Dedicated to the memory of my Father
Seyed Mostafa who dedicated his life to educating the people of our town.

Though he did not have the opportunity to pursue his education past grade eleven, when I explained problems to him during my studies he solved them intuitively faster than me.

And to my mother Fatemeh who has always kept me in her heart.

Electroviscous Particle-Wall Interactions

by

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Abstract - A theoretical analysis is presented to determine the forces of interaction between an electrically charged cylindrical or spherical particle and a charged plane boundary wall when the particle translates parallel to the wall and rotates around its axis in a symmetric electrolyte at rest. The electroviscous effects, arising from the coupling between the electrical and hydrodynamic equations, are determined as a solution of three partial differential equations, derived from Cox's general theory, for electroviscous ion concentration, electroviscous potential and electroviscous flow field. It is a priori assumed that the double layer thickness surrounding each charged surfaces is much smaller than the length scale of the problem. Using the matched asymptotic expansion technique, the electroviscous forces experienced by the cylinder and by the sphere are explicitly determined analytically for low and intermediate Peclet numbers, but small particle-wall distances. The solution for the sphere-wall interactions is extended to arbitrary particle-wall distances analytically for the tangential component of the force and numerically for the normal component of the force by the use of a bipolar coordinate system. The tangential and normal components of the electroviscous force experienced by the sphere-wall interactions for both arbitrary particle-wall distances and arbitrary Peclet numbers are also determined numerically by the use of the finite difference approximation in the bipolar coordinate system. It is found that the tangential force usually increases the drag above the purely hydrodynamic drag, although for certain conditions the drag can be reduced. Similarly the normal force is usually repulsive, i.e. it is an electrokinetic lift force, but under certain conditions the normal force can be attractive.

Résumé - Une analyse théorique est présentée afin de déterminer les forces d'interaction entre une particule cylindrique ou sphérique chargée électriquement et une paroi plane également chargée lorsque la particule est en translation parallèlement à la paroi et en rotation autour de son axe dans un électrolyte symétrique au repos. Les effets électrovisqueux, provenant du couplage entre les équations électriques et hydrodynamiques, sont déterminés par la résolution de trois équations aux dérivées partielles, provenant de la théorie générale de Cox, pour une concentration ionique électrovisqueuse, un potentiel électrovisqueux et un champ d'écoulement électrovisqueux. On fait l'hypothèse que l'épaisseur de la double couche entourant chaque surface chargée est bien plus petite que les dimensions du problème. En utilisant une technique d'expansion asymptotique, les forces électrovisqueuses auxquelles sont soumis le cylindre et la sphère sont déterminées explicitement analytiquement pour de faibles et intermédiaires nombres de Peclet et distances particule - paroi. La solution pour les interactions sphère - paroi est étendue aux distances particule - paroi arbitraires de façon analytique pour la composante tangentielle de la force et numérique pour la composante normale en utilisant un système de coordonnées bipolaires. Les composantes tangentielle et normale des forces électrovisqueuses auxquelles sont soumises les interactions sphère-paroi pour des distances particule - paroi arbitraires et des nombres de Peclet arbitraires sont aussi déterminées numériquement en utilisant l'approximation de la méthode des différences finies dans un système de coordonnées bipolaires. Les résultats montrent que la force tangentielle augmente la résistance, en génerale, au dessus de la valeur purement hydrodynamique, mais, pour certaines conditions, la résistance est diminuée. Egalement, la force normale est en génerale une force répulsive, mais pour certains conditions elle peut être attractive.

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Chapter One

Introduction

1.1 - Introduction

Suspensions of colloid particles in Newtonian fluids are well known for their complex rheology and their sensitivity to their electrochemical state. For example, Freundlich & Jones (1936) had difficulty to distinguish between systems for which the shear viscosity increases with increasing rate of strain (shear-thickening) and those for which it decreases (shear-thinning), solely based on particle size and shape, concentration and solvent type. This failure is due to the fact that these parameters do not characterize all the dominant forces. Fryling (1963) demonstrated the critical role of electrical forces by transforming a low-viscosity suspension of 0.1 μm polymer latex spheres into a gel by removing free electrolyte which screens (or neutralizes) surface charges. Alexander and Prieve (1987) observed the change in particle-wall distance of a 9 μm latex particle moving with a velocity of 50 μm/s parallel to a glass wall in a slit-like flow cell apparatus containing a glycerol-water solution. These phenomena along with many others appearing in the literature indicate that surface charges play a major role in the behavior of suspensions of colloidal particles.

When a solid surface comes into contact with a liquid it often acquires a charge. In a suspension of charged particles containing electrolyte, ions of opposite charge (counterions) are attracted toward the surface of the particles and ions of like charge (coions) are repelled from the surface. Therefore, each particle is surrounded by a charged cloud which total charge is equal in magnitude and opposite in sign to its own. This charged cloud together with the surface charge is referred to as electric or diffuse double layer.

When fluid flow or electric fields are applied to such a system, so-called electrokinetic phenomena arise. They owe their unusual character to the interaction among viscous, Brownian and electrical forces in the diffuse double layer. For systems subject to fluid flow, this behavior has been qualitatively explained for many years in terms of the 'primary', 'secondary' and 'tertiary' electroviscous effects [Dobry (1953)]. The first or primary effect arises from the deformation of the diffuse double layer around a single particle by the flow. The secondary effect arises from charged particle interactions and has been studied theoretically by Russel (1976, 1978 a). The tertiary effects appears when electrical forces cause particles to change their shape, as happens with polyelectrolytes [Sherwood

(1980)].

The first theory for the primary electroviscous effect was presented without any proof by Smochulowski (1916) for the limiting case of a thin double layer. Krasny-Ergen (1936) calculated the viscous dissipation in the same limit to obtain a result similar to Smochulowski's, but differing from it by a numerical factor. Booth (1950b) presented a complete analysis of the primary effect for spherical particles with an arbitrary thick charged cloud in the limits of weak flow and weak electrical effects, which leads to a modification of the Einstein coefficient characterizing viscosity in the dilute limit. Russel (1978b) extended the theory to flows with arbitrary strength. Lever (1979) considered the problem with the same assumption but for a large deformation of the charged cloud. All these theories were developed for small surface potentials. They also assumed that the fluid motion around the sphere was changed only slightly by the presence of the charged cloud. Sherwood (1980) removed these restriction. Hinch and Sherwood (1983) extended and complemented Sherwood's asymptotic results for high surface potential and high Hartmann numbers. Oshima *et all.* (1984) derived the electrokinetic force superimposed on the Stokes drag in the sedimentation of a charged sphere in unbounded liquid. Dukhin & van de Ven (1993, 1994) studied theoretically the behavior of a charged sphere in a simple shear flow in an unbounded medium with a symmetric electrolyte.

When sliding motion or squeezing flow is present, the unbounded restriction is released, and hence the so called electroviscous effects have been an interesting subject for study, not only because of the complexity and unusual behavior of the force experienced by the particle, but also because of a practical demand for explaining experimental observations. Among pioneers who paid attention to this line of investigation we may mention the works by Prieve & Bike (1987), Bike (1988), Bike & Prieve (1990), Bike & Prieve (1992), van de Ven, Warszynski & Dukhin (1993a, b), Bike & Prieve (1995), Bike, Lazaro & Prieve (1995) and Wu,Warszynski & van de Ven (1996). All these papers consider the problem of a particle with a thin double layer. With the exception of the numerical work by Wu, Warszynski & van de Ven (1996), the common problem encountered in these theories is that the Maxwell stress tensor, used to calculate the force, does not seem to be the dominant contribution to the force. It was Cox (1997) who pointed out that the main contribution to the force experienced by a charged particle comes from the non-zero normal hydrodynamic stress originating from the tangential flow of the ions in the diffuse double-layer as a result of the streaming potential built up outside it. This contribution is two orders of magnitude greater than that predicted from the perturbation of the electrical field due to the presence of the flow (the streaming potential). Consequently, he provided a general recipe to calculate the normal and tangential components of the force to be applied to different geometries.

The objective of this research is to calculate the electroviscous force experienced by cylindrical and spherical particles under translation and rotation parallel to a wall based on *Cox's general theory (1997)*. Thus, following the historical background, Cox's theory (1997) is presented in detail. The problem of a cylinder moving near a wall is investigated in Chapter two. Analytical solutions for a sphere moving near a wall for low and intermediate Peclet numbers (characteristic of the relative importance of hydrodynamic motion to Brownian motion), and small clearance of particle-wall are presented in Chapter three. In Chapter four the restriction on particle wall distances is released. Analytical-numerical solutions for low and also arbitrary Peclet numbers are obtained in this chapter. Chapter five contains the overall conclusion of this dissertation.

Throughout this research I tried to present the subjects in a relatively self-contained way with the mathematical procedures, containing most details of calculations, as simple as to be easily followed. Whenever it was felt needed a figure accompanies the material. Finite difference approximations are used in the numerical calculations. For the sake of simplicity it is programmed in Matlab. An electric copy of the programs is available upon request. Some properties of coordinate systems employed are discussed in Appendix A. Tables of theoretical results are located in Appendix B. Finally, Appendix C contains some of the analytical calculations of Chapter four.

1.2 - Historical Background

1.2.1 - Electrophoretic Mobility

Many attempts have been made in the past to determine the relation between the motion of charged particles, the applied electric field and other relevant physical quantities. Helmholtz (1879) was the first to pay attention to this problem. He made a theoretical study of electrokinetic phenomena in general. He presented a qualitative discussion of cataphoresis, now commonly called electrophoresis. Consequently, he formulated the electroosmotic velocity in a single capillary upon imposing an external eclectic field it. He also presented a relation for the streaming potential (electroviscous potential) arising from the motion of the electrolyte in a simple capillary, upon imposing a pressure drop along it.

Smoluchowski (1918) improved Helmholtz's theory and derived the relationship

$$\frac{U}{E} = \frac{\varepsilon_m \zeta}{\eta} \tag{1.2.1a}$$

presented without any proof. E is the strength (magnitude) of the applied electric field $\vec{E}$, i.e. $E = |\vec{E}|$, (in modern physics a field is described by an "action-at-distance" theory) defined by[1]

$$\vec{E} = -\nabla \psi \tag{1.2.1.b}$$

in which the gradient, ∇, is defined as the directional rate of variation (derivation) with respect to space, and ψ is a scalar physical quantity known as potential; U is the electrophoretic velocity of non-conducting particles (U/E is known as the electrophoretic mobility denoted by E.M.). The parameter ε_m is the permittivity of the medium (or dielectric permittivity), defined by

$$\varepsilon_m = \varepsilon_r \varepsilon_0 \tag{1.2.1c}$$

where ε_r is the relative permittivity of the liquid (dielectric constant) and ε_0 is the permittivity of free space (the vacuum); η is the viscosity of the solution surrounding the colloid particles; ζ represents the difference potential between the surface of the solid and

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Throughout this dissertation, the physical quantities or geometry descriptions, which is described by a scalar quantity and a direction (vector), such as velocity, force and position of a point relative to a reference (coordinate system), are denoted by an arrow (→), and those which is described by a scalar quantity and two directions (tensor of the second rank), such as hydrodynamic and electric stress tensor (directional derivative of the force per unit area), by two arrows, an arrow rides another arrow.

the liquid at infinity, known as the electrokinetic potential of the surface, and it is well known as the Zeta-potential (ζ-potential).

Later works by Hückel (1924), Henry (1931), Overbeek (1943) and Booth (1948) have shown that the validity of Eq. (1.2.1) is rather restricted. In the case of a spherical colloid particle, it is valid only when $\kappa^{-1} << a$, in which a is the radius of the particle and κ is the reciprocal double layer thickness.

