_{m=1}^{\infty} q_m^i \frac{(-1)^{n+s-1} (mk)^{2n+2s-1} r^{2n+1}}{(2n+1)!} - z_i E_0 r \delta_{n,0} \right. \\ & + G_{2n+2}^i (2n+1)! \frac{1}{r^{2n+2}} \\ & \left. + \sum_{s=1}^{\infty} G_{2s}^i (2s-1)! H(2n+1 | 2s-1) S_{2(n+s)} r^{2n+1} \right\} P_{2n+1}(\mu_0). \end{aligned} \quad (4.21)$$

Substituting this expression for μ_i in (4.4), making use of the relation $\Delta'_s P_l = -l(l+1)P_l$ and of the orthogonality of the Legendre polynomials P_l we find the following infinite set of equations for the spherical multipole moments G_{2s}^i :

$$\begin{aligned} & \sum_{s=1}^{\infty} G_{2s}^i \delta_1^i \lambda^{4n+3} - z_i E_0 \lambda^3 \delta_{n,0} - G_{2n+2}^i (2n+2)! + \sum_{s=1}^{\infty} G_{2s}^i \omega_1 \lambda^{4n+3} \\ & = \beta_i^* \left\{ \sum_{s=1}^{\infty} G_{2s}^i \delta_2^i \lambda^{4n+3} - 2z_i E_0 \lambda^3 \delta_{n,0} + G_{2n+2}^i (2n+2)! (2n+1) + \sum_{s=1}^{\infty} G_{2s}^i \omega_2 \lambda^{4n+3} \right\}, \end{aligned} \quad (4.22)$$

with the following definitions:

$$\delta_1^i = \sum_{m=1}^{\infty} q_m^i \frac{(-1)^{n+s-1} (mk)^{2n+2s-1}}{(2n)!}, \quad (4.23 a)$$

$$\delta_2^i = \sum_{m=1}^{\infty} q_m^i \frac{(2n+2)(-1)^{n+s-1} (mk)^{2n+2s-1}}{(2n)!}, \quad (4.23 b)$$

$$\omega_1 = (2s-1)! (2n+1) H(2n+1 | 2s-1) S_{2(n+s)}, \quad (4.23 c)$$

$$\omega_2 = (2s-1)! (2n+1)(2n+2) H(2n+1 | 2s-1) S_{2(n+s)}. \quad (4.23 d)$$

We can find solutions for the spherical multipoles moments G_{2s}^i by truncating this set of linear equations by taking into account only a finite number of spherical multipole moments and a finite number of cylindrical multipole moments q_m^i . By increasing the number of multipole moments the precision of the solution is increased until the required accuracy in the result is obtained. To obtain a certain accuracy the number of cylindrical multipole moments has to be increased, when β increases, and the number of spherical multipole moments has to be increased when λ increases.

5. Governing equations, boundary conditions and solution for the velocity field

5.1. Governing equations for the velocity field

The solution for the ionic function μ_i as found in the previous section enables us to construct the solution for the velocity field. Outside the double layer the velocity field has to satisfy the Stokes equations. The problem without surface charges, to be referred to as the uncharged case, has already been studied by Wang & Skalak (1969, referred to hereafter as W & S). We will present a modified version of their calculation to include the charge effects. In order to illustrate the solution method we will use we will sketch the way the problem is solved for the uncharged case (W & S) and how this treatment is modified by the presence of the double layers, a situation we will refer to as the charged case. Following W & S we define, in addition to (4.2), the following non-dimensionalized variables (unprimed) which are defined in terms of the dimensional variables (primed) as

$$V = \frac{RV'}{\nu}, \quad p = \frac{p'R}{\rho\nu^2}, \quad \tau_{ij} = \frac{\tau'_{ij}R^2}{\rho\nu^2}, \quad D = \frac{D'}{\rho\nu^2}, \quad \psi = \frac{\psi'}{a\nu}, \quad Q = \frac{Q'}{R\nu}. \quad (5.1)$$

Here V is the velocity, p the pressure, τ_{ij} the stress tensor, ψ the stream function, D the drag, ρ the fluid density, ν the kinematic viscosity and R the radius of the tube. Owing to the symmetry of our system we are dealing with an axisymmetric flow and we can

define a Stokes stream function ψ (not to be confused with the electrostatical potential Ψ), which fulfils the following fourth-order differential equation (Happel & Brenner 1965):

$$\mathbf{E}^2(\mathbf{E}^2\psi(\mathbf{r})) = 0, \quad (5.2)$$

with the following form for \mathbf{E}^2 :

$$\mathbf{E}^2 = \left[\frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial \rho^2} - \frac{1}{\rho} \frac{\partial}{\partial \rho} \right] \quad \text{in cylindrical coordinates,} \quad (5.3)$$

$$\mathbf{E}^2 = \left[\frac{\partial^2}{\partial r^2} + \frac{(1 - \cos^2(\theta))}{r^2} \frac{\partial^2}{\partial \cos^2(\theta)} \right] \quad \text{in spherical coordinates.} \quad (5.4)$$

The fluid velocity is related to the stream function ψ by the following expressions:

$$v_z(\rho, z) = -\frac{1}{\rho} \frac{\partial \psi}{\partial \rho}; \quad v_\rho(\rho, z) = \frac{1}{\rho} \frac{\partial \psi}{\partial z} \quad \text{in cylindrical coordinates,} \quad (5.5)$$

$$v_r(r, \theta) = -\frac{1}{r^2 \sin(\theta)} \frac{\partial \psi}{\partial \theta}; \quad v_\theta(r, \theta) = \frac{1}{r \sin(\theta)} \frac{\partial \psi}{\partial r} \quad \text{in spherical coordinates.} \quad (5.6)$$

The total discharge Q of the fluid and the spheres is given by

$$Q = 2\pi \int_0^1 v_z(\rho, z) \rho \, d\rho = -2\pi \int_0^1 \frac{\partial \psi}{\partial \rho} \, d\rho = -2\pi [\psi(\rho, z)]_0^1. \quad (5.7)$$

We now choose the value of stream function at the axis of the cylinder equal to zero. Using this (5.7) becomes

$$Q = -2\pi\psi(1). \quad (5.8)$$

5.2. Boundary conditions for the stream function ψ

Because we have to solve a fourth-order differential equation we must have also four boundary conditions. At the wall of the cylinder we have the following two conditions for the ψ and the derivative of ψ . First we demand that the total discharge equals Q , so it follows from (5.8) that

$$\psi(\rho, z) \Big|_{\rho=1} = -\frac{Q}{2\pi} \Big|_{\rho=1}. \quad (5.9)$$

This expression is independent of the z -coordinate, which means that the stream function ψ is constant along the wall of the cylinder. As a result the wall of the tube is followed by a streamline of the fluid flow. We now have to set the value for this velocity. In case of hard uncharged spheres, where no-slip boundary conditions apply, we have in a reference system fixed to the spheres

$$v_z \Big|_{\rho=1} = -\frac{1}{\rho} \frac{\partial \psi}{\partial \rho} \Big|_{\rho=1} = 0. \quad (5.10)$$

Boundary condition (5.10) for the uncharged case will change when we consider the influence of the thin double layer of the wall of the tube. From (2.15) we know that for the charged case the velocity at and relative to the cylinder wall in cylindrical coordinates is given by

$$v_z = -\frac{kT}{\nu\eta} \sum_{i=1}^2 \nabla_z \mu_i \left[\int_0^\infty y' (n_i^0 - n_i^\infty) \, dy' \right]_{\xi=\xi_w}. \quad (5.11)$$

When the flow in the tube is undisturbed by the spheres or charge effects a pure Poiseuille flow develops. It is convenient to use a reference system fixed to the centre of a reference sphere. The spheres are supposed to be moving relative to the tube with a velocity U in the positive z -direction. Relative to the spheres the Poiseuille flow has the following stream function:

$$\psi_{\text{pois}} = \left(\frac{1}{2}U - \frac{1}{2}V\right)\rho^2 + \frac{1}{4}V\rho^4. \quad (5.12)$$

From (5.5) it follows that the velocity field of the Poiseuille flow is given by

$$v_z = -\frac{1}{\rho} \frac{\partial \psi}{\partial \rho} = -U + (1 - \rho^2)V. \quad (5.13)$$