The next major advance was made by Henry (1931). He confined attention to spherical particles but generalized Smoluchowski's theory in two ways. He examined both conducting and non-conducting particles and did not impose any restrictions on the double layer thickness, but assumed that the ζ-potential is low. For the case of non-conducting particles he obtained the relationship

$$\frac{U}{E} = \frac{\varepsilon_m \zeta}{\eta} f(b) \tag{1.2.2a}$$

where $b = \kappa a$; $1/\kappa$ is known as the double layer thickness and is defined by

$$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon_m kT}{\sum_{i=1}^{m} c_i z_i^2 e^2}} \tag{1.2.2b}$$

z_i is the ion valency of species i, e the charge of a poroton, c_i the number concentration of ions of type i far from the particle; k is Boltzmann's constant and T the absolute temperature. The summation is over the m different ionic species in the electrolyte. The function f(b) is plotted by Henry and varies from the value of 2/3 for small b to 1 for large b, that is, $⅔ < f(b) < 1$. Hence, for large b (i.e. for thin double layers), Henry's equation reduces to that of Smoluchowski. In deriving Eq. (1.2.2), Henry used two main simplifying assumptions. He assumed in the first place that the so-called ' inertia terms' in the hydrodynamic equations of motion would be negligible, that is the Reynolds number, which describes the relative importance of the inertia effects to viscous effects, is low. Secondly, he regarded the field near the particle as simply the resultant of the applied field and the field due to the electrical double layer in its equilibrium state. The first assumption is almost certainly valid for the range of the particle sizes and of velocities encountered experimentally. But, the second assumption is open to criticism. As the particle moves through the electrolyte, the ions in the double layer will tend to lag behind. In front of the particle we would expect the charge density at a given position in the ionic double layer to be less than its equilibrium value, whereas behind the particle it will be greater. This behavior is well known as the 'relaxation effect' in the Debye-Hückel theory of the conductance of electrolytes. In addition, the applied field will modify the charge density in the atmosphere, quite apart from any effects due to the finite mobilities of the ions. For moderate values of κa (say, $0.2 < \kappa a < 50$), the so-called relaxation effect leads to important corrections, which increase with increasing electrokinetic potential. This was found by Overbeek (1943) and, independently, by Booth (1950a).

Although Komagata (1935) and Hermans (1938) had attempted to improve Henry's theory, only Overbeek and Booth' s results are in fair agreement with each other, though their methods and scope of their studies are different. Both authors expressed the E.M. as a power series in the dimensionless ζ-potential, hereafter denoted by $\tilde{\psi}$, defined by (1.2.28e), unless otherwise stated.

Overbeek (1943), under the following assumptions, calculated the electrophoretic velocity, U, correct to order $\tilde{\psi}^4$:

a - Interactions between colloid particles are negligible and only a single particle is considered (i.e. low concentration of particles, a dilute suspension).

b - This particle (plus the adjacent layer of the liquid which remains stationary relative to the particle) is treated as a rigid sphere.

c - The dielectric constant is supposed to be same everywhere in the sphere.

d - The electric conductivity of the sphere is assumed to be zero. This implies that the charge within the surface of shear does not move relative to the particle when a D.C. electrical field is applied.

e - The charge of the sphere is supposed to be uniformly distributed on the surface.

f - The mobile part of the electric double layer is described by the classical Gouy Chapman theory.

g - Only one type of the positive and one type of negative ions are considered to be present in the ionic atmosphere.

h - The dielectric constant of the liquid surrounding the sphere is supposed to be independent of position.

i - The viscosity of the surrounding liquid is assumed to be independent of position.

j - Brownian motion of the colloid particle is negligible.

k - Finally, because colloidal suspensions follow Ohm's law at the moderate field strengths (i.e. a few volts per second) which are employed in electrophoresis experiments, in the computation only linear terms in the field are taken into account.

Booth (1950a) analyzed the electrophoresis (cataphoresis) of a spherical, non-conducting solid particle, suspended in a fluid, under the action of an applied electric field. He demonstrated that the steady velocity (U) of the particle may be expressed as:

$$U = \sum_{n=1}^{\infty} c_n Q^n = \sum_{n=1}^{\infty} d_n \widetilde{\psi}^{\,n} \qquad (1.2.3a)$$

where Q is the number of charges, i.e. Qe is the absolute value of the total charge of the sphere and where either of the coefficients c_n and d_n is an infinite set of coefficients to be determined, proportional to the strength of the applied field, and depending on particle size, and the concentrations, valencies and also mobilities of the ions in the electrolyte. Booth outlined a general method for calculation of c_n or d_n and could calculate the coefficient c_n for four terms involved in Eq. (1.2.3a) under the following assumptions:

(1) - The dielectric constant, the viscosity and the ionic mobilities are uniform throughout the fluid phase.

(2) - The cataphoretic velocity is proportional to the field strength; this assumption simplifies the theory very much and is generally fulfilled in practice.

(3) - The electrolyte is incompressible.

(4) - The inertia terms in the equations of motion of the electrolyte is negligible. It can be shown that this is justified provided that (2) is fulfilled.

(5) - The electrolyte is symmetrical, that is, it contained of equal numbers of ions of

equal ion valency but with opposite charge.

(6) - Finally, some extra assumptions on the behavior at the surface of the particle are required. By purely thermodynamical arguments, the difference of potential between the interior of the particle and the electrolyte far from the interface, ψ, is derived as

$$\psi = \psi_0 + \frac{RT}{z_i F_r} \ln a_i \tag{1.2.3b}$$

in which ψ_0 is a constant potential; R is the gas constant, F_r the Faraday's constant (RT/F_r sometimes is refereed to as *Nernst potential* and has a value of 25.7 mV at 25°C), and a_i is the activity of ion of type i. The potential ψ can not be identified with the electrokinetic potential, since ζ and ψ behave quite differently as the ionic concentrations are varied. It is therefore necessary to postulate a region or 'surface phase' on the solid side of the boundary, in which the potential varies. The four assumptions on conditions in the surface phase are:

(i) - The thickness of the surface phase is small compared with the particle radius.

(ii) - The charge in the surface phase is immobile; there is no surface conductance.

(iii) - The surface charge density when the field is applied satisfies

$$S(\vec{r}_O) = -\frac{3}{2}\vec{E}\,\varepsilon_S \cos\theta + S_1(\vec{r}_O) \tag{1.2.3c}$$

in which $S(\vec{r}_0)$ and $S_1(\vec{r}_0)$ represent the density of the surface charge at point O, ($\vec{r}_0$ is the position vector of point O relative to a reference coordinate system) with and without applied field ($\vec{E}$), respectively; ε_s is the permittivity of the solid, and θ the angle between the directions of field $\vec{E}$ and position vector $\vec{r}_0$ at the point under consideration, O. The first term represents a small charge due to the difference between the conductivities of solid and liquid. In fact, this assumption [Eq. (1.2.3c)] was first made by Henry who then concluded that the first term is negligible, i.e. field remained unchanged [$S(\vec{r}_0) \approx S_1(\vec{r}_0)$].

(iv) - Finally, the potential difference across the surface phase retains its equilibrium state when the external field is applied.

As mentioned by Booth himself, the last two assumptions are open to criticism, since both the surface charge and potential jump must depend, somehow, on conditions in the electrolyte such as on the ionic concentrations and the local field strength, whilst neither of them is taken into account.

However, because of mathematical complications, both authors [Overbeek (1943) and Booth (1950a)], as mentioned above, were able to calculate only a few terms of the series in electrokintic potential under the above assumptions. Therefore, quantitative validity of their results could be claimed only for small potentials, ζ < 25 mV [for ζ = 25.7 mV, in a univalent electrolyte at the room temperature, $\widetilde{\psi} = 1$, c.f., relation (1.2.28.e)].

Wiersema *et al.* (1966) considered the problem under the same assumption as Overbeek (1943)'s work improving the results by obtaining a more general calculation numerically. Comparison of the result with those of Overbeek (1943) and Booth (1950a) shows that, for high ζ together with the double layer thickness, $(\kappa)^{-1}$, in the range of, 0.2< κa < 50, the preceding calculations generally overestimate the relaxation effect.

Dukhin & Semenikhin (1970) derived an analytical expression for electro- and diffusio-phoresis of spherical particles.

O'Brien &White (1978) improved the numerical method used by Wiersema *et al.* (1966) and removed its convergence difficulty for high Zeta potentials. They obtained a more general calculation for 1:1 and 2:1 electrolytes.

1.2.2 - Brownian Motion and Diffusion[2]

1.2.2.1 - Brownian Motion

A major characteristic of colloidal dispersion is the perpetual motion of the suspended particles. This motion was first observed by Robert Brown (1928), who observed the motion of pollen grains suspended in water. The phenomenon is widely known as Brownian motion. Initially, it was believed that the particles were alive and their motion caused by vital forces. Gouy (1888) observed that the motion decreases with increasing

[2] The reference of the following discussions is "Colloid Hydrodynamics" by van de Ven (1989).

viscosity and increasing with the particle size. Consequently, he concluded that the idea of the vital force is incorrect. Exner (1900) attempted to measure the velocity of the particles and to compare it with the value deduced from the kinetic theory of gases:

$$\frac{1}{2} m < v^2 > = \frac{3}{2} kT, \tag{1.2.4}$$

in which m is mass of the particle. Since the velocity changes, its mean square of its magnitude [$v = |\vec{v}|$], denoted by the symbol $< >$, appears in the mechanical energy. Exner observed that the velocity v is about 1000 times smaller than that predicted by Eq. (1.2.4). This failure is due to the fact, that the actual path of a particle changes direction so often, that the time interval Δt needed to measure the velocity, $v = \Delta x/\Delta t$, is extremely small.

In classical mechanics the motion of the particle is determined from the force balance equation. The drag force, $\vec{F}$, experienced by a particle may be determined by Stokes' law, that is

$$\vec{F} = -f\vec{v} \tag{1.2.5a}$$

in which f is the friction coefficient [for spherical particle of radius a, $f = 6\pi\eta a$, c.f., Eq. (1.2.17)], and $\vec{v}$ is the particle velocity. When the velocity is non-uniform (i.e. the particle accelerates or decelerates), it experiences a force, $\vec{F}$, described by the Newton's second law which may be written as

$$\vec{F} = m\frac{d^2\vec{r}(t)}{dt^2} \tag{1.2.5b}$$

where $\vec{r}$ is the position vector of the particle, function of time, t, which describes the path of the particle. The velocity of the particle [with initial velocity $\vec{v}_0$ at time t = 0] is determined, upon combining Eq.s (1.2.5a, b), i.e. writing down the force balance, and then integrating it once:

$$\vec{v}(t) = \frac{d\vec{r}}{dt} = \vec{v}_0 e^{-\frac{t}{\tau}}, \qquad \tau = \frac{m}{f} \tag{1.2.6a}$$

and the path of the particle [with the initial position $\vec{r}(t) = 0$, at time t = 0], upon integrating it once more:

$$\vec{r}(t) = \tau\vec{v}_0\left(1 - e^{-\frac{t}{\tau}}\right), \tag{1.2.6b}$$

in which the parameter τ has a dimension of time and is known as "relaxation time" [i.e. a time in which the particle velocity decays to 1/e times its initial value]. Typically, it is of order 10^{-9} sec, depending on the size and mass density of the particle, and its friction coefficient in the medium.

To see how this classical mechanics works for Brownian motion, suppose we would film the motion of a Brownian particle with a film speed of n frames per second. Projecting the film at low speed (for example 4 frames per second) and observing the trajectory of the particle for one second, we would observe the trajectory of the particle at 4 subsequence positions, such as that shown in Fig. 1.1a. If we would project this trajectory with a film speed of 2n frames (8 frames) per second we would observe a different trajectory, as shown in Fig. 1.1b.

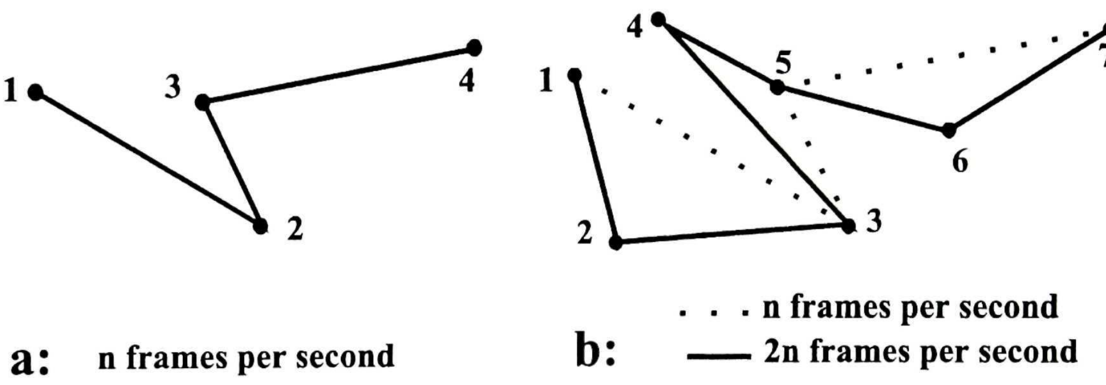

Fig. 1.1 -Trajectory of a particle with two speeds of observation [after van de Ven(1989)].

Thus, increasing the film speed, increases the apparent distance a particle has to travel, as can be seen upon comparing the two trajectories for the same particle at the same period of time, but with two speeds of observation. This increase in path will continue until the film speed reaches about 10^9 frames per second. In addition, the position of the particle also depends on the speed of observation. Stated mathematically, the trajectory of a

Brownian motion is non-differentiable curve. It is impossible to fix a tangent at a given point, because it changes direction with changing the speed of observation. Since velocity in classical mechanics is described as the tangent of the path (which has magnitude and direction), given by the relation (1.2.6a), it is clear that the velocity of a Brownian motion is a meaningless quantity. What is meaningful, instead, is its displacement from a given origin. This was first realized by Einstein (1905), and independently by Smoluchowski (1906).

Therefore, since a Brownian particle is subject to a random displacement, besides the forces described by Eq.s (1.2.5a, b), it experiences a "random" forces denoted by $\vec{A}$ a function of time, due to fluctuations in the random motion of the suspending fluid molecules. According to quantum mechanics, these fluctuations are truly non-deterministic, only statistical averages can be determined:

$$< \vec{A}(t) >= 0 \tag{1.2.7a}$$

$$< \left|\vec{A}(t_1)\right|\left|\vec{A}(t_2)\right| >= 2\frac{kTm^2}{f}\delta(t_1 - t_2) \tag{1.2.7b}$$

in which δ is Dirac delta function defined by

$$\delta(t_1 - t_2) = \begin{cases} \infty & \text{if } t_1 = t_2 \\ 0 & \text{if } t_1 \neq t_2 \end{cases} \tag{1.2.7c}$$

Eq. (1.2.7b) is a mathematical expression of a Markov-process, which is a process in which a future motion is independent of the motion's history.

Combining Eq.s (1.2.5a, b, 7) yields the following force-balance:

$$\frac{d^2\vec{r}}{dt^2} = -\frac{1}{\tau}\vec{v} + \vec{R}, \qquad \vec{R} = \frac{1}{m}\vec{A}(t) \tag{1.2.8a}$$

known as the Langevin equation. Its solution is

$$\vec{r} = \tau\left[\vec{v}_0\left(1 - e^{-\frac{t}{\tau}}\right) + \int_0^t\left(1 - e^{-\frac{t}{\tau}}\right)\vec{R}(t)dt\right] \tag{1.2.8b}$$

Statistical averages can be obtained by averaging Eq. (1.2.8b), upon the use of relations (1.2.4, 7):

$$< |\vec{r}(t)|^2 >= \frac{2kT}{m}\tau^2\left[\frac{t}{\tau} - 1 + e^{-\frac{t}{\tau}}\right] \tag{1.2.8c}$$

Since τ is of order 10^{-9}, in real life $t >> \tau$, and hence the second and third term in the square bracket is much smaller than the first term. Thus, Eq. (1.2.8c) reduces to

$$< |\vec{r}(t)|^2 >= 2\frac{kT}{f}t, \qquad \text{for } t >> \tau \tag{1.2.8d}$$

and for $t << \tau$, in view of the expansion

$$e^{-\frac{t}{\tau}} = 1 - \frac{t}{\tau} + \frac{1}{2}\left(\frac{t}{\tau}\right)^2 - \cdots, \tag{1.2.8e}$$

to

$$< \frac{|\vec{r}(t)|^2}{t^2} >=< v^2 >= \frac{kT}{m}, \qquad \text{for } t << \tau = O\left(10^{-9}\right) \tag{1.2.8f}$$

in agreement with the equipartition of energy, given by (1.2.4), so that Exter was right in postulating this equation, but the difficulty he encountered was that its condition could not be satisfied (as observation times are much larger than τ). The above theory also provides another interpretation of the relaxation time, τ. For times $t << \tau$, the motion is correlated with the motion at the initial time, $t = 0$, while for $t >> \tau$, no correlation between the motion at a given time and time $t = 0$ exist (Markov-process).

1.2.2.2 - Diffusion

Diffusion is the spontaneous equalization of the concentration of colloidal (or other) particles as a result of the chaotic Brownian motion of each particle. It can be easily understood if we consider a container divided in two parts by an imaginary wall. Let each part contains a suspension with different concentration (say, c_1 for the left part and c_2 for the right, with $c_1 > c_2$), and let the imaginary wall have no excess resistance to the motion of the particles. Each particle on each side of the dividing surface undergoes random Brownian displacements. Thus, each particle is equally likely to move to the right or to the left, and hence it does not know it must diffuse in a certain direction. But, since there are more particle available in the intermediate neighborhood of the left side of the imaginary wall than on the right side, on average more particles will move from left to the right than vice versa. Hence, there will be a net transport of particles from higher to the lower concentrations. This is quantitatively described by the Fick's first law:

$$\vec{J} = -D\nabla c, \qquad \nabla = \vec{i}_x \frac{\partial}{\partial x} + \vec{i}_y \frac{\partial}{\partial y} + \vec{i}_z \frac{\partial}{\partial z} \tag{1.2.9a}$$

in which $\vec{J} = J_x \vec{i}_x + J_y \vec{i}_y + J_z \vec{i}_z$ is the flux or number of particles passing a unit area on the surface normal to the direction of concentration changes (concentration gradient) per unit time. In a Cartesian coordinate system of reference, with unit base vectors $\left(\vec{i}_x, \vec{i}_x, \vec{i}_x\right)$, it has three component in the (x, y, z)- direction (for concentration changes in the x-direction, $\partial/\partial x$, in the y-direction, $\partial/\partial y$, and in the z-direction, $\partial/\partial z$, respectively). D is proportionality constant, termed diffusion constant (diffusivity), with a dimension of surface per time (length^2 time^{-1}). Regarding the mass balance in an element volume of the dispersion, the change in the mass with respect to time is equal to the change in the flux of mass in the volume. And since the flux of the particles is proportional to the gradient of the concentration, the mass balance process is determined by the divergence of the flux ($\nabla \cdot \vec{J}$), that is [c.f., Eq. (1.2.9a)]

$$\frac{\partial c}{\partial t} = -\nabla \cdot \vec{J} = D\nabla^2 c, \qquad \nabla \cdot \nabla = \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{1.2.9b}$$

which is Fick's second Law of diffusion. ∇^2 is known as the Laplacian, defined as the dot product of two gradients (or divergence of gradient), and hence it is a scalar operator. Both equations (1.2.9a, b) are equally valid for ions in a solution. In fact, Ficks laws were first developed for diffusion of molecules in a solvent, and because of the similarity between such a system and colloidal dispersions, they have also been applied to the latter. Fick's second Law, Eq. (1.2.9b), can either be considered as describing the diffusion of a single particle, for which c must be interpreted as the probability of finding the particle at a certain position at time t, or for many particle systems, for which c is considered as particle concentration at a given time and position.

Eq. (1.2.9b), is function of both time and position, the solution of which, for particles initial at origin at time $t = 0$, is

$$c(|\vec{r}|, t) = \frac{1}{2\sqrt{\pi D t}} e^{-\frac{|\vec{r}|^2}{4Dt}} \tag{1.2.9c}$$

Here c is the concentration per unit length. From Eq. (1.2.9c) the mean square displacement is determined by

$$< |\vec{r}|^2 > = \int_{-\infty}^{+\infty} |\vec{r}|^2 c(|\vec{r}|, t) d|\vec{r}| = \int_{-\infty}^{+\infty} r^2 \frac{1}{2\sqrt{\pi D t}} e^{-\frac{r^2}{4Dt}} dr = 2Dt, \qquad r = |\vec{r}| \tag{1.2.9d}$$

Now, in view of (1.2.8d, 9d), it is observed that

$$D = \frac{kT}{f} \tag{1.2.10}$$

which is known as Stokes-Einstein (or sometimes as Einstein-Sutherland) equation. This equation is a fundamental equation, relating diffusion to the friction coefficient of a particle. The Stokes-Einstein equation allows Avogadro's number, N_A (= R/k), to be determined from diffusion experiments. This was first done by Perrin (1909). In fact, by this experiment he proved the reality of atoms and molecules, for which he received a Nobel prize.

1.2.3 - Rheology of Suspensions

1.2.3.1 - Viscosity of Suspensions

The first investigation for the viscosity of suspensions (effective viscosity) was made by Albert Einstein (1906). He derived analytically the effective viscosity of a suspension of solid spheres in a liquid of viscosity η_0 as

$$\eta = \eta_0 \left[1 + \frac{5}{2} \frac{v_T}{V_T} + O\left(\frac{v_T}{V_T} \right)^2 \right] \tag{1.2.11}$$

(V_T is the total volume of the mixture; v_T is the total volume of the solid particles assumed to be much smaller than V_T), though he had made a mistake in the coefficient of the volume fraction (5/2) in his first calculation which was corrected by himself, after an analysis of experimental data by Perrin [Perrin (1913)]. In fact, among others, he developed this theory, in his doctoral dissertation (1905) to obtain a model for the resistance to shear of a molecular solution in which the dissolved molecules are large enough (compared to solvent molecules) to be considered to be dissolved in a continuous fluid in the macroscopic scale.

Smoluchowski (1916) pointed out that for a charged particle in an electrolyte, the electrical double layer around the particle might be expected to increase the effective viscosity of the suspension. Hence, he added a term due to the electroviscous effect to the Einstein formula. He assumed that the thickness of the double layer, compared with the particle radius, is small and calculated the effective viscosity as

$$\eta = \eta_0 \left\{ 1 + \frac{5v_T}{2V_T} \left[1 + \frac{1}{\eta_0 \sigma} \left(\frac{2\varepsilon_W \zeta}{a} \right)^2 \right] \right\} \tag{1.2.12}$$

where σ is the specific conductivity of the electrolyte, a the radius of the solid particles and ε_w the the permittivity of water.

Jeffery (1922) extended Einstein's work to ellipsoidal particles, with a different approach, and found that for this case the factor 5/2 in the formula (1.2.11) is replaced by a coefficient depending on the axial ratio of the particles and their orientation with respect to the flow.

Gouth & Simha (1936) improved the Einstein's approximation and obtained the formula correct up to the third power of the volume fraction as

$$\eta = \eta_0 \left[1 + \frac{5v_T}{2V_T} + \frac{109}{14} \left(\frac{v_T}{V_T} \right)^2 + O\left(\frac{v_T}{V_T} \right)^3 \right] \tag{1.2.13}$$

Batchelor & Green (1972) proved that the coefficient of the third term in the expansion (1.2.13) depends on Peclet number and type of flow which varies from 5.2 to 7.6.