The total discharge Q , as measured relative to the cylinder wall, cf. (5.8), is given by

$$Q = -2\pi\psi(\rho = 1) = \frac{1}{2}\pi V. \quad (5.14)$$

In a reference system fixed to the spheres, the total discharge Q^* is given by

$$Q^* = Q - \pi U, \quad (5.15)$$

with Q and U still measured relative to the cylinder wall. The boundary conditions (5.9) and (5.10) at the wall of the tube become, for the uncharged case,

$$\psi(\rho, z)|_{\rho=1} = -\frac{Q}{2\pi} + \frac{1}{2}U, \quad (5.16)$$

$$v_z(\rho, z)|_{\rho=1} = -\frac{1}{\rho} \frac{\partial \psi}{\partial \rho} \Big|_{\rho=1} = -U. \quad (5.17)$$

According to (5.11) these boundary conditions become, for the charged case,

$$\psi(\rho, z)|_{\rho=1} = -\frac{Q}{2\pi} + \frac{1}{2}U, \quad (5.18)$$

$$v_z(\rho, z)|_{\rho=1} = -\frac{1}{\rho} \frac{\partial \psi}{\partial \rho} \Big|_{\rho=1} = -U - \frac{kT}{v\eta} \sum_{i=1}^2 \nabla_z \mu_i \left[\int_0^\infty y'(n_i^0 - n_i^\infty) dy' \right]_{\zeta=\zeta_w}. \quad (5.19)$$

Note that (5.16)–(5.19) apply for a reference system fixed to one of the spheres. We now have formulated the problem in such a way that the total discharge Q , as measured relative to the wall of the tube, is completely determined by V . To derive the remaining two boundary conditions for the stream function ψ at the surfaces of the spheres, we first must realize that there must be a streamline that has to follow the surfaces of the spheres so the stream function must be a constant along these surfaces. We have already set the value of ψ equal to zero on the centreline of the cylinder, and because the poles of the sphere are on this line ψ has to be zero on the surfaces of spheres. For the uncharged case no-slip boundary conditions on the spheres would apply and in a reference system fixed one of the spheres we have

$$v_\theta = \frac{\partial \psi}{\partial r} = 0, \quad (5.20)$$

$$\psi = 0. \quad (5.21)$$

Again, these boundary conditions will change when we consider the charged case,

where the influence of the thin double layers of the spheres is taken into account, to become

$$v_\theta = -\frac{kT}{\nu\eta} \sum_{i=1}^M \left(\frac{\partial \mu_i}{r \partial \theta} \right) \left[\int_0^\infty y' (n_i^0 - n_i^\infty) dy' \right]_{\xi=\xi_p}, \quad (5.22)$$

$$\psi = 0. \quad (5.23)$$

5.3. The solution of the stream function

We will construct a solution of (5.1) that fulfils the boundary conditions (5.18) and (5.19) at the wall of the tube and (5.22) and (5.23) at the surface of the spheres. The solution is obtained using a modification of a method applied to the uncharged case, described by (5.1) with boundary conditions (5.16), (5.17), (5.20) and (5.21) that has already been studied by W & S. In this work a solution is constructed by writing the total solution for the stream function as

$$\psi_{\text{tot, unch}} = \psi_1 + \psi_{\text{pois}}, \quad (5.24)$$

with

$$\psi_1 = \psi_{\text{sph}} + \psi_{\text{cyl}}. \quad (5.25)$$

Here $\psi_{\text{tot, unch}}$ is the total solution for the uncharged case, ψ_{sph} represents the influence of the spheres and ψ_{cyl} represents the influence of the wall of the cylinder on the flow field. Substituting (5.24) into boundary conditions (5.16) and (5.17), we find that ψ_1 has to fulfil the following boundary conditions at the wall of the tube:

$$v_z = -\frac{1}{\rho} \frac{\partial \psi_1}{\partial \rho} = 0, \quad (5.26)$$

$$\psi_1 = 0. \quad (5.27)$$

The essential step in the analysis of W & S is to construct two fundamental solutions, ψ_1^1 and ψ_1^2 , given by

$$\psi_1^1 = \psi_{\text{sph}}^1 + \psi_{\text{cyl}}^1 \quad (5.28)$$

and

$$\psi_1^2 = \psi_{\text{sph}}^2 + \psi_{\text{cyl}}^2, \quad (5.29)$$

with ψ_{cyl}^1 and ψ_{cyl}^2 the full solution of (5.1) in cylindrical coordinates which remains finite at $\rho = 0$ and containing unknown cylindrical multipole moments A_0, B_0, A_m, B_m , and C_0, D_0, C_m, D_m . The stream function ψ_{sph}^2 belongs to a Stokeslet and ψ_{sph}^1 belongs to a potential doublet, the two basic solutions necessary for constructing the stream function of a sphere moving in an unbounded fluid. By writing ψ_{sph}^1 and ψ_{sph}^2 in cylindrical coordinates one obtains (W & S)

$$\psi_1^1 = \sum_{n=-\infty}^{\infty} \frac{\rho^2}{2(\rho^2 + (z - nd)^2)^{3/2}} + A_0 \rho^4 + B_0 \rho^2 + \sum_{m=1}^{\infty} \{A_m \rho I_1(mk\rho) + B_m \rho^2 I_0(mk\rho)\} \cos(mkz), \quad (5.30)$$

$$\psi_1^2 = \sum_{n=-\infty}^{\infty} \left\{ \frac{\rho^2}{2(\rho^2 + (z - nd)^2)^{1/2}} - \frac{\rho^2}{nd} \right\} + C_0 \rho^4 + D_0 \rho^2 + \sum_{m=1}^{\infty} \{C_m \rho I_1(mk\rho) + D_m \rho^2 I_0(mk\rho)\} \cos(mkz). \quad (5.31)$$

The term $-\rho^2/nd$ is added in (5.31) to remove the singularity that arises due to the summation over all the Stokeslets. The I_1 and I_2 denote modified Bessel functions of

the first kind. The boundary conditions (5.26) and (5.27) at the wall of the tube are used to determine the cylindrical multipole moments $A_0, A_m, B_0, B_m, C_0, C_m, D_0, D_m$. At this point ψ_1^1 and ψ_1^2 are completely determined and satisfy (5.1), (5.26) and (5.27). Further progress is made by the observation all derivatives of higher order with respect to z of ψ_1^1 and ψ_1^2 also fulfil (5.1), (5.25) and (5.26). All linear combinations of these terms with derivatives of even order, to keep the solution even in z , and unknown spherical multipole coefficients E_{2s} and F_{2s} also satisfy these equations and we may write the total solution $\psi_{\text{tot, unch}}$ of the (5.1) satisfying (5.26) and (5.27) as

$$\psi_{\text{tot, unch}} = \sum_{s=1}^{\infty} \frac{1}{(2s-2)!} \frac{\partial^{2s-2}}{\partial z^{2s-2}} \{E_{2s} \psi_1^1 + F_{2s} \psi_1^2\} + \psi_{\text{pois}}. \quad (5.32)$$

After transforming (5.32) into spherical coordinates the boundary conditions (5.20) and (5.21) at the surface of the spheres will be used to solve the spherical multipole moments E_{2s} and F_{2s} (see W & S for details). This solution method may be compared to the construction of the solution for the ionic function μ_i in §4.2, where at first only the dipole term was taken into account, and then arising from the presence of the spheres higher-order terms were taken into account following similar lines as the analysis of W & S. The central point in the analysis of W & S is that (5.1) and the boundary conditions at the wall of the cylinder (5.26) and (5.27) are homogeneous. In the charged case this property is lost as a result of (5.19) where a surface velocity enters the problem. Fortunately, we may take care of this problem by introducing the stream function ψ_{cyl}^* fulfilling (5.1), (5.18) and (5.19). The total stream function for the charged case is

$$\psi_{\text{tot, ch}} = \psi_{\text{tot, unch}} + \psi_{\text{cyl}}^*, \quad (5.33)$$

with $\psi_{\text{tot, unch}}$ as defined in (5.32) with unknown spherical multipole moments E_{2s} and F_{2s} , but the functions ψ_1^1 and ψ_1^2 in (5.32) are still given by the solution for the uncharged case and are given by W & S. The spherical multipole moments E_{2s} and F_{2s} are to be determined from boundary conditions (5.22) and (5.23) at the spheres:

$$\psi_{\text{tot, ch}} = 0 \quad (5.34)$$

and

$$\frac{1}{r \sin \theta} \left(\frac{\partial \psi_{\text{tot, ch}}}{\partial r} \right) = v_\theta, \quad (5.35)$$

with v_θ given by (5.22). In order to generate a solution we first have to construct ψ_{cyl}^* , which has to satisfy the equation

$$\mathbf{E}^2(\mathbf{E}^2 \psi_{\text{cyl}}^*) = 0, \quad (5.36)$$

with the following boundary conditions at the wall of the cylinder:

$$\psi_{\text{cyl}}^* = 0, \quad (5.37)$$

$$\frac{1}{\rho} \frac{\partial \psi_{\text{cyl}}^*}{\partial \rho} = \frac{kT}{\nu \eta} \sum_{i=1}^M \nabla_z \mu_i \left[\int_0^\infty y' (n_i^0 - n_i^\infty) dy' \right]_{\zeta=\zeta_w}. \quad (5.38)$$