Krasny & Ergen (1936) improved Smoluchowski's theory, given by (1.2.12), upon increasing the electroviscous term by a factor 3/2, which may be written as

$$\eta = \eta_0 \left\{ 1 + \frac{5v_T}{2V_T} \left[1 + \frac{6}{\eta_0 \sigma} \left(\frac{\varepsilon_w \zeta}{a} \right)^2 \right] \right\} \tag{1.2.14}$$

Booth (1950b) modified the primary electroviscous effect by combining his theory, given by (1.2.3), with the Einstein formula as

$$\eta = \eta_0 \left\{ 1 + \frac{5 v_T}{2 V_T} \left[1 + \sum_{n=1}^{\infty} b_n \left(\frac{e\zeta}{kT} \right)^n \right] \right\} \tag{1.2.15}$$

in which b_n is an infinite set of constants to be determined (n is an integer). However, He computed only the first two terms of the infinite series.

Dukhin & van de Ven (1993) found a solution for particles with thin double layers, but arbitrary ζ- potentials as

$$\eta = \eta_0 \left\{ 1 + \frac{5 v_T}{2 V_T} \left\{ 1 + \frac{180}{(\kappa a)^2} \ln\cosh\tilde{\psi} \left\{ m_+ f_+(\tilde{\psi}) + m_- f_-(\tilde{\psi}) - \tilde{\psi}\left[m_+ f_+(\tilde{\psi}) - m_- f_-(\tilde{\psi}) \right] \right\} \right\} \right\} \tag{1.2.16a}$$

in which the mobility of ions, $m_\pm$, is related to their diffusion coefficients, $D_\pm$, by

$$m_\pm = \frac{2\varepsilon_m k^2 T^2}{3\eta e^2 z^2 D_\pm}, \tag{1.2.16b}$$

and $\tilde{\psi}$ is the dimensionless ζ-potential defined by the authors as

$$\tilde{\psi} = \frac{ez\zeta}{4kT} \tag{1.2.16c}$$

1.2.3.2 - Motion of a Single Particle

The flow field produced by the motion of a single particle in a quiescent liquid has attracted considerable attention. When a suspension of colloid particles is dilute, that is each particle is far enough from the others not to be influenced by the reflection of the others, the rheology of the suspension can be analysed by studying the behavior of a single particle. Thus, each particle in the suspension can be considered moving in an unbounded medium. Though, this idealization is justified and works for most particles inside such a dilute suspension, for those close to the suspension container the particle-wall interactions should always be taken into account, and play a major role to predict the behavior of such particles in deposition or detachment processes. Particle-wall interactions are discussed in the next section. The most common particle shapes encountered in suspensions of colloid particles are of a simple geometry or can be approximated to a simple geometry, either sphere, cylinder, or ellipsoid. For prescribed translational and angular particle velocities, the macroscopic parameters of primary physical interest are the hydrodynamic forces and torques exerted on the particles by the fluid. Once these parameters are known for a particle, one may immediately solve the inverse problem of determining the state of motion of such a particle from the known gravitational body forces and torques acting on it. Since the problem of the motion of a particle in a quiescent liquid is hydrodynamically similar to the problem of the flow of the liquid on the fixed particle, in the following discussions, sometimes the former is replaced by the latter, or vice versa.

Many of the early contributions to low Reynolds number hydrodynamics are summarized in the book by the Swedish physicist, Carl W. Oseen (1927); of special interest are the contributions of Hilding Faxen, his co-worker, the early papers of whom are discussed by Oseen. His later papers are discussed in a famous book by Happel & Brenner (1965).

The problem of the motion of a sphere in a viscous incompressible fluid first received attention by Stokes (1851) who derived the force, F, experienced by the particle as

$$\vec{F} = -6\pi a\eta \vec{U} \tag{1.2.17}$$

(a is the radius of the sphere, U its uniform velocity) which is the well-known Stokes drag formula for sedimenting a sphere in an unbounded liquid. For an infinite circular cylinder, Stokes equations (the low Reynolds number version of the Navier-Stokes equation) failed to give any solution. The non-existence of a Stokes solution for any two dimensional body fixed in unbounded flow is usually referred to as *Stokes' paradox.*

Oberbeck (1876) considered a spheroid, with semi-axis a and b, aligned along the symmetry axis, b, by neglecting the inertia effects too, leading to a value for the force F (also along the symmetry axis) of magnitude

$$F = -16\pi\eta bU\left\{-\frac{2\left(\frac{a}{b}\right)}{\left(\frac{a}{b}\right)^2-1}+\frac{2\left(\frac{a}{b}\right)^2-1}{\left[\left(\frac{a}{b}\right)^2-1\right]^{3/2}}\ln\frac{\left(\frac{a}{b}\right)+\left[\left(\frac{a}{b}\right)^2-1\right]^{1/2}}{\left(\frac{a}{b}\right)-\left[\left(\frac{a}{b}\right)^2-1\right]^{1/2}}\right\} \tag{1.2.18}$$

Whitehead (1889) attempted to improve the Stokes solution for a sphere by obtaining higher order approximations to the flow when the Reynolds number is not negligibly small.

The method proposed by Whitehead was an iterative procedure to take the inertia effects into account. The particular difficulty encountered by Whitehead was that the second approximation to the velocity of flow remains finite at infinity in a way which is incompatible with the uniform-stream condition. This mathematical phenomenon appears to be common to all problems of uniform streaming past bodies of finite length and is sometimes referred to as *Whitehead's paradox* [Proudman & Pearson (1957)].

The paradox was resolved by Oseen (1910). Oseen pointed out its physical origin and developed a mathematical device for overcoming the difficulties associated with Whitehead's paradox. Oseen found a uniformly valid first approximation to the velocity and all its derivatives, which is itself a linear problem that can be solved analytically, resulting in the Oseen equation. In contrast to Stokes equations, Oseen's equation provided a solution for a two dimensional flow past an infinite cylinder of finite cross-sectional length. The first such solution to be obtained was by Lamb (1911), for which Lamb retained some of the "inertia terms" but omitted the others in his solution. Oseen himself gave a solution for flow past a sphere of radius a and an infinite circular cylinder of radius b (placed perpendicular to the uniform flow), respectively, as

$$F = 6\pi\eta a U\left[1+\frac{3}{8}Re_a\right] \tag{1.2.19a}$$

and

$$F = \frac{4\pi\eta U}{2\ln 2 - \ln Re_b - \gamma + 1/2} \tag{1.2.19b}$$

where Re_a and Re_b are the Reynolds number based on the characteristic length of a and b, and γ is Euler's constant. These parameters are defined by

$$Re_a = \frac{aU}{\nu}, \qquad Re_b = \frac{bU}{\nu}, \qquad \gamma = 0.5772\cdots \tag{1.2.19c}$$

Burgers (1938) derived the force on a long slender ellipsoid of revolution with the result exactly the same as the asymptotic result of the Oberbeck (1876)'s formula, given by (1.2.18), for large b/a. He also applied his method to determine the force acting on a circular cylinder of finite length fixed in a uniform stream flowing in the direction of its symmetry axis. For this case, he obtained the total force acting on the cylinder as

$$F = \frac{4\pi\eta a U}{\ln\left(2\frac{a}{b}\right) - 0.72} \tag{1.2.20}$$

where a and b are, respectively, the semi-length and the cross-sectional radius of the cylinder.

Lagerstorm & Cole (1955) introduced Oseen and Stokes variables and obtained Oseen and Stokes expansions which followed naturally from the limit processes they adopted.

A well-known paper by Proudman & Pearson (1957) considered the problem in more detail giving an intensive theoretical study of the subject. Proudman & Pearson (1957) and also Kaplun & Lagerstorm (1957) demonstrated that it is possible to obtain higher order approximations to the flow past a sphere and a circular cylinder by applying the method of Stokes and Oseen expansions, the so called *matched asymptotic expansion* technique, which is also the main tool used in Chapters two and three of this thesis. Proundman & Pearson 's studies (1957) led to improving the approximation of the Oseen drag force acting on a sphere and on an infinite circular cylinder, respectively, as

$$F = 6\pi a\eta U\left[1 + \frac{3}{8}Re_a + \frac{9}{40}Re_a^{\,2}\ln Re_a + O\left(Re_a^{\,2}\right)\right] \tag{1.2.21}$$

and

$$F = -4\pi\eta U\left[\frac{1}{\ln Re_b} + \left(\frac{1}{\ln Re_b}\right)^2\left(\gamma + \frac{1}{2} - 2\ln 2\right)\right] + O\left(\frac{1}{\ln Re_b}\right)^3 \tag{1.2.22}$$

Broersma (1960) improved the method outlined by Burgers (1938). He took the disturbance produced by a cylindrical body as being that due to a line of force of magnitude

$$\left.\begin{aligned} f(z) &= B_0 + B_2\left(\frac{z}{a}\right)^2 + B_4\left(\frac{z}{a}\right)^4 + \cdots \qquad \text{if}\,|z| < a \\ f(z) &= 0 \qquad\qquad\qquad\qquad\qquad\qquad \text{otherwise} \end{aligned}\right\} \tag{1.2.23a}$$

where B_0, B_2, B_4 ... are an infinite set of constants to be determined. Broersma computed the values of these constants numerically (for the case of a circular cylinder of finite semi-length a and cross-sectional radius b being fixed in a fluid with uniform velocity U flowing in the direction of the symmetry axis) and obtained the force on the cylinder as

$$F = \frac{4\pi\eta a U}{\ln\left(2\frac{a}{b}\right) - 0.81} \qquad (1.2.23b)$$

which is similar to the formula (1.2.20), but differs from it by a numerical factor.

Taylor (1969) proved that if the Reynolds number is very small, a slender body of revolution falls twice as fast axially as it does transversely.

Cox (1970), by neglecting inertia effects, derived the force density (force per unit length) on a fixed curved slender body of circular cross-sections (the radius may varies along the body centerline) with length l and with the characteristic dimension of the body cross-section b by expanding the solution directly in powers of $1/\ln\delta$ (δ is the slenderness parameter defined by $\delta = b/l$) up to $O(1/\ln \delta)^3$. He obtained a solution for the force per unit length, for examples involving bodies having a curved centerline. For the special case of sedimenting of a torus (with constant circular cross section falling normal to its centre line), he derived the total force:

$$F = \frac{6\pi^2\eta a U}{\frac{1}{3} - \ln\frac{\pi}{4} - \ln\delta} + O\left(\frac{1}{\ln\delta}\right)^3 \qquad (1.2.24)$$

Batchelor (1970) adopted the slender body theory to a straight non-axisymmetric body. From an investigation of the local inner flow field in the vicinity of a section of the body, and the condition that it should join smoothly with the outer flow which is determined by the body as a whole, Batchelor observed that a given shape and size of the local cross-section is equivalent, in all cases of transverse relative motion, to an ellipse of certain dimensions and orientation, and in all cases of longitudinal relative motion, to a circle of certain radius. The equivalent circle and the equivalent ellipse (characteristic tensor) of the cross-sectional shape may be found from certain boundary-value problems by solving the harmonic and biharmonic equations, respectively [Details of such a solution by complex variable method is given in Tabatabaei (1995), Appendix A].

Batchelor (1972) devised a method for calculation of the mean velocity of the sedimentation of the spherical particles in a dilute dispersion.