The ionic function μ_i enters the Stokes stream function through boundary condition (5.28). The general solution of (5.36) that is periodic and even in z and stays finite when $\rho = 0$, is given by

$$\psi_{\text{cyl}}^*(\rho, z) = A_0^* \rho^4 + B_0^* \rho^2 + \sum_{m=1}^{\infty} \{A_m^* \rho I_1(mk\rho) + B_m^* \rho^2 I_0(mk\rho)\} \cos(mkz). \quad (5.39)$$

The unknown cylindrical multipole moments A_0^* , B_0^* , A_m^* and B_m^* have to be determined in such a way that the boundary conditions (5.37) and (5.38) are satisfied. Boundary condition (5.37) simply gives

$$A_0^* + B_0^* + \sum_{m=1}^{\infty} \{A_m^* I_1(mk) + B_m^* I_0(mk)\} \cos(mkz) = 0. \quad (5.40)$$

Boundary condition (5.38) is more involved because it contains the term $\nabla_z \mu_i$. We use (4.20) where μ_i is given in spherical coordinates to derive an expression for $\nabla_z \mu_i$ in cylindrical coordinates (Appendix E) with the result

$$\begin{aligned} & \nabla_z \mu_i \\ &= \sum_{s=1}^{\infty} G_{2s}^i (-1)^{s+1} \sum_{m=1}^{\infty} \left\{ \frac{4}{\beta} (mk)^{2s} K_0(mk) + q_m^i (mk)^{2s-1} I_0(mk) \right\} \cos(mkz) - z_i E_0. \end{aligned} \quad (5.41)$$

After substituting (5.39) and (5.41) into (5.38), we find

$$\begin{aligned} & 4A_0^* + 2B_0^* + \sum_{m=1}^{\infty} \{mkA_m^* I_0(mk) + B_m^* (2I_0(mk) + mkI_1(mk))\} \cos(mkz) \\ &= \left\{ \sum_{i=1}^2 \sum_{s=1}^{\infty} G_{2s}^i (-1)^{s+1} \sum_{m=1}^{\infty} \left[\frac{4}{\beta} (mk)^{2s} K_0(mk) + q_m^i (mk)^{2s-1} I_0(mk) \right] \cos(mkz) - z_i E_0 \right\} \\ & \quad \times \frac{kT}{v\eta} \left[\int_0^{\infty} y' (n_i^0 - n_i^{\infty}) dy' \right]_{\xi=\xi_w}, \end{aligned} \quad (5.42)$$

where we have made use of the recurrence relations between modified Bessel functions. The spherical multipole moments G_{2s}^i of the ionic function μ_i are to be found from solution of (4.23). From (5.40) and (5.42) we are able to find the coefficients A_0^* , B_0^* , A_m^* and B_m^* as

$$A_0^* = -\frac{kT}{2\eta v} \sum_{i=1}^2 z_i E_0 \left[\int_{\xi=\xi_w}^{\infty} y' (n_i^0 - n_i^{\infty}) dy' \right], \quad (5.43)$$

$$B_0^* = \frac{kT}{2\eta v} \sum_{i=1}^2 z_i E_0 \left[\int_{\xi=\xi_w}^{\infty} y' (n_i^0 - n_i^{\infty}) dy' \right], \quad (5.44)$$

$$A_m^* = -\frac{I_0}{I_1} B_m^*, \quad (5.45)$$

with

$$\begin{aligned} B_m^* &= \frac{\sum_{i=1}^2 \sum_{s=1}^{\infty} G_{2s}^i (-1)^{s+1} \left\{ \frac{4}{\beta} (mk)^{2s} I_1 K_0 + q_m^i (mk)^{2s-1} I_1 I_0 \right\}}{2I_0 I_1 + mk(I_1^2 - I_0^2)} \\ & \quad \times \frac{kT}{\eta v} \left[\int_{\xi=\xi_w}^{\infty} y' (n_i^0 - n_i^{\infty}) dy' \right]. \end{aligned} \quad (5.46)$$

At this point ψ_{cyl}^* is completely determined and we may use boundary conditions (5.34) and (5.35) to determine the spherical multipole moments E_{2s} and F_{2s} . For this purpose (5.33) has to be written in terms of spherical coordinates. From W & S we know the

expression $\psi_{\text{tot,unch}} + \psi_{\text{pois}}$ in spherical coordinates. We rewrite ψ_{cvl}^* in spherical coordinates as (Appendix C)

$$\begin{aligned} \psi_{\text{cvl}}^*(\rho, z) = & \rho \left\{ -B_0^* r P_1^1(\mu_0) + A_0^* r^3 \left(-\frac{4}{5} P_1^1(\mu_0) + \frac{2}{15} P_3^1(\mu_0) \right) \right\} \\ & + \rho \sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \left\{ A_m^* \frac{(-1)^{n+1} (mk)^{2n+1} r^{2n+1}}{(2n+2)!} \right. \\ & \left. + B_m^* \frac{(-1)^{n+1} (mk)^{2n} r^{2n+1}}{(2n+2)!} \left[\frac{(2n+2)(2n+1)}{(4n+1)} + \frac{(mkr)^2}{(4n+5)} \right] \right\} P_{2n+1}^1(\mu_0). \end{aligned} \quad (5.47)$$

Here P_l^m are the associated Legendre polynomials of the m th order and l th degree, given by (Hobson 1955)

$$P_l^m(\mu) = (-1)^m (1 - \mu^2)^{m/2} \frac{d^m P_l(\mu)}{d\mu^m}. \quad (5.48)$$

The total stream function $\psi_{\text{tot,ch}}$ expanded around R_λ may now be written in spherical coordinates as

$$\begin{aligned} \psi_{\text{tot,ch}} = & \sin(\theta) \sum_l \left\{ F_{2l+4} \left[\frac{1}{2(4l+5)r^{2l+1}} \right] - F_{2l+2} \left[\frac{1}{2(4l+1)r^{2l-1}} \right] \right. \\ & + F_2 \left[-\frac{r^2}{2\beta} (-2 \ln(2\beta) + 2E - 1) - \frac{4r^2}{10\beta} \right] \delta_{l,0} + F_2 \left[\frac{4r^4}{60\beta} \right] \delta_{l,1} \\ & + \sum_{s=1} F_{2s} \{ r^{2l+2} (-\tau + \beta_2 + \gamma_2) + r^{2l+4} (\xi + \sigma_2) \} + E_{2l+2} \left\{ \frac{-1}{2r^{2l+1}} \right\} \\ & + E_2 \left\{ \left(\frac{2}{\beta} r^2 - \frac{4}{5\beta} r^4 \right) \delta_{l,0} + \frac{4}{30\beta} r^4 \delta_{l,1} \right\} + \sum_{s=1} E_{2s} \left\{ r^{2l+2} (-\alpha + \beta_1 + \gamma_1) + r^{2l+4} \sigma_1 \right. \\ & \times \left[\left(\frac{V}{2} - \frac{U}{2} \right) r^2 - \frac{V}{5} r^4 \right] \delta_{l,0} + \frac{V}{30} r^4 \delta_{l,1} + (-B_0^* r^2 - \frac{4}{5} A_0^* r^4) \delta_{l,0} \\ & \left. + \frac{2}{15} r^4 A_0^* \delta_{l,1} + A_l r^{2l+2} + \Pi_l^1 r^{2l+2} + \Pi_l^2 r^{2l+4} \right\} P_{2l+1}^1(\mu_0), \end{aligned} \quad (5.49)$$

where equations for τ , ξ , β_1 , γ_1 , σ_1 , β_2 , γ_2 , σ_2 , α , A_m , B_m , C_m , D_m may be found in W & S. A_l , Π_l^1 , Π_l^2 represent the influence of the double layers:

$$A_l = \sum_{m=1}^{\infty} \frac{B_m^* (-1)^l (mk)^{2l+1} I_0}{(2l+2)! I_1}, \quad (5.50 a)$$

$$\Pi_l^1 = \sum_{m=1}^{\infty} \frac{B_m^* (-1)^{l+1} (mk)^{2l}}{(2l)! (4l+1)}, \quad (5.50 b)$$

$$\Pi_l^2 = \sum_{m=1}^{\infty} \frac{B_m^* (-1)^{l+1} (mk)^{2l+2}}{(2l+2)! (4l+5)}. \quad (5.50 c)$$