Johnson & Wu (1979) considered the Stokes flow passing a slender torus of circular cross-section. By the method of distribution of singularities (stokeslets, doublets, rotlets, sources, stresslets and quadrupoles) on the body centreline, they satisfied the no slip boundary condition on the body surface, in closed form, up to an error of $O(\varepsilon^2 \ln\varepsilon)$ (ε is the semi-slenderness parameter, ratio of the radius of cross-section to the half length), and hence they obtained the force (correct up to order ε^2) and/or the torque the torus experienced for the individual cases of the broadwise translation (motion along the longitudinal axis), translation normal to the longitudinal axis, rotation of a torus on its edge, spinning and expanding of a torus. For the case of axial translation of a torus with cross-sectional radius b and body centreline radius a, their studies results in

$$F = -\frac{4\pi\eta U}{\ln 8/\varepsilon + 1/2} + O(\varepsilon^2) \tag{1.2.25a}$$

where $\varepsilon = b/a$, and F is the axial component of the force per unit length acting on the torus. For the case of transverse motion perpendicular to the torus axis, they obtained the total drag as

$$F = \frac{2\pi^2 \eta a U (3\ln 8/\varepsilon - 17/2)}{(\ln 8/\varepsilon - 1/2)(\ln 8/\varepsilon - 2) - 2} + O(\varepsilon^2) \tag{1.2.25b}$$

where by neglecting terms of order $(1/\ln\varepsilon)^3$ this leads to Cox's result given by (1.2.24).

Johnson (1980) generalised the method used by Johnson & Wu (1979) (singularity method) for flow past slender bodies of finite centreline curvature. He applied his theory to a torus of a circular cross-section with the same result as that obtained directly by Jonson & Wu (1979), given by (1.2.25a).

Khayat & Cox (1989) took inertia effects into account and adopted Batchelor (1970)'s observation for a non-axisymmetric body to Cox (1970)'s theory. They assumed the Reynolds number Re based on the body length is arbitrary and derived the force per unit length on a curved slender body of arbitrary transverse cross-section (at rest in unbounded fluid undergoing undisturbed uniform velocity U) in terms of the semi slenderness parameter, ϵ, correct up to order $(1/\ln \epsilon)^3$. They applied the force equation to the uniform flow past a long straight slender body of arbitrary cross-section, and derived the force density experienced by the body, F(s), as

$$\frac{F(s)}{2\pi\eta U} = \frac{1}{\ln\varepsilon}\left(\vec{t}\cos\theta - 2\vec{i}\right) + \left(\frac{1}{\ln\varepsilon}\right)^2 \left\{\frac{1}{4}\left[2\vec{i}\cos\theta - \left(2 - \cos\theta + \cos^2\theta\right)\vec{t}\right] \times \right.$$
$$\left[\frac{1 - e^{-\frac{1}{2}Re(1-\cos\theta)(1+s)}}{\frac{1}{2}Re(1-\cos\theta)(1+s)} - 1\right] - \frac{1}{4}\left[2\vec{i}\cos\theta - \left(2 + \cos\theta + \cos^2\theta\right)\vec{t}\right] \times$$
$$\left[\frac{1 - e^{-\frac{1}{2}Re(1+\cos\theta)(1-s)}}{\frac{1}{2}Re(1+\cos\theta)(1-s)} - 1\right] - \frac{1}{2}\left(\vec{t}\cos\theta - 2\vec{i}\right)\left\{E_1\left[\tfrac{1}{2}Re(1-\cos\theta)(1+s)\right]\right.$$
$$\left. + \ln(1-\cos\theta)\right\} - \frac{1}{2}\left(\vec{t}\cos\theta - 2\vec{i}\right)\left\{E_1\left[\tfrac{1}{2}Re(1+\cos\theta)(1-s)\right] + \ln(1+\cos\theta)\right\}$$
$$\left. -\left(\vec{t}\cos\theta - 2\vec{i}\right)\left(\gamma + \ln\frac{Re\lambda_s}{4}\right) + \frac{3}{2}\vec{t}\cos\theta - \vec{i} + 2\vec{i}\cdot\vec{\vec{Q}} + \vec{t}\cos\theta\ln q \right\} + O\left(\frac{1}{\ln\varepsilon}\right)^3 \qquad (1.2.26a)$$

where $\epsilon = b/a$ (b being the characteristic length of the cross-sectional shape and a is the half length of the body); $\vec{t}$ is a unit vector, representing the direction of the body centreline; $\vec{i}$ is the unit vector in the direction of velocity U; θ is the angle between the unit vectors $\vec{t}$ and $\vec{i}$ (i.e. $\vec{i}\cdot\vec{t} = \cos\theta$); γ is Euler's constant; Re is the Reynolds number based on the body half-length; λ_s is the radius of the equivalent circle of the cross-section at the point under consideration, s [where s ($-1 \le s \le +1$) is the arch length along the body centreline measured from its midpoint]; $\vec{\vec{Q}}$ is the characteristic tensor of the transverse cross-sectional shape; q is the charateristic scalar which depends on the cross-sectional shape (charateristic scalar of the cross-section for longitudinal relative motion), for a sphere q = 1, and where $E_1(x)$ is the exponential integral defined by

$$E_1(x) = \int_x^\infty \frac{e^{-\tau}}{\tau}d\tau \qquad (1.2.26b)$$

in which the argument x for the formula (1.2.26a) is $\left[\frac{1}{2}Re(1-\cos\theta)(1+s)\right]$ and $\left[\frac{1}{2}Re(1+\cos\theta)(1-s)\right]$. While they applied their theory to an infinite straight slender body, with large Re, they realized that it fails to give a uniform valid solution, and hence a minor modification is needed. They gave a theoretical reason for this violation and pointed out that for an infinite slender body together with large Re the force should be expanded in $(\ln R_b)^{-1}$ (R_b being the Reynolds number based on the characteristic length of the cross-sectional shape) instead of $(\ln\delta)^{-1}$ and lengths, in the outer region, should be made dimensionless by (ν/U) (ν being the kinematic viscosity of the fluid) rather than a (half length of the body). By this modification, their research for the special case of an infinite straight cylinder of constant circular cross-section, placed perpendicular to uniform flow, leads to the Proudman & Pearson's result, given by (1.2.22).

Cox (unpublished), in his last sabbatical (1992 or 93), improved the inertia effects in the slender body theory of circular cross-section, but with an arbitrary body centreline configuration. He derived a force integral equation by considering the Reynold numbers based on the body length being of order unity. For low Reynolds number fluid flows, his theory leads to the Johnson's theory (1980). He applied his theory to derive the force on the sedimentation of a torus which, for low Reynolds number flows, leads to a different result than that obtained by Jonson & Wu (1979) and Jonson (1980), given by (1.2.25a).

Tabatabaei (1995) extended Cox's theory to arbitrary body cross-sectional shapes. He applied his theory to a straight slender body of arbitrary cross-section and to a torus of uniform arbitrary cross-sectional shape. For the former he obtained a result in a complete agreement with the formula (1.2.26), directly obtained by Khayat & Cox (1989). For the latter he derived the radial and normal components of the force density (F_ρ, F_z) experienced by the torus correct up to $O(\delta)$ as

$$F_\rho = \frac{-8\pi\eta U\left(\frac{2\pi}{Re}A_1 + A_2 2Q_{13}\right)}{\left(\frac{2\pi}{Re}A_1 + A_2 2Q_{13}\right)^2 - \left(A_1 - 1 - \frac{4\pi}{Re}A_2 + \frac{4\pi^2}{Re} - 2\ln\frac{\pi\lambda_s\delta}{4} - 2Q_{11}\right)\left(A_1 + 1 - 2\ln\frac{\pi\lambda_s\delta}{4} - 2Q_{33}\right)} \quad (1.2.27a)$$

$$F_z = \frac{-8\pi\eta U\left(A_1 - 1 - \frac{4\pi}{Re}A_2 + \frac{4\pi^2}{Re} - 2\ln\frac{\pi\lambda_s\delta}{4} - 2Q_{11}\right)}{\left(\frac{2\pi}{Re}A_1 + A_2 2Q_{13}\right)^2 - \left(A_1 - 1 - \frac{4\pi}{Re}A_2 + \frac{4\pi^2}{Re} - 2\ln\frac{\pi\lambda_s\delta}{4} - 2Q_{11}\right)\left(A_1 + 1 - 2\ln\frac{\pi\lambda_s\delta}{4} - 2Q_{33}\right)} \quad (1.2.27b)$$

in which Q_{ij} are the characteristic tensor of the cross-sectional shape, λ_s is the radius of its equivalent circle (i.e. $2\pi\lambda_s$ is the perimeter of the local cross-section), and (A_1, A_2) are function of Re, determined by the integrals:

$$A_1 = \int_0^\pi \left[\frac{e^{-\frac{1}{2\pi}Re\sin\frac{\theta}{2}}}{\sin\frac{\theta}{2}} - \frac{1}{\sin\frac{\theta}{2}}\right]d\theta, \qquad A_2 = \int_0^\pi e^{-\frac{1}{2\pi}Re\sin\frac{\theta}{2}}\,d\theta \quad (1.2.27c)$$

For an elliptical cross-section with semi-diameters a and b (with a $>$ b) and with the direction of larger principal axis (2a) given by unit vector $\vec{t}$, Q_{ij} are determined by

$$Q_{11} = \ln\frac{a+b}{2\lambda_s} + \frac{a-b}{(a+b)}\cos^2\alpha,\ Q_{13} = \frac{a-b}{2(a+b)}\sin 2\alpha,\ Q_{33} = \ln\frac{a+b}{2\lambda_s} + \frac{a-b}{(a+b)}\sin^2\alpha \tag{1.2.27d}$$

in which α is the angle between the direction of larger principal axis and uniform velocity U (i.e. $\cos\alpha = \vec{t}\cdot\vec{i}_z$) and λ_s is determined by

$$\lambda_s = \frac{2a}{\pi}E\left[\sqrt{1-\frac{b^2}{a^2}}, \frac{\pi}{2}\right], \qquad E\left[K, \frac{\pi}{2}\right] = \int_0^{\frac{\pi}{2}}\sqrt{1-K^2\sin^2\phi}\,d\phi \tag{1.2.27e}$$

where E(K, $\pi/2$) is the complete elliptic integral of the second kind the values of which, for various values of $K = (1 - b^2/a^2)^{1/2}$, are available in tables. For a torus of a circular cross-section (i.e. a = b and $\lambda_s = 1$), Q_{ij} in formula (1.27a, b) vanish [c.f., (1.2.27d)]. For circular cross-section, by neglecting the inertia effects, i.e. in the limit as Re $\rightarrow$ 0, the only non-zero component of the force, F_z, leads to Jonson & Wu (1979) and Johnson (1980)'s results, given by (1.2.25a), and for Re of order unity to the correction for the Cox's solution.

Russel (1978a, b) formulated a theory of the rheology of suspensions of charged rigid spheres. He calculated the bulk stresses due to the deformation of the electrical double layer surrounding a charged sphere. These stresses are derived for a dilute dispersion of spheres which have small surface charges and with a thin double layer.

Lever (1979) studied the large distortion of the electric double layer around a charged particle by a shear flow. For weak flows, a second-order-fluid approximation was obtained for the stress contribution for a dilute suspension of such particles. For arbitrary strong flows an integral representations of the charge density and the numerical calculations of the stress contribution are given for three representative flows, simple shear, axisymmetric strain and two-dimensional straining motion.

Sherwood (1980) assumed an arbitrary value for the surface potential of the particles and found that for non-dimensional potential value smaller than two, $\tilde{\psi} < 2$, the predictions are altered by less than10 %, whilst for higher values, specially when the charge cloud is much thinner than the radius of the charged sphere, the differences between linear and non-linear theory are not negligible.