Substituting (5.49) in boundary conditions in (5.34) and (5.35) together with

$$\mu_i = \sum_{l=0}^{\infty} a_l^i(r) P_{2l+1}(\mu_0), \quad (5.51)$$

where the definition of $a_l^i(r)$ is clear from (4.19), using the orthogonality of the

associated Legendre polynomials $P_{2l+1}^1(\mu_0)$ leads to two linear sets of equations for the spherical multipole coefficients E_{2s} and F_{2s} which may be combined to give

$$\begin{aligned}
& -F_{2l+2} \frac{1}{4l+1} + F_2 \left[-\frac{3\lambda}{2\beta} (-2 \ln(2\beta) + 2E - 1) - \frac{2\lambda^3}{\beta} \right] \delta_{l,0} + F_2 \left[\frac{16\lambda^5}{60\beta} \right] \delta_{l,1} \\
& + \sum_{s=1} F_{2s} \{ (4l+3) \lambda^{4l+1} (-\tau + \beta_2 + \gamma_2) + (4l+5) \lambda^{4l+3} (\xi + \sigma_2) \} \\
& + E_2 \left\{ \left(\frac{6}{\beta} \lambda - \frac{4}{\beta} \lambda^3 \right) \delta_{l,0} + \frac{28}{30\beta} \lambda^5 \delta_{l,1} \right\} + \sum_{s=1} E_{2s} \{ (4l+3) \lambda^{4l+1} (-\alpha + \beta_1 + \gamma_1) \\
& + (4l+5) \lambda^{4l+3} \sigma_1 \} + \left\{ 3 \left(\frac{V}{2} - \frac{U}{2} \right) \lambda - V \lambda^3 \right\} \delta_{l,0} + \frac{7V}{30} \lambda^5 \delta_{l,1} \\
& + (-3B_0^* \lambda - 4A_0^* \lambda^3) \delta_{l,0} + \frac{14}{15} \lambda^5 A_0^* \delta_{l,1} + (4l+3) A_l \lambda^{4l+1} + (4l+3) \Pi_l^1 \lambda^{4l+1} \\
& + (4l+5) \Pi_l^2 \lambda^{4l+3} = -\lambda^{2l} \sum_{i=1}^2 a_i^l(\lambda) \frac{kT}{\eta\nu} \left[\int_{\xi=\xi_p} y'(n_i^0 - n_i^\infty) dy' \right], \quad (5.52)
\end{aligned}$$

and

$$\begin{aligned}
& -F_{2l+4} \frac{1}{4l+5} + E_{2l+2} + F_2 \left[-\frac{\lambda^3}{2\beta} (-2 \ln(2\beta) + 2E - 1) - \frac{12\lambda^5}{10\beta} \right] \delta_{l,0} + F_2 \left[\frac{\lambda^7}{3\beta} \right] \delta_{l,1} \\
& + \sum_{s=1} F_{2s} \{ (4l+1) \lambda^{4l+2} (-\tau + \beta_2 + \gamma_2) + (4l+3) \lambda^{4l+5} (\xi + \sigma_2) \} \\
& + E_2 \left\{ \left(\frac{2}{\beta} \lambda^3 - \frac{12}{5\beta} \lambda^5 \right) \delta_{l,0} + \frac{2}{3\beta} \lambda^7 \delta_{l,1} \right\} + \sum_{s=1} E_{2s} \{ (4l+1) \lambda^{4l+3} (-\alpha + \beta_1 + \gamma_1) \\
& + (4l+3) \lambda^{4l+5} \sigma_1 \} + \left\{ \left(\frac{V}{2} - \frac{U}{2} \right) \lambda^3 - \frac{3}{5} V \lambda^5 \right\} \delta_{l,0} + \frac{5V}{30} \lambda^7 \delta_{l,1} \\
& + (-B_0^* \lambda^3 - \frac{12}{5} A_0^* \lambda^5) \delta_{l,0} + \frac{10}{15} \lambda^7 A_0^* \delta_{l,1} + (4l+1) A_l \lambda^{4l+3} + (4l+1) \Pi_l^1 \lambda^{4l+3} \\
& + (4l+3) \Pi_l^2 \lambda^{4l+5} = -\lambda^{2l+2} \sum_{i=1}^2 a_i^l(\lambda) \frac{kT}{\eta\nu} \left[\int_{\xi=\xi_p} y'(n_i^0 - n_i^\infty) dy' \right]. \quad (5.53)
\end{aligned}$$

Ignoring the electro-kinetic effects by setting $E_0 = 0$, (5.52) and (5.53) reduce to equations given by W & S. Because we restrict ourselves to a symmetrical electrolyte, with an absolute valence Z , the integrals occurring in (5.52) and (5.53) simplify (Chen & Keh 1992) to give

$$\int_0^\infty y'(n_i^0 - n_i^\infty) dy' = \frac{\epsilon_0 \epsilon_r kT}{2e^2 Z^2} [4T_i \bar{\xi} + 4 \ln \cosh(\bar{\xi})], \quad (5.54)$$

with

$$\bar{\xi} = Ze\xi/4kT, \quad (5.55)$$

and $T_i = -1$ when we are dealing with co-ions, and $T_i = 1$ when we are dealing with counter-ions. After introducing the values for the system parameters we can solve (5.52) and (5.53) for F_{2s} and E_{2s} . Similarly as in the case of the ionic function (cf. §4.2) we solve these infinite sets of linear equations numerically by taking into account a finite number of spherical multipole moments and cylindrical multipole moments. By increasing these numbers of multipole moments the precision of the solution is increased until the required accuracy in the result is obtained. To obtain a certain accuracy the number of cylindrical multipole moments has to be increased when β increases, and the number of spherical multipole moments has to be increased when λ increases.

6. Transport properties

After solving for the ionic function μ_i using (4.23), one may solve for the coefficients E_{2s} and F_{2s} from (5.52) and (5.53) and the total solution for the flow problem is obtained. From this the transport properties of the system may be determined. For this we find the viscous drag on the spheres and the mean pressure drop in terms of the multipole moments. The viscous drag D on the spheres and the mean pressure gradient is obtained in a similar way as W & S, using (5.49) for the total stream function. By integrating the expression for the stress tensor over the surface of the sphere this gives for the viscous drag (W & S)

$$D = 4\pi F_2. \quad (6.1)$$

The mean pressure gradient $\Delta p/\beta$ per sphere is evaluated as (W & S)

$$\frac{\Delta p}{\beta} = -\frac{8}{\beta}(F_2 + 2E_2) - 4(V + 4A_0^*). \quad (6.2)$$

The electrical force F_e on the sphere is given by

$$F_e = \int \rho \nabla \Psi \, dr, \quad (6.3)$$

with ρ the charge density of the double layer. Because with the thin double layer theory we choose the surface of the particle just outside the double layer, the net charge is zero. However, the charge density will have a dipole moment due to the polarization of the double layer induced by the external electrical field E_0 . This dipole moment is proportional to E_0 which will lead to an electrical (Maxwellian) force on the particle of $O(|E_0|^2)$. Since we are only considering disturbance linear in E_0 we may neglect this force (O'Brien & White 1978). Because we are dealing with a linear problem the general form for the coefficients F_{2s} and E_{2s} may be written as

$$F_{2s} = F_{2u} U + F_{2v} V + F_{2e} \left(\frac{\epsilon_0 \epsilon_r (kT)^2}{e^2 \nu \eta} \right) E_0, \quad (6.4)$$

$$E_{2s} = E_{2u} U + E_{2v} V + E_{2e} \left(\frac{\epsilon_0 \epsilon_r (kT)^2}{e^2 \nu \eta} \right) E_0. \quad (6.5)$$

Note that we have related the coefficients to the applied undisturbed electrical field E_0 . In general this field is not equal to the electrical field one measures in the system, which is the volume average of $\nabla \Psi$ given by

$$\langle \nabla \Psi \rangle = \frac{1}{V} \int_V \nabla \Psi \, dr, \quad (6.6)$$

with V denoting a volume large compared to the characteristic dimensions of the inhomogeneities of the system. Since we are dealing with a periodic system, i.e. the system might be thought of as being built up from replicas of just one (Wigner–Seitz) cell containing one particle, we may restrict the averaging to the volume of just one cell denoted by Ω . However because $\nabla \Psi$ is a period function with the periodicity of the system, after averaging only the non-periodic part of the function survives, which gives

$$\langle \nabla \Psi \rangle = \frac{1}{\Omega} \int_{\Omega} \nabla \Psi \, dr = E_0. \quad (6.7)$$

From this it follows that we may simply replace E_0 by $\langle \nabla \Psi \rangle$ when we want to relate the results to the volume-averaged electrical field instead of the external undisturbed field. In dimensional form that the viscous drag D' and the total pressure drop per sphere $\Delta p'$ may be written as

$$D' = 6\pi\eta\lambda R \left(-K_u U' + K_v V' + K_e \left(\frac{\epsilon_0 \epsilon_r \zeta_p}{\eta} \right) E_0' \right), \quad (6.8)$$

$$\Delta p' = \frac{\eta}{R} \left\{ P_u U' - (P_v + 4\beta) V' + \left[P_e - 16 \left(\frac{\zeta_w}{\zeta_p} \right) \beta W \right] \left(\frac{\epsilon_0 \epsilon_r \zeta_p}{\eta} \right) E_0' \right\}. \quad (6.9)$$

Here W is given by

$$W = \sum_{i=1}^2 \left\{ \frac{T_i \bar{\zeta}_w + \ln(\cosh(\bar{\zeta}_w))}{2\bar{\zeta}_w} \right\}, \quad (6.10)$$

with T_i and $\bar{\zeta}_w$ as defined in (5.55). The dimensionless coefficients $K_u, K_v, K_e, P_u, P_v, P_e$ have to be determined now as a function of system parameters like $\lambda, \beta, \zeta_p, \zeta_w$ and κa . These coefficients are given in terms of $F_{2v}, F_{2u}, F_{e2}, E_{2v}, E_{2u}$ and E_{2e} as

$$K_u = -\frac{2}{3\lambda} F_{2u}; \quad K_v = \frac{2}{3\lambda} F_{2v}; \quad K_e = \frac{2}{3\lambda} \left(\frac{e\zeta_p}{kT} \right)^{-1} F_{e2}; \quad (6.11)$$

$$P_u = -8F_{2u} - 16E_{2u}; \quad P_v = -8F_{2v} - 16E_{2v}; \quad P_e = \left(\frac{e\zeta_p}{kT} \right)^{-1} (-8F_{e2} - 16E_{2e}). \quad (6.12)$$

The coefficients K_u, K_v, P_u, P_v only depend on the parameters β and λ and were calculated by W & S. The results of the computer program for numerically solving the coefficients were tested against the results of W & S and good agreement was found (relative error $< 1\%$). The values for K_u, K_v, P_u, P_v are tabulated in W & S. In order to make comparison with the work of W & S feasible the tables presented here have the same range of β and λ as in their work. The coefficients K_e and P_e which also have to be determined do not only depend on β and λ , but also on the parameters describing the electrical state of the system, like $\kappa a, \zeta_p, \zeta_w, m_i$ and Z . The results for these coefficients K_e and P_e were tested in two ways. First, we have calculated the electrophoretic mobility of an array of small spheres moving in the tube, for different values for $\kappa a, \zeta_p$ and Z , by setting $\zeta_w = 0, \lambda = 0.01, \beta = 40, V' = 0$. Because the spheres are very small relative to the radius of the tube and the spheres are separated by 2000 diameters from each other we may compare this situation to one isolated sphere in an infinite medium. The behaviour of the electrophoretic mobility including the polarization effect has been well studied for several values of $\kappa a, \zeta_p$ and Z . We have checked our results with those of Chen & Keh (1992, table 1) and their results were almost exactly recovered. Secondly, by using the above mentioned values for the parameters ζ_w, β and V' , but by increasing λ , we could study the influence of the uncharged wall on the electrophoretic mobility of a single sphere. This situation has been studied by Keh & Anderson (1985) who neglected the polarization effects of the double layer and obtained an expression for the electrophoretic mobility valid up to $O(\lambda^6)$. This limit is reached in our model by choosing a sufficiently large value for κa , so that condition (1.2) is fulfilled and polarization effects can be ignored, and comparison with their results is allowed. Again almost identical results for the electrophoretic mobility were found. In principle it is possible to determine the coefficients $K_u, K_v, K_e, P_u, P_v, P_e$ for arbitrary values of the system parameters, provided a sufficient number of multipoles are taken into account. Some examples of the results

	λ	$\beta = 2\lambda$	$\beta = 1.0$	$\beta = 1.4$	$\beta = 2.0$	$\beta = 4.0$	$\beta = 40.0$
(a)	0.1	0.460	1.200	1.234	1.240	1.241	1.241
	0.2	0.810	1.488	1.597	1.623	1.630	1.635
	0.3	1.316	1.871	2.116	2.196	2.228	2.254
	0.4	2.098	2.439	2.873	3.078	3.184	3.275
	0.5	3.377	3.376	4.056	4.502	4.807	5.089
	0.6	5.661	—	6.132	7.008	7.839	8.693
	0.7	10.40	—	10.40	12.13	14.44	17.21
	0.8	23.21	—	—	25.78	33.28	44.94
	0.9	87.07	—	—	92.48	133.5	225.5
(b)	0.1	0.536	1.415	1.455	1.462	1.463	1.464
	0.2	1.782	3.351	3.604	3.665	3.681	3.693
	0.3	4.065	5.908	6.740	7.013	7.115	7.198
	0.4	8.057	9.477	11.34	12.23	12.65	13.02
	0.5	15.09	15.09	18.46	20.72	22.15	23.45
	0.6	28.21	—	30.80	35.71	40.04	44.40
	0.7	56.07	—	56.07	66.26	79.17	94.42
	0.8	132.3	—	—	147.7	191.3	258.3
	0.9	514.0	—	—	546.3	789.9	1334

TABLE 1. The coefficients (a) K_e and (b) P_e for the following set of parameters: $e\zeta_p/kT = 1$; $e\zeta_w/kT = 0$; $Z = 1$; $\kappa a = 100$; $m_i = 0.4$.

	λ	$\beta = 2\lambda$	$\beta = 1.0$	$\beta = 1.4$	$\beta = 2.0$	$\beta = 4.0$	$\beta = 40.0$
(a)	0.1	0.926	2.408	2.474	2.486	2.487	2.488
	0.2	1.625	2.962	3.168	3.215	3.228	3.239
	0.3	2.629	3.702	4.156	4.298	4.356	4.407
	0.4	4.166	4.812	5.605	5.961	6.154	6.329
	0.5	6.657	6.657	7.888	8.662	9.218	9.750
	0.6	11.08	—	11.92	13.45	14.97	16.57
	0.7	20.24	—	20.24	23.32	27.55	32.71
	0.8	45.07	—	—	49.75	63.59	83.61
	0.9	168.6	—	—	178.5	254.2	358.4
(b)	0.1	1.089	2.855	2.934	2.948	2.949	2.951
	0.2	3.675	6.796	7.280	7.390	7.421	7.446
	0.3	8.482	12.12	13.68	14.17	14.36	14.53
	0.4	16.92	19.71	23.21	24.78	25.59	26.31
	0.5	31.71	31.71	38.11	42.17	44.91	47.50
	0.6	59.07	—	63.98	72.98	81.31	89.99
	0.7	116.5	—	116.5	135.6	160.7	190.8
	0.8	271.5	—	—	301.0	385.6	507.9
	0.9	1031	—	—	1093	1557	2213

TABLE 2. The coefficients (a) K_e and (b) P_e for the following set of parameters: $e\zeta_p/kT = 1$; $e\zeta_w/kT = 1$; $Z = 1$; $\kappa a = 100$; $m_i = 0.4$.

for parameters K_e and P_e as a function of β and λ for different values of the parameters describing the electrical double layer are given in tables 1(a, b) and 2(a, b). From the expressions for the total force on the particle and pressure gradient the transport properties can be determined.

7. Electro-kinetic transport properties

We will discuss some modes of electro-kinetic transport that may occur in the system. When the system parameters like β , λ , κa , ζ_p , ζ_w , Z and m_i are known, we are able to evaluate the coefficients K_u , K_v , K_e , P_u , P_v , and P_e , from which the transport properties are fully determined by (6.8) and (6.9). Depending on the constraints on the system different modes of electro-kinetic transport may be observed, as the following examples show.