Ohshima, Healy, White & O'Brien (1984) did a theoretical study on the sedimentation velocity (electroviscous velocity) and potential (streaming potential) in a dilute suspension of charged spherical colloidal particles. They derived a general expression for the sedimentation velocity (U_{SED}) and potential in a dilute suspension of charged spherical rigid particles in an electric solution in terms of the liquid flow and the potential of the electrolyte ions. They obtained the exact numerical result for the sedimentation velocity and potential as functions of the ζ-potential and κa. They also derived analytical expressions for small $\tilde{\psi}$ and for large κa with arbitrary $\tilde{\psi}$. For the latter, they formulated the sedimentation velocity (U_{SED}) as [Eq. (78) in their paper]

$$U_{SED} = \left\{1 + \frac{12}{(\kappa a)^2}\left[m_1 G_P^2 + \frac{m_2 H_P^2}{(1+I)}\right] + O\left[\frac{1}{(\kappa a)^3}\right]\right\} U_{SED}^{ST} \qquad (1.2.28a)$$

where m_1 and m_2 are the scaled ionic mobilities for counterions and coions, respectively, given by [c.f., Eq. (1.2.16b)]

$$m_i = \frac{2\varepsilon_m kT}{3\eta(z_i e)^2}\lambda_i \qquad (1.2.28b)$$

in which λ_i is the drag coefficient of the i^{th} ionic species related to the limiting conductance of the same ionic species (A^0_i) or molar conductivity (A_i) by

$$\lambda_i = \frac{N_A e^2 |z_i|}{A_i^0} = \frac{N_A e^2}{A_i} \qquad (1.2.28c)$$

(N_A is Avogadro number); U_{SED}^{ST} is the Stokes velocity for uncharged particle; G and H are defined by relationships (1.2.32c) and I by

$$I = \frac{2}{\kappa a}\left(1 + \frac{2\varepsilon_m kT}{\eta(z_2 e)^2}\lambda_2\right)\left[\exp\left(\tilde{\psi}/2\right) - 1\right] \qquad (1.2.28d)$$

in which $\tilde{\psi}$ is th7e dimensionless electrokinetic potential (particle surface ζ- potential), defined [differently than (1.2.16c)] by

$$\widetilde{\psi} = \frac{ez\zeta}{kT} \qquad (1.2.28e)$$

Although it was not mentioned by the authors, Cox(1997) pointed out that this theory is valid for low Peclet numbers.

Schumacher & van de Ven (1987) studied the diffusion coefficients of charged colloidal particles surrounded by electrical double layers by the use of photon correlation spectroscopy. They found that the diffusion constant equals the value of a neutral sphere at high and low electrolyte concentrations, but is reduced by several percent when the electrical double layer is comparable to the radius of the particle. The reduction depends on the ζ-potential of the particle and the sizes of the ions in the double layer. They also found that the diffusion of charged particle can be explained by the Ohshima *et al* (1984)'s theory, assuming that the friction coefficient of a charged sphere in Brownian motion equals the equilibrium friction coefficient of a sedimenting sphere.

van de Ven (1988) studied streamlines around a charged sphere in simple shear flow and found that the region of closed streamlines is larger than for a neutral sphere. He concluded that a small neutral particle approaching a large charged sphere feels an additional repulsion on approach and an additional attraction after the encounter.

Schumacher & van de Ven (1991), by using photon correlation spectroscopy, determined translational diffusion coefficients of electrostatically stabilized rod shaped colloidal particles, TMV (tobacco mosaic virus). They found that when the double layer thickness is comparable to the radius of an equivalent sphere of the rod, the diffusion constant reduces by a few percent, depending on both the sizes of the ions and the charge on the rod. The experimental data is found to indicate that, at the salt concentrations used, TMV behaves like a model colloidal particle. They also obtained the effective charge on the individual TMV particles, as well as an estimate of their ζ-potential.

Dukhin & van de Ven (1994) studied the trajectories of charged tracer particles around a charged sphere in a simple shear flow. They found several new types of trajectory, besides the closed and open trajectories. They concluded that the richness of possible trajectories is due to three electrokinetic phenomena: electro-osmotic slip, electrophoretic motion and diffusiophoretic motion.

1.2.3.3 - Squeezing and Sliding Motion

The study of hydrodynamic interactions of rigid particles, under the slow motion induced by an external force, was initiated by Smoluchowski (1911). He outlined a method, known as 'reflections method', to determine the flow field for an array of particles that are sufficiently close to each other to be hydrodynamically interacting, and the whole system is far enough from the wall to be considered an unbounded flow. An extensive review of such solutions is presented in the book by Happel & Brenner (1965).

Stimpson & Jeffery (1926) obtained the exact solution of Stokes equations for two spheres (equal or unequal size) falling parallel to their line of centres (an axisymmetric flow), by employing a bipolar coordinate system, upon the use of Jeffery's (1912) solution of Laplace's equation. The bipolar coordinates, discussed in Appendix A, best described the geometry of the problem of two sphere or a sphere and wall, and hence allows one to simultenuously satisfy the boundary conditions on the solid surfaces for such a boundary value problem. The details of such a solution for interaction of sphere and wall is presented in the hydrodynamic part of Chapter four of this dissertation.

Oseen (1927) improved the inertia effects, in the Smoluchowski (1911)'s theory, for the case of two sphere, by replacing the Stokes field with Oseen's field.

Kynch (1952) presented general formulas to provide an analytic analysis for the case of three or more spheres. This expressions are so complicated that generalization are only possible for a simple geometry of configuration. So far the hydrodynamic interaction of particles has been solved for not more than three particles, done by Kynch himself.

A number of authors have contributed to the development of purely hydrodynamic interactions of two particles or in general two surfaces. Among them we may mention the work by Dean & O'Neill (1963), O'Neill (1964), Cooley & O'Neill (1967), Goldman, Cox & Brenner (1966, 67), Darabaner & Raasch & Mason (1967), O'Neilll & Stewartson (1967), Cox & Brenner (1967, 68, 71), Cox & Zia & Mason (1968), Curtis & Hocking (1969), Lin & Lee & Sather (1969), Batchelor (1972), Batchelor & Green (1972), Cox (1974), van de Van & Mason (1976) and Kao & Cox & Mason (1977).

Darabaner *et al.* (1967) have investigated both theoretically (by the use of bipolar coordinates) and experimentally the interaction of two infinitely long cylinders in a Couette flow. They showed that the cylinders move either along open orbits extending to infinity in both upstream and downstream directions or in closed orbits around each other forming a permanent doublet. They have illustrated that in the limiting case where the radius of one cylinder tends to zero while the other remains constant one would expect the orbit of the smaller cylinder to be the streamline around the larger one.

Cox *et al.* (1968) studied theoretically the streamlines around an infinitely long cylinder and around a sphere moving freely in Couette shear flow. For flow around a cylinder, they obtained the streamline, Ψ as

$$\Psi = -\frac{1}{4}G\left[\rho^2 - 1 + \left(\rho^2 - 2 + \rho^{-2}\right)\cos 2\phi\right] \qquad (1.2.29a)$$

from which the velocity components $\left(u_\rho, u_\phi\right)$ are obtained by

$$u_\rho = \frac{1}{\rho}\frac{\partial \Psi}{\partial \phi}, \qquad u_\phi = -\frac{\partial \Psi}{\partial \rho} \qquad (1.2.29b)$$

in which G = 2 Ω is the shear rate (Ω being angular velocity of the cylinder relative to polar axes (ρ, Φ). For free spheres, they obtained the streamline which satisfies the following relations in spherical polar coordinates (r, θ, Φ) with the origin at the centre of the moving sphere:

$$\frac{1}{r}\frac{\partial r}{\partial t} = \frac{1}{4}G\sin^2\theta\sin 2\phi\left[3r^{-5} - 5r^{-3} + 2\right], \qquad (1.2.30a)$$

$$\frac{\partial \theta}{\partial t} = -\frac{1}{4}G\sin 2\theta\sin 2\phi\left[r^{-5} - 1\right] \qquad (1.2.30b)$$

$$\frac{\partial \phi}{\partial t} = -\frac{1}{4}G\left[2\cos\phi\, r^{-5} - \cos 2\phi - 1\right] \qquad (1.2.30c)$$

In both cases, they obtained open and closed streamlines separated by a limiting streamline or surface. These correspond to separating and permanent collision doublets of cylinders and of spheres in the limiting case in which the ratio of diameters of the two interacting particles (two cylinders or two spheres) is zero. Their theory is in complete agreement with Darabaner *et al.*'s theoretical study (1967) and experimental observation.

Lin *et al.* (1969) solved the Stokes equations for two spheres of arbitrary size and orientation with respect to the shear field by the use of spherical bipolar coordinates. They calculated numerically the trajectory of the free motion of the sphere for the two cases of (1) two equal-sized spheres in a simple shear flow, and (2) a sphere near a wall in a rotational shear flow between two parallel disks rotating at different rates, where the results for the first case agrees fairly well with those observed experimentally.

Batchelor & Green (1972) studied the purely hydrodynamic interaction of two unequal sized spheres in unbounded flow whose velocity at infinity is assumed to be a linear function of position. They found the velocity either of each sphere relative to the other together with the force dipole strength tensors of the two spheres as a function of the position vector of the either sphere relative to the other. Both the velocity and the force dipole strengths depend linearly on the rate of strain at infinity which can be expressed as a function of scalar quantities r/a and b/a (r being the magnitude of the position vector $\vec{r}$; a and b radius of the spheres). They determined the asymptotic solution of the functions for both cases of $r/(a+b) >> 1$ and $r - (a+b) << $ either a or b whichever is smaller. For the special case of two equal spheres in a steady simple shearing motion they analysed the closed trajectories of one of them relative to the other both analytically and numerically.

Kao *et al.* (1977) investigated a general two dimensional linear flow having pure shear flow as one limiting case and pure rotation as the other one, with simple shear flow as an intermediate case. They calculated the streamlines around a rigid, neutral sphere in creeping flow and found that for flow regimes between pure and simple shear both types of closed and open streamlines exist, whilst only closed ones exist between simple shear and pure rotation. There is no closed streamlines for pure shear. They also calculated the trajectories of interaction of two equal sized spheres for these types of flow and found that closed trajectories do not exist in a large regime of flows near pure shear.

Boluk & van de Ven (1989) studied the deposition of titanium dioxide particles onto cellophane and glass surfaces in a stagnation point flow. They concluded that the discrepancies between observations and DLVO theory [after Derjaguin & Landau (1943) and Verwey & Overbeek (1948)] can be explained by including ion-size effects in the hydrodynamic correction functions which describe hydrodynamic particle-wall interactions.

Warszynski & van de Ven (1990) did a theoretical study of electroviscous forces in a suspension of charged particles. Using the squeezing-flow approximation, they analysed the interaction of charged disks, and calculated the total friction coefficient. Using the Derjaguin approximation, they also calculated the relative friction coefficient for two charged spherical particles to obtain the theoretical rates of the coagulation and/or deposition process. They compared the theory with experimental data and found a good agreement between the theory and coagulation, but a significant discrepancy for the deposition process.

Bike & Prieve (1990) applied lubrication theory to study the squeezing motion and also sliding motions of two surfaces bearing thin double layers in an electrolyte solution for the cases when the double layer is much thinner than the minimum distance separating the two bodies. For sliding motion of a spherical particle along a plane wall they obtained a general integral expression for the force the fluid exerts on the body in the direction normal to the wall (F_z) and evaluated it numerically as

$$F_z = \frac{\pi a \varepsilon_m^3 U^2}{K^2 h^3}\left[0.3840.0\zeta^2 + 0.1810\zeta\Delta\zeta + 0.0242(\Delta\zeta)^2\right] \qquad (1.2.31)$$

in which a is the particle radius, h the minimum clearance between the particle and the wall, K is the conductivity of the medium, ζ the average of ζ-potentials of the particle and the wall, and $\Delta\zeta$ is their differences. They concluded that always $F_z \geq 0$, regardless of the sign and magnitude of ζ-potential, and so they called F_z the electrokinetic lift force. However, experimental observations show that this theory and some other theories which appeared in the literature underestimate the force by several orders of magnitude. It was pointed out by Cox (1997) that the discrepancy between the experimental observations and these theories is due to the fact that the authors *a priori* assumed that the dominant electroviscous force, arising from the coupling between electrical and hydrodynamic equations, would be due to the contribution of the Maxwell stress tensor resulting from the streaming potential. In reality the contribution to the electroviscous force from hydrodynamic effects is two orders of magnitude greater than that of electric effects.