(i) Electrophoretic and electro-osmotic transport in a closed system

When an electrical field is applied and the spheres move force free through the fluid the spheres will attain an electrophoretic velocity U' , measured relative to the wall of the tube. In addition to this an electro-osmotic flow will develop in the tube as a result of the double layer near the wall of the tube. The total discharge of particles and fluid through the tube is in our calculation given by Q' , as measured relative to the wall of the tube. In a closed system the total discharge equals, by definition, zero. This situation is established by the system by developing a counter-pressure that induces a balancing counterflow in the tube. For this situation we have in (6.8) and (6.9):

$$D' = 0; \quad U' \neq 0; \quad Q' = \frac{1}{2}\pi R^2 V' = 0; \quad \Delta p' \neq 0. \quad (7.1)$$

From (6.8) it follows that the electrophoretic velocity U' is given by

$$U' = \frac{K_e(\epsilon_0 \epsilon_r \zeta_p / \eta) E'_0}{K_u}, \quad (7.2)$$

and from (6.9) that the pressure drop per sphere $\Delta p'$ is given by

$$\Delta p' = \frac{\epsilon_0 \epsilon_r \zeta_p E'_0}{R} \left(\frac{P_u K_e}{K_u} + P_e - 16 \frac{\zeta_w}{\zeta_p} W \beta \right). \quad (7.3)$$

(ii) Electrophoretic and electro-osmotic transport in an open system

In this case we have the same conditions on D' and U' as in (i), but in this case we have by definition a zero pressure gradient. So, we have

$$D' = 0; \quad U' \neq 0; \quad Q' = \frac{1}{2}\pi R^2 V' \neq 0; \quad \Delta p' = 0. \quad (7.4)$$

Again, from (6.8) the electrophoretic velocity U' is given by

$$U' = \frac{K_e(\epsilon_0 \epsilon_r \zeta_p / \eta) E'_0}{K_u}. \quad (7.5)$$

Equation (6.9) for the pressure drop per sphere with $\Delta p' = 0$, together with (5.14), gives a linear relation between the total discharge Q' , as measured relative to the wall of the tube, and the applied electrical field E'_0 :

$$Q' = \frac{\pi R^2 [P_u K_e / K_u + P_e - 16(\zeta_w / \zeta_p) W \beta]}{2[P_v + 4\beta]} \left(\frac{\epsilon_0 \epsilon_r \zeta_p}{\eta} \right) E'_0. \quad (7.6)$$

(iii) Pure electro-osmotic transport in a closed system

In this case we assume that the spheres are fixed to their positions relative to the wall of the tube. They will experience a drag force that is balanced by an external force of an undefined nature. In case of a closed system, we have

$$D' \neq 0; \quad U' = 0; \quad Q' = \frac{1}{2}\pi R^2 V' = 0; \quad \Delta p' \neq 0, \quad (7.7)$$

which leads to the relations

$$D' = 6\pi\eta\lambda R(K_e(\epsilon_0 \epsilon_r \zeta_p/\eta) E'_0), \quad (7.8)$$

$$\Delta p' = [P_e - 16(\zeta_w/\zeta_p) W\beta](\epsilon_0 \epsilon_r \zeta_p/R) E'_0. \quad (7.9)$$

Closely related to this mode of transport is the possibility of an applied pressure gradient opposing the electro-kinetic motion of the spheres. In this case we have $D' = 0$, instead of $D' \neq 0$. From (6.8) and (6.9) we find the total discharge and the required pressure gradient as

$$Q' = -(\pi R^2 K_e/2K_v)(\epsilon_0 \epsilon_r \zeta_p/\eta) E'_0, \quad (7.10)$$

$$\Delta p' = \{(P_v + 4\beta) K_e/K_v + P_e - 16(\zeta_w/\zeta_p) W\beta\}(\epsilon_0 \epsilon_r \zeta_p/\eta) E'_0. \quad (7.11)$$

(iv) Pure electro-osmotic transport in an open system

Again, we assume that the spheres are fixed to their positions in the tube and that they experience a viscous drag force that is balanced by an external force of an undefined nature. In case of an open system, we have

$$D' \neq 0; \quad U' = 0; \quad Q' = \frac{1}{2}\pi R^2 V' \neq 0; \quad \Delta p' = 0, \quad (7.12)$$

which leads to

$$D' = 6\pi\eta\lambda R\{K_e(\epsilon_0 \epsilon_r \zeta_p/\eta) E'_0 + (2K_v Q'/\pi R^2)\}, \quad (7.13)$$

$$Q' = \frac{\pi R^2 [P_e - 16(\zeta_w/\zeta_p) W\beta]}{2[P_v + 4\beta]} \left(\frac{\epsilon_0 \epsilon_r \zeta_p}{\eta} \right) E'_0, \quad (7.14)$$

where (7.14) gives a linear relation between the total discharge Q' and the electrical field E'_0 .

8. Properties of the streamlines

When we characterize the streamline pattern (as measured relative to the spheres) by the number and location of the vortices, one of the following four situations may occur, depending on the system parameters: (i) no vortices at all; (ii) vortices between subsequent spheres; (iii) vortices near the surface of the spheres; (iv) situation (ii) and (iv).

To illustrate this we have plotted in figure 2(a-d) the streamlines, measured relative to the spheres, in the region $-1 \leq \rho \leq 1$ and $-0.7 \leq z \leq 0.7$. Owing to the periodicity of the system the float at every point of the system may be constructed by translation. The parameters in these plots are chosen as follows: $\beta = 1.4$ and $\lambda = 0.5$, $\kappa a = 50$, $m_i = 0.4$, $Z = 1$, $U = 0$ and $(\epsilon_0 \epsilon_r (kT)^2/2Z^2 e^2 \nu \eta) E_0 = 1$ and we have varied V , $e\zeta_p/kT$ and $e\zeta_w/kT$ in the different plots. Because we have chosen $U = 0$, the spheres are fixed relative to wall of the tube, so in this case the streamlines and the discharge Q as measured relative to the spheres are also the streamlines and the discharge as measured relative to the tube. The number of grid points in the z -direction is 41 and in the ρ -direction there are 51. The corresponding transport coefficients K_e and P_e for the case $e\zeta_p/kT = 1$ and $e\zeta_w/kT = 2$ may be found in tables 3(a) and 3(b). We will first discuss the case where $V = -5$, $e\zeta_p/kT = 1$ and $e\zeta_w/kT = 2$ plotted in figure 2(a). Both the wall of the cylinder and the spheres are positively charged, and the electrical field E'_0 points in the positive z -direction. Because V is negative there has to be a discharge in the negative z -direction. The electrical double layer introduces a slip velocity at the bounding surfaces, directed in the negative z -direction. These requirements makes it possible to develop a flow without vortices. When V increases to $V = -1.5$, as plotted in figure 2(b), the total discharge must be reduced, still satisfying the slip boundary

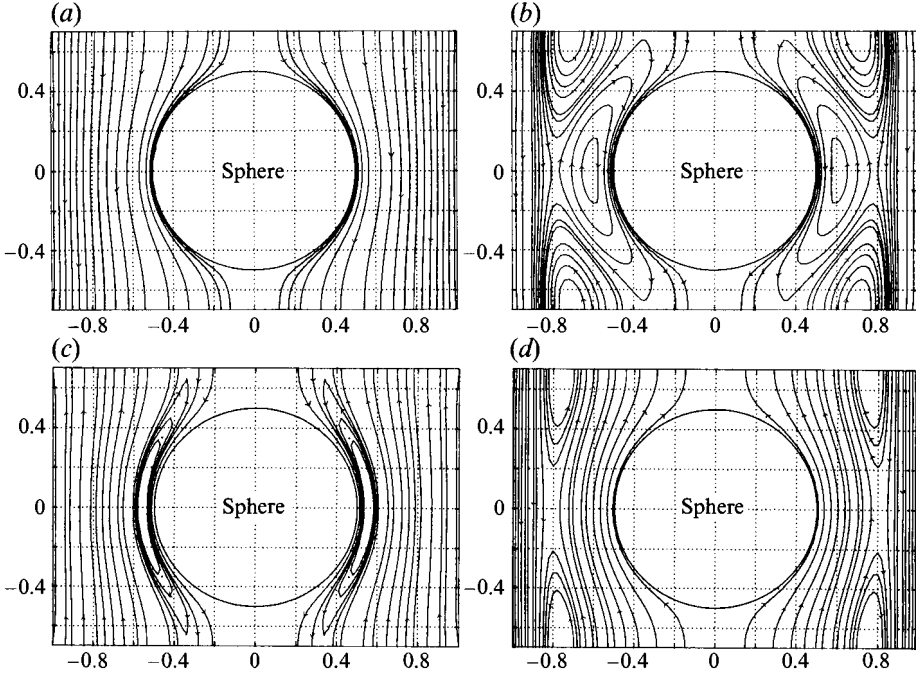


FIGURE 2. Streamlines, as measured relative to the sphere, for the following sets of parameters: (a) $e\zeta_p/kT = 1, e\zeta_w/kT = 2; V = -5$; (b) $e\zeta_p/kT = 1, e\zeta_w/kT = 2; V = -1.5$; (c) $e\zeta_p/kT = 1, e\zeta_w/kT = -2; V = 5$; (d) $e\zeta_p/kT = -1, e\zeta_w/kT = 2; V = 0$. In all cases, $Z = 1, U = 0; \beta = 1.4; \lambda = 0.5; \kappa a = 50; \epsilon_0 \epsilon_r (kT)^2 E_0 / 2e^2 v \eta = 1, m_i = 0.4$.

	λ	$\beta = 2\lambda$	$\beta = 1.0$	$\beta = 1.4$	$\beta = 2.0$	$\beta = 4.0$	$\beta = 40.0$
(a)	0.1	1.384	3.593	3.691	3.709	3.710	3.712
	0.2	2.427	4.408	4.709	4.776	4.794	4.809
	0.3	3.922	5.502	6.158	6.354	6.432	6.499
	0.4	6.205	7.149	8.285	8.773	9.026	9.255
	0.5	9.889	9.889	11.64	12.70	13.41	14.10
	0.6	16.40	—	17.58	19.64	21.57	23.56
	0.7	29.77	—	29.77	33.85	39.13	45.33
	0.8	65.48	—	—	71.42	88.24	111.7
	0.9	236.8	—	—	248.7	336.6	458.2
(b)	0.1	1.635	4.268	4.384	4.405	4.408	4.409
	0.2	5.543	10.18	10.89	11.05	11.09	11.12
	0.3	12.84	18.23	20.50	21.17	21.43	21.66
	0.4	25.67	29.79	34.87	37.04	38.11	39.08
	0.5	48.11	48.11	57.40	63.02	66.62	70.01
	0.6	89.40	—	96.46	108.9	119.7	130.8
	0.7	175.2	—	175.2	201.3	233.2	270.2
	0.8	402.2	—	—	440.8	545.8	691.6
	0.9	1468	—	—	1543	2090	3207

TABLE 3. The coefficients (a) K_e and (b) P_e for the following set of parameters: $e\zeta_p/kT = 1; e\zeta_w/kT = 2; Z = 1; \kappa a = 50; m_i = 0.4$.

conditions at the bounding surfaces. This is achieved by the system developing two vortices, one rotating in a clockwise direction and the other counterclockwise. When V becomes positive and the zeta-potential of the wall of the tube changes sign, so that $e\zeta_w/kT = -2$ and $e\zeta_p/kT = 1$, a flow with only one vortex near the surface of the sphere develops (figure 2c). The vortex near the wall of the tube is not present since the negative zeta-potential of the wall of the cylinder induces a surface flow in the positive z -direction which is compatible with the demand of a positive discharge. When the sphere has negative charge, so that $e\zeta_p/kT = -1$ with $e\zeta_w/kT = 2$, $U = 0$, $V = 0$ we are dealing with a purely electro-osmotic motion. In this case one vortex develops between the spheres in the neighbourhood of the wall of the tube (figure 2d). The presence of vortices will be of importance for the convective transport of molecules in the system. One may, for instance, think of the molecules of the sample to be separated in the case of micellar electro-kinetic capillary chromatography. The efficiency of the separation by the micelles will be influenced significantly by the vortices.

9. Conclusions

In this paper we have shown how to use the thin double layer theory to derive the electro-kinetic transport properties in a system consisting of a cylindrical tube containing a linear array of identical charged spheres. Polarization effects of the electrical double layer are taken into account and the theory is valid for arbitrary zeta-potentials and for thin electrical double layers, introducing a typical error of $O(1/\kappa a)$. All interactions, electrical double layer and hydrodynamical interactions, between of the spheres and between the spheres and the wall of the tube are taken into account. By increasing the number of multipole moments it is possible to obtain the transport coefficients to any desired accuracy. Expressions for the pressure drop per sphere and the hydrodynamical drag on the spheres are given in terms of the velocity of the spheres, the total discharge and the applied electrical field. The coefficients in these expressions depend on the system parameters and have to be evaluated numerically by truncating an infinite set of linear equations for the multipole moments. Depending on the conditions placed on the system, e.g. an open or closed system, a backflow may develop resulting in complex flow behaviour. This results in rather complex plots for the streamlines, sometimes with vortices, which will have significant influence on the convective transport properties of small molecules present in the system. Applications of this work may be found in the electro-kinetic displacement of charged solid particles or charged emulsion droplets through porous media, e.g. tertiary oil recovery, micellar electro-kinetic capillary chromatography and soil cleaning.

The author wishes to express his gratitude to Professor Dr H. N. Stein for stimulating discussions and useful remarks during the preparation of this paper.

Appendix A

We will focus on a symmetrical salt so that

$$z_+ = -z_- = Z \quad \text{and} \quad n_+^\infty = n_-^\infty = n^\infty. \quad (\text{A } 1)$$

The Poisson-Boltzmann equation reads

$$\frac{d^2\phi}{dx^2} = \frac{2eZn^\infty}{\epsilon_0 \epsilon_r} \sinh\left(\frac{Ze\phi}{kT}\right), \quad \phi(\infty) = 0 \quad \text{and} \quad \phi(0) = \phi_0. \quad (\text{A } 2)$$

The solution for a flat-plate geometry is

$$\phi(x) = \frac{2kT}{Ze} \ln \left[\frac{1 + \gamma \exp(-\kappa x)}{1 - \gamma \exp(-\kappa x)} \right], \quad (\text{A } 3)$$

$$\text{with} \quad \gamma = \tanh(Ze\phi_0/4kT) \quad \text{and} \quad \kappa^2 = (2e^2/\epsilon_0\epsilon_r kT) n^\infty Z^2. \quad (\text{A } 4)$$

Appendix B

Multiplying (4.11) by $\sin(mkz)$ and integrating from $-\frac{1}{2}\beta$ to $\frac{1}{2}\beta$ using

$$\int_{-\beta/2}^{\beta/2} \sin(mkz) \sin(m'kz) dz = \frac{1}{2}\beta \delta_{m,m'}, \quad (\text{B } 1)$$

we may evaluate the following integrals as

$$\sum_{n=-\infty}^{\infty} \int_{-\beta/2}^{\beta/2} \frac{(z-n\beta) \sin(mkz)}{((1+(z-n\beta)^2)^{5/2})} dz = \int_{-\infty}^{\infty} \frac{z \sin(mkz)}{(1+z^2)^{5/2}} dz = \frac{2}{3}(mk)^2 K_1(mk) \quad (\text{B } 2)$$

and

$$\begin{aligned} \sum_{n=-\infty}^{\infty} \int_{-\beta/2}^{\beta/2} \sin(mkz) \frac{\partial^2}{\partial z^2} \left(\frac{(z-n\beta)}{((1+(z-n\beta)^2)^{3/2})} \right) dz &= \int_{-\infty}^{\infty} \sin(mkz) \frac{\partial^2}{\partial z^2} \left(\frac{z}{(1+z^2)^{3/2}} \right) dz \\ &= 2(mk)^3 K_0(mk). \end{aligned} \quad (\text{B } 3)$$

To derive (B 2) we start from the expression (Watson 1944)

$$\int_{-\infty}^{\infty} \frac{\cos(mkz)}{(1+z^2)^{5/2}} dz = \frac{2}{3}(mk)^2 K_2(mk). \quad (\text{B } 4)$$

Differentiating (B 4) once to (mk) we find

$$\int_{-\infty}^{\infty} \frac{z \sin(mkz)}{(1+z^2)^{5/2}} dz = \frac{2}{3}(mk)^2 K_1(mk), \quad (\text{B } 5)$$

where we have used the recursion relation

$$2K_2(mk) + mkK_2'(mk) = -mkK_1(mk). \quad (\text{B } 6)$$

Integral (B 3) is partially integrated twice, which leads to

$$\int_{-\infty}^{\infty} (mk)^2 \sin(mkz) \left(\frac{z}{(1+z^2)^{3/2}} \right) dz. \quad (\text{B } 7)$$

For evaluating this integral we use (Watson 1944)

$$\int_{-\infty}^{\infty} \frac{\cos(mkz)}{(1+z^2)^{3/2}} dz = 2mkK_1(mk). \quad (\text{B } 8)$$