Wu, Warszynski & van de Ven (1996) calculated numerically the lift force per unit length experienced by a long cylinder in a sliding motion along a plane wall for an arbitrary Peclet number and $\kappa^{-1} << h << a$. They also conducted experiments on a sphere and a wall under the same conditions. Using the Derjaguin approximation, they converted their calculation and also Cox's analytical expression for the lift force (reported in the same paper) from a cylinder-wall system to a sphere-wall system and observed that there was a good agreement between these two theories and their experiment. Cox's formula for the electroviscous lift force per unit length experienced by an infinite cylinder under translation and rotation parallel to a plane wall in a symmetric electrolyte, obtained from his general theory, for low Peclet numbers and $\kappa^{-1} \ll h \ll a$, is presented as

$$F_z = \frac{\sqrt{2}\pi}{8}\frac{(\varepsilon_r\varepsilon_0)^2(kT)^3}{(z_1 e)^4 c_\infty}\frac{a\sqrt{a}}{h^2\sqrt{h}}\left\{\left[\frac{(G_P+G_W)(9G_P+G_W)}{D_1^2}+\frac{(H_P+H_W)(9H_P+H_W)}{D_2^2}+\frac{2(9G_PH_P+5G_PH_W+5G_WH_P+G_WH_W)}{D_1D_2}\right]V^2+4Va\Omega\left[\frac{(G_P+G_W)(4G_P+3G_W)}{D_1^2}+\frac{(8G_PH_P+7G_PH_W+7G_WH_P+6G_WH_W)}{D_1D_2}+\frac{(H_P+H_W)(4H_P+3H_W)}{D_2^2}\right]+8(a\Omega)^2\left[\frac{G_P+G_W}{D_1}+\frac{H_P+H_W}{D_2}\right]^2\right\} \tag{1.2.32a}$$

where a is the radius of the cylinder; Ω is its angular velocity with the clockwise direction; V is the velocity of the nearest point of the cylinder to the wall, that is

$$V = U - a\Omega \tag{1.2.32b}$$

(U is its translation velocity parallel to the wall); c_∞ is the number ionic bulk concentration, z_1 is ion valency of either species; D_1 and D_2 are ions diffusion coefficients (diffusivity) of counterions and coions, respectively, and where (G_P, H_P) and (G_W, H_W) are defined by

$$G_J = \ln\frac{1+\exp\left(-\frac{\tilde{\psi}_J}{2}\right)}{2},\quad H_J = \ln\frac{1+\exp\left(+\frac{\tilde{\psi}_J}{2}\right)}{2} \qquad J=(P,W) \tag{1.2.32c}$$

in which $\tilde{\psi}_P$ and $\tilde{\psi}_W$ are the dimensionless particle and wall ζ-potentials, defined by relation (1.2.28e). Cox also obtained the tangential component of the force as

$$\begin{aligned} F_x = &-2\sqrt{2}\pi\eta\sqrt{\frac{a}{h}}(V+a\Omega)\\ &-\frac{\sqrt{2}\pi}{2}\frac{(\varepsilon_r\varepsilon_0)^2(kT)^3}{(z_1e)^4c_\infty}\frac{\sqrt{a}}{h^2\sqrt{h}}\left\{\left[\frac{5G_P^2+2G_PG_W+G_W^2}{D_1}+\frac{5H_P^2+2H_PH_W+H_W^2}{D_2}\right]V\right.\\ &\left.+2\left[\frac{3G_P^2+4G_PG_W+G_W^2}{D_1}+\frac{3H_P^2+4H_PH_W+H_W^2}{D_2}\right]a\Omega\right\} \end{aligned} \tag{1.2.32d}$$

The first term is the purely hydrodynamic drag and the second one is the electroviscous drag.

Warszynski & van de Ven (2000), applying lubrication theory, obtained, in a direct fashion, an analytical expression for the electroviscous forces per unit length experienced by an infinite cylinder moving normal to its centerline parallel to a plane wall in a symmetric electrolyte with velocity U, for low Peclet numbers and $\kappa^{-1} << h << a$. The lift component of the force may be expressed as

$$\begin{aligned} F_z = &\frac{\sqrt{2}\pi}{8}\frac{(\varepsilon_r\varepsilon_0)^2(kT)^3}{(z_1e)^4c_\infty}\frac{a\sqrt{a}}{h^2\sqrt{h}}\left(\frac{G_W}{D_1}+\frac{H_W}{D_2}\right)\left(\frac{9G_P}{D_1}+\frac{9H_P}{D_2}+\frac{G_W}{D_1}+\frac{H_W}{D_2}\right)U^2\\ &+\frac{\pi\sqrt{2}}{16}\frac{(\varepsilon_r\varepsilon_0)^3(kT)^4}{(z_1e)^6c_\infty^2}\frac{\sqrt{a}}{h^3\sqrt{h}}\left[7\left(\frac{G_P}{D_1}-\frac{H_P}{D_2}\right)^2+\left(\frac{G_W}{D_1}-\frac{H_W}{D_2}\right)^2\right.\\ &\left.+4\left(\frac{G_P}{D_1}-\frac{H_P}{D_2}\right)\left(\frac{G_W}{D_1}-\frac{H_W}{D_2}\right)\right]U^2 \end{aligned} \tag{1.2.33}$$

The first term is due to the hydrodynamic effects and the second one is due to the Maxwell stress tensor resulting from deformation of the potentials (streaming potential). Warszynski & van de Ven (2000) also derived an expression for the drag component of the force containing an integral which is evaluated numerically. Their results agree with Wu, *et al.*'s numerical solution (1996) for arbitrary Peclet numbers.

1.3 - Cox's General Theory

1.3.1 - Problem Statement

Cox considered 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.

At position $\vec{r}$ relative to some fixed origin and at time t, the velocity of the liquid is taken as $\vec{v}$ and the pressure as p. The ion concentration of the species i is taken as c_i the electric potential as ψ and the charge density as ρ. The concentrations of the ions each satisfy the convective diffusion equation which may be written as

$$\nabla \cdot \left[D_i \nabla c_i - c_i \left(\pm \vec{v}_{iE} + \vec{v} \right) \right] = \frac{\partial c_i}{\partial t} \quad (1.3.1a)$$

(with + sign for counter-ions and - one for co-ions) in which D_i is the diffusion coefficient of ion i, and where $\vec{v}_{iE}$ is the velocity of the ion i, produced by the electric field, $\vec{E}$, induced by the charged particle and/or wall. Introducing the Lorentz- Stokes-Einstein equation,

$$\vec{v}_{iE} = \frac{\vec{F}_{iE}}{f_i} = -\frac{D_i z_i e}{kT} \nabla \psi \quad (1.3.1b)$$

[$\vec{F}_{iE} = -(z_i e) \nabla \psi$, (Lorentz equation) is the electric force experienced by the ion i, f_i is Stokes friction coefficient, obtained by the relation (1.2.10)], to Eq. (1.3.1a) results in

$$\nabla \cdot \left[D_i \nabla c_i + c_i \left(\pm \frac{D_i z_i e}{kT} \nabla \psi - \vec{v} \right) \right] = \frac{\partial c_i}{\partial t} \quad (1.3.1c)$$

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 $-z_1 e$ for i = 1 and i = 2, respectively, so that only symmetric electrolytes are considered, that is electrolytes in which both species of ion have the same valency z_1.

The variables are made dimensionless by the length scale, L (L being for example the particle size or the distance between the particle and wall), velocity V (an appropriate characteristic velocity), the liquid viscosity, η, and the ion concentration, c_∞ (where c_∞ is the characteristic value of the ion concentration and is taken to be the value of c_1 or c_2 at infinity). Therefore, the independent variables $\vec{r}$, t and dependent variables $\vec{v}$, p, c_1, c_2, ψ and ρ may be expressed in terms of corresponding dimensionless quantities (shown with a tilde) as

$$\vec{r} = L\tilde{\vec{r}} \qquad t = \frac{L}{V}\tilde{t} \tag{1.3.2a}$$

and

$$\vec{v} = V\tilde{\vec{v}} \qquad p = \frac{\eta V}{L}\tilde{p} \qquad \psi = \frac{kT}{z_1 e}\tilde{\psi}$$
$$c_i = c_\infty \tilde{c}_i \qquad (i = 1, 2) \qquad \rho = 2\tilde{c}_\infty z_1 e\tilde{\rho} \tag{1.3.2b}$$

Thus, the concentrations of the ions, given by Eq.s. (1.3.1c), for species 1 may be expressed in terms of the dimensionless (tilde) variables as

$$\frac{1}{L}\tilde{\nabla}\cdot\left\{D_1\left(\frac{1}{L}\tilde{\nabla}\right)\left(c_\infty\tilde{c}_1\right)+\left(c_\infty\tilde{c}_1\right)\left[\frac{D_1 z_1 e}{kT}\left(\frac{1}{L}\tilde{\nabla}\right)\left(\frac{kT}{z_1 e}\right)-V\tilde{\vec{v}}\right]\right\}=\frac{n_\infty\partial\tilde{c}_1}{\left(L/V\right)\partial\tilde{t}}$$

or

$$\tilde{\nabla}\cdot\left[\tilde{\nabla}\tilde{c}_1+\tilde{c}_1\tilde{\nabla}\tilde{\psi}-\mathrm{Pe}\,\tilde{c}_1\tilde{\vec{v}}\right]=\mathrm{Pe}\frac{\partial\tilde{c}_1}{\partial\tilde{t}} \tag{1.3.3a}$$

in which Pe is a Peclet number defined by

$$\mathrm{Pe}=\frac{VL}{D_1} \tag{1.3.4}$$

and a tilde over the gradient operator denotes evaluation with respect to dimensionless position vector $\tilde{\vec{r}}$. Similarly, a dimensionless convection diffusion equation for the other species, $\tilde{c}_2$, may be obtained as

$$\tilde{\nabla}\cdot\left[\tilde{\nabla}\tilde{c}_2-\tilde{c}_2\tilde{\nabla}\tilde{\psi}-\mathrm{Pe}\left(\frac{D_1}{D_2}\right)\tilde{c}_2\tilde{\vec{v}}\right]=\mathrm{Pe}\left(\frac{D_1}{D_2}\right)\frac{\partial\tilde{c}_2}{\partial\tilde{t}} \tag{1.3.3b}$$

In Eq.s. (1.3.3a, b) the first, second and third terms in the 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 is given by Poisson equation as

$$\nabla^2\psi = -\frac{\rho}{\varepsilon_m}$$

It may be expressed in terms of the dimensionless (tilde) variables defined by (1.3.2), as

$$\left(\frac{1}{L^2}\tilde{\nabla}^2\right)\left(\frac{kT}{z_1 e}\tilde{\psi}\right) = -\frac{(2c_\infty z_1 e\tilde{\rho})}{\varepsilon_r\varepsilon_o}$$

But, the characteristic double layer thickness for two species of ions is [c.f., (1.2.2b)]

$$\frac{1}{\kappa} = \left(\frac{\varepsilon_r\varepsilon_o kT}{2z_1^2 e^2 c_\infty}\right)^{1/2} \quad (1.3.5)$$

Therefore,

$$\tilde{\nabla}^2\tilde{\psi} = -(L\kappa)^2\tilde{\rho}$$

or

$$\epsilon^2\,\tilde{\nabla}^2\tilde{\psi} = -\tilde{\rho} \quad (1.3.3c)$$

in which ϵ defined by

$$\epsilon = (\kappa L)^{-1} \quad (1.3.6)$$

is the ratio of the inverse of the Debye-Hückel parameter κ to the length scale L.