Differentiating (B 8) once to (mk) leads to

$$(mk)^2 \int_{-\infty}^{\infty} \sin(mkz) \left(\frac{z}{(1+z^2)^{3/2}} \right) dz = 2(mk)^3 K_0(mk), \quad (\text{B } 9)$$

where we have used the recursion relation

$$mkK_1'(mk) + K_1(mk) = -mkK_0(mk). \quad (\text{B } 10)$$

Appendix C

Using the relation (MacRobert 1948)

$$\sum_{n=0}^{\infty} \frac{R^n}{n!} P_n(\mu) = e^x J_0(y), \quad (\text{C } 1)$$

$$\text{with} \quad x = R \cos(\theta), \quad y = R \sin(\theta), \quad I_0(z) = J_0(iz), \quad (\text{C } 2)$$

$$\text{we find} \quad I_0(mk\rho) \cos(mkz) = \sum_{n=0}^{\infty} \frac{(-1)^n (mk\rho)^{2n}}{2n!} P_{2n}(\mu). \quad (\text{C } 3)$$

Differentiating (C 3) once to z gives

$$I_0(mk\rho) \sin(mkz) = \sum_{n=0}^{\infty} \frac{(-1)^n (mk)^{2n+1} \rho^{2n+1}}{(2n+1)!} P_{2n+1}(\mu). \quad (\text{C } 4)$$

Appendix D

In order to write expand the last term in (4.18) around the lattice point $R_n = 0$, we start from the following generalized form of the addition theorem for spherical harmonics (McKenzie, McPhedran & Derrick 1978):

$$\frac{1}{r_2^{l_2+1}} Y_{l_2,0}(\theta_2, \varphi_2) = \sum_{l_1=0}^{\infty} H'(l_1 0 | l_2 0) \frac{Y_{l_1,0}(\theta_R, \varphi_R)}{R^{l_1+1}} r_1^{l_1} Y_{l_1,0}(\theta_1, \varphi_1), \quad (\text{D } 1)$$

valid for $r_1 \leq R$, with the definitions

$$r_1 = r - R_1; \quad r_2 = r - R_2; \quad R = R_1 - R_2, \quad (\text{D } 2)$$

$$Y_{l_1,0}(\theta_0, \varphi_0) = \left\{ \frac{2l_1+1}{4\pi} \right\}^{1/2} P_{l_1}(\mu_0) \quad \text{and} \quad \mu_0 = \cos(\theta_0), \quad (\text{D } 3)$$

with

$$H'(l_1 0 | l_2 0) = (4\pi)^{1/2} (-1)^{l_2} \left[\frac{(2l_2+1)}{(2l_1+1)(2l_1+1)} \right]^{1/2} \frac{l!}{l_1! l_2!} \quad \text{and} \quad l = l_1 + l_2. \quad (\text{D } 4)$$

Using this we find

$$\frac{1}{r_2^{l_2+1}} P_{l_2}(\mu_2) = \sum_{l_1=0}^{\infty} H(l_1 | l_2) \frac{P_{l_1}(\mu_R)}{R^{l_1+1}} r_1^{l_1} P_{l_1}(\mu_1), \quad (\text{D } 5)$$

$$\text{with} \quad H(l_1 | l_2) = (-1)^{l_2} \frac{l!}{l_1! l_2!} \quad \text{and} \quad l = l_1 + l_2. \quad (\text{D } 6)$$

Using this expression we can write (4.15) as

$$\sum_{n=-\infty}^{\infty} \frac{1}{r_n^{l_2+1}} P_{l_2}(\mu_n) = \sum_{n=-\infty}^{\infty} \sum_{l_1} H(l_1 | l_2) \frac{P_{l_1}(\mu_R)}{R^{l_1+1}} r_1^{l_1} P_{l_1}(\mu_1); \quad l = l_1 + l_2. \quad (\text{D } 7)$$

Introducing the lattice sum S_l :

$$S_l = \sum_{n=-\infty}^{\infty} \frac{P_{l_1}(\mu_R)}{R^{l_1+1}} \quad (\text{D } 8)$$

we may write

$$\sum_{n=-\infty}^{\infty} \frac{P_{2s-1}(\mu_n)}{r_n^{2s}} = \sum_{l_1=0}^{\infty} H(2l_1+1 | 2s-1) S_l r_1^{2l_1+1} P_{2l_1+1}(\mu_0), \quad l = 2(l_1+s). \quad (\text{D } 9)$$

Here we have used that $S_l = 0$ for l odd. This is because in our geometry we have $\mu_R = 1$ or $\mu_R = -1$ and the property $P_l(-1) = (-1)^l$ and $P_l(1) = 1$. For l even we find

$$S_l = \sum_{n=1}^{\infty} \frac{2}{(n\beta)^{l+1}}. \quad (\text{D } 10)$$

Appendix E

$$\frac{\partial \mu_i}{\partial z} = \frac{\partial}{\partial z} \left(\sum_{s=1}^{\infty} G_{2s}^i \frac{\partial^{2s-2}}{\partial z^{2s-2}} \left\{ \sum_{n=-\infty}^{\infty} \frac{(z-n\beta)}{((\rho^2 + (z-n\beta)^2)^{3/2}} + \sum_{m=1}^{\infty} q_m^i I_0(mk\rho) \sin(mkz) \right\} - z_i E_0 z \right). \quad (\text{E } 1)$$

With $\rho = 1$

$$\frac{\partial \mu_i}{\partial z} = \frac{\partial}{\partial z} \left(\sum_{s=1}^{\infty} G_{2s}^i \frac{\partial^{2s-2}}{\partial z^{2s-2}} \left\{ \sum_{n=-\infty}^{\infty} \frac{(z-n\beta)}{((1 + (z-n\beta)^2)^{3/2}} + \sum_{m=1}^{\infty} q_m^i I_0(mk) \sin(mkz) \right\} - z_i E_0 z \right). \quad (\text{E } 2)$$

We now first expand the first term in a Fourier series, and because this term is odd in z we must expand it in a sin series:

$$\sum_{n=-\infty}^{\infty} \frac{(z-n\beta)}{((1 + (z-n\beta)^2)^{3/2}} = \sum_{m=1}^{\infty} A_m \sin(mkz) \quad \text{with} \quad k = \frac{2\pi}{\beta}. \quad (\text{E } 3)$$

So we find

$$\begin{aligned} A_m \frac{1}{2}\beta &= \int_{-\infty}^{\infty} \frac{z \sin(mkz)}{(1+z^2)^{3/2}} dz = -\frac{\partial}{\partial(mk)} \left\{ \int_{-\infty}^{\infty} \frac{\cos(mkz)}{(1+z^2)^{3/2}} dz \right\} \\ &= -\frac{\partial}{\partial(mk)} (2mkK_1(mk)) = -(2K_1(mk) + 2mkK_1'(mk)) = 2mkK_0(mk), \end{aligned} \quad (\text{E } 4)$$

where we have used the recursion relations for the modified Bessel functions, so

$$A_m = (4/\beta) mkK_0(mk). \quad (\text{E } 5)$$

Substituting this in (E 1) gives

$$\begin{aligned} \frac{\partial \phi_{tot}^i}{\partial z} &= \frac{\partial}{\partial z} \left(\sum_{s=1}^{\infty} G_{2s}^i \frac{\partial^{2s-2}}{\partial z^{2s-2}} \left\{ \sum_{m=1}^{\infty} \frac{4}{\beta} mkK_0(mk) \sin(mkz) \right. \right. \\ &\quad \left. \left. + \sum_{m=1}^{\infty} q_m^i I_0(mk) \sin(mkz) \right\} \right) - z_i E_0 \\ &= \sum_{s=1}^{\infty} G_{2s}^i \frac{\partial^{2s-1}}{\partial z^{2s-1}} \sum_{m=1}^{\infty} \left\{ \frac{4}{\beta} mkK_0(mk) + q_m^i I_0(mk) \right\} \sin(mkz) - z_i E_0 \\ &= \sum_{s=1}^{\infty} G_{2s}^i (-1)^{s+1} \sum_{m=1}^{\infty} \left\{ \frac{4}{\beta} (mk)^{2s} K_0(mk) \right. \\ &\quad \left. + q_m^i (mk)^{2s-1} I_0(mk) \right\} \cos(mkz) - z_i E_0. \end{aligned} \quad (\text{E } 6)$$

This expression gives v_z at $\rho = 1$. Note that $v_z(\rho = 1)$ is indeed an even function in z so this is consistent with our assumption that the stream function is an even function in z .

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