The electric charge density (charge per unit volume of the liquid), defined by

$$\rho = \sum_1^j c_i z_i e \qquad (j = 2)$$

may be written in terms of the our dimensionless (tilde) variables as

$$(2c_\infty z_1 e\tilde{\rho}) = (c_\infty z_1 e\tilde{c}_1) + (-c_\infty z_1 e\tilde{c}_2)$$

or

$$\tilde{\rho} = \frac{1}{2}(\tilde{c}_1 - \tilde{c}_2) \quad (1.3.3d)$$

It is assumed 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. Thus, momentum and continuity equations for the liquid flow in the presence of the electric body force, $\vec{F}_E = -\rho \nabla \psi$, may be written as

$$\eta \nabla^2 \vec{v} - \nabla p = \rho \nabla \psi, \qquad \nabla \cdot \vec{v} = 0$$

It may be expressed in terms of our dimensionless variables, defined by (1.3.2), as

$$\eta \left(\frac{\tilde{\nabla}^2}{L^2} \right) \left(V \vec{\tilde{v}} \right) - \left(\frac{\tilde{\nabla}}{L} \right) \left(\frac{\eta V}{L} \tilde{p} \right) = \left(2c_\infty z_1 e \tilde{\rho} \right) \left(\frac{\tilde{\nabla}}{L} \right) \left(\frac{kT}{z_1 e} \tilde{\psi} \right), \quad \left(\frac{\tilde{\nabla}}{L} \right) \cdot \left(V \vec{\tilde{v}} \right) = 0$$

or

$$\tilde{\nabla}^2 \vec{\tilde{v}} - \tilde{\nabla} \tilde{p} = \lambda \tilde{\rho} \tilde{\nabla} \tilde{\psi} \tag{1.3.3e}$$

$$\tilde{\nabla} \cdot \vec{\tilde{v}} = 0 \tag{1.3.3f}$$

in which the parameter λ defined by

$$\lambda = \frac{2c_\infty kTL}{\eta V} \tag{1.3.7}$$

measures the relative importance of the electrical body forces on the flow field.

Thus, there are eight scalar equations, given by Eq.s (1.3.3a-f), for the eight dependent variables (denoted by $\vec{\tilde{v}}$, $\tilde{p}$, $\tilde{c}_1$, $\tilde{c}_2$, $\tilde{\psi}$ 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

$$\tilde{c}_1 = \tilde{c}_2 = \text{constant}; \qquad \tilde{\rho} = 0$$

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

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

and with a purely hydrodynamic flow

$$\tilde{\nabla}^2 \vec{\tilde{v}} - \tilde{\nabla} \tilde{p} = 0; \qquad \tilde{\nabla} \cdot \vec{\tilde{v}} = 0$$

Thus, at large distances we will take a solution of this form with $\tilde{\psi} = 0$, since it is assumed that there is no applied electric field at infinity. If we take the characteristic ion concentration c_∞ to be that at infinity (i.e., $c_\infty =$ the bulk concentration), then the boundary conditions will be

$$\tilde{c}_1 \to 1; \qquad \tilde{c}_2 \to 1 \tag{1.3.8a}$$

$$\tilde{\psi} \to 0 \tag{1.3.8b}$$

$$\tilde{\vec{v}} \to (\text{given flow at infinity}) \tag{1.3.8c}$$

as $|\tilde{\vec{r}}| \to \infty$. On the surface S_p of the particle P and on the surface S_w of the wall W the no-slip boundary condition is required to be satisfied, so that if at a general point on S_p the velocity of the solid surface is $\tilde{\vec{U}}_P$ (and on S_w is $\tilde{\vec{U}}_W$), then

$$\tilde{\vec{v}} = \tilde{\vec{U}}_P \quad \text{on } S_P; \qquad \tilde{\vec{v}} = \tilde{\vec{U}}_W \quad \text{on } S_W \tag{1.3.8d}$$

where $\tilde{\vec{U}}_P$ and $\tilde{\vec{U}}_W$, defined by

$$\tilde{\vec{U}}_P = \frac{\vec{U}_P}{V} \qquad \text{and} \qquad \tilde{\vec{U}}_W = \frac{\vec{U}_W}{V} \tag{1.3.9}$$

are the dimensionless velocities of the solid surface S_p and S_w, respectively.

It is also assumed 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, or mathematically stated, the ion flux (of either species) normal to the surface (relative to the surface) must be zero, that is

$$\vec{n} \cdot \left[\tilde{\nabla}\tilde{c}_1 + \tilde{c}_1 \tilde{\nabla}\tilde{\psi}\right] = 0 \qquad \text{on } S_P \text{ and } S_W \tag{1.3.8e}$$

$$\vec{n} \cdot \left[\tilde{\nabla}\tilde{c}_2 - \tilde{c}_2 \tilde{\nabla}\tilde{\psi}\right] = 0 \qquad \text{on } S_P \text{ and } S_W \tag{1.3.8f}$$

where $\vec{n}$ is the unit vector normal to the surface directed into the liquid. In deriving Eq.s (1.3.8e, f), it was noted that, by the aid of Eq. (1.3.8d), the convective flux due to the fluid relative to the solid surface is zero. Boundary conditions (1.3.8e, f) are usually referred as the no-penetration boundary conditions.

It is assumed that the surface potential of the particle is everywhere equal to a constant on S_P, $\tilde{\psi}_P$, and that of the wall is everywhere equal to another constant, say $\tilde{\psi}_W$. Then it is required that

$$\tilde{\psi} = \tilde{\psi}_P \qquad \text{on} \quad S_P \tag{1.3.8g}$$

$$\tilde{\psi} = \tilde{\psi}_W \qquad \text{on} \quad S_W \tag{1.3.8h}$$

where

$$\tilde{\psi}_P = \left(\frac{z_1 e}{kT}\right)\zeta_P; \qquad \tilde{\psi}_W = \left(\frac{z_1 e}{kT}\right)\zeta_W \tag{1.3.10}$$

are the dimensionless surface potentials of the particle P and wall W, respectively.

The solution of Eq.s (1.3.3a-f) with B.C.s (1.3.8a-h) depend, in addition to the shapes, relative positions and motions of the particle and wall (and flow at infinity), on the following six parameters:

Pe = Peclet number for ions of species 1 [c.f., Eq. (1.3.3a, b)].

D_1/D_2 = Ratio of diffusivities of the two species of ion [c.f., Eq. (1.3.3b)].

ϵ = Ratio of double layer thickness to the length scale, L [c.f., Eq. (1.3.3c)].

λ = Parameter measuring effect of electrical forces on the flow [c.f., Eq.(1.3.3e)].

$\tilde{\psi}_p$ = Dimensionless particle surface potential [c.f., B.C. (1.3.8g)].

$\tilde{\psi}_w$ = Dimensionless wall surface potential [c.f., B.C. (1.3.8h)].

Cox considered the problem for small ϵ with all the other five parameters being held fixed and of order unity, i.e. there is no restriction on the other parameters. He was interested in obtaining a general solution under the above assumptions to determine the force and torque experienced by the particle P in the limit as $\epsilon \to 0$. Thus, it is assumed that the double layer thickness is very much smaller than the particle size or the distance from particle to the wall.

Since the total stress tensor σ_{ij} is the sum of the hydrodynamic and electrostatic Maxwell stress tensors, then if one defines a dimensionless stress tensor $\tilde{\sigma}_{ij}$ by

$$\sigma_{ij} = \frac{\eta V}{L}\tilde{\sigma}_{ij} \tag{1.3.11}$$

the dimensionless stress tensor may be expressed as[1]

$$\tilde{\sigma}_{ij} = -\tilde{P}\delta_{ij} + \left(\tilde{v}_{i,j} + \tilde{v}_{j,i}\right) + \lambda\varepsilon^2\left(-\frac{1}{2}\tilde{\psi}_{,k}\tilde{\psi}_{,k}\delta_{ij} + \tilde{\psi}_{,i}\tilde{\psi}_{,j}\right), \quad (i,j) = (1,2,3) \tag{1.3.12a}$$

were all derivatives are with respect to the $\tilde{r}_j$ variables, that is

$$\tilde{v}_{i,j} = \frac{\partial \tilde{v}_i}{\partial \tilde{r}_j}, \quad \tilde{\psi}_{,i} = \frac{\partial \tilde{\psi}}{\partial \tilde{r}_i}, \qquad \tilde{\psi}_{,k}\tilde{\psi}_{,k} = \left(\frac{\partial \tilde{\psi}}{\partial \tilde{r}_1}\right)^2 + \left(\frac{\partial \tilde{\psi}}{\partial \tilde{r}_2}\right)^2 + \left(\frac{\partial \tilde{\psi}}{\partial \tilde{r}_3}\right)^2, \text{etc} \cdots \tag{1.3.12b}$$

---

[1]Einstein summation convention is imposed on the repeated index, unless otherwise stated.

and where δ_{ij} is the Kronecker delta defined by

$$\delta_{ij} = \begin{cases} 1 & \text{for} \quad i = j \\ 0 & \text{for} \quad i \neq j \end{cases} \qquad (1.3.12c)$$

It may then, by using (1.3.3c, e, f), be readily shown that the conservation of total momentum defined by

$$\tilde{\nabla} \cdot \vec{\vec{\tilde{\sigma}}} = 0 \qquad \text{or} \qquad \tilde{\sigma}_{ij,j} = 0 \qquad (1.3.13)$$

is satisfied. It is noted that the external angular momentum for structureless fluids considered here is always satisfied [Happel & Brenner 1975, p. 25].

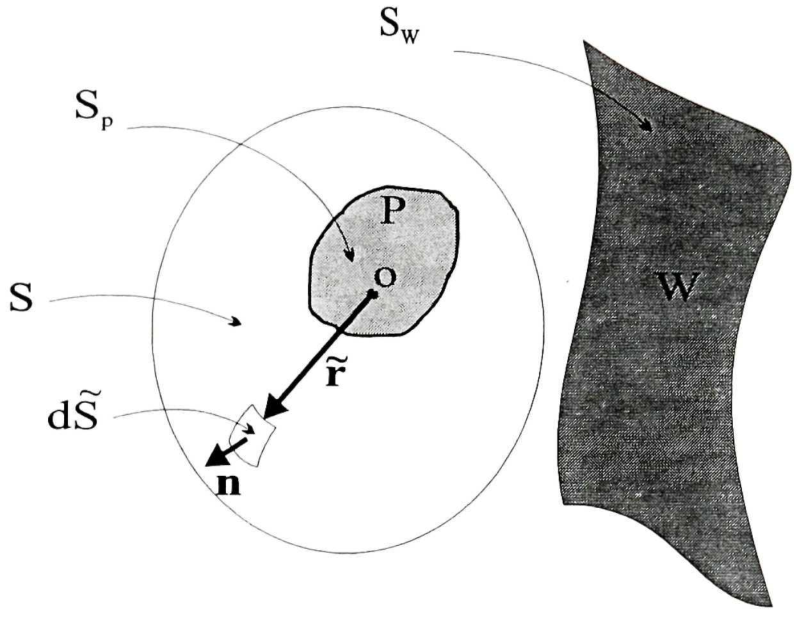

Fig. 1.2 - Surface S enclosing particle P near the wall W.

The total dimensionless force, $\vec{\tilde{F}}$, acting on the particle P may be determined by

$$\tilde{F}_i = \int_{S_P} \tilde{\sigma}_{ij} n_j d\tilde{S} = \int_{S} \tilde{\sigma}_{ij} n_j d\tilde{S} \qquad (1.3.14)$$

where $\vec{\tilde{F}}$ is defined by

$$\vec{F} = \eta L V \vec{\tilde{F}} \qquad (1.3.15)$$

and where $d\tilde{S}$ is a dimensionless infinitesimal element of area; $\vec{n}$ is the unit vector normal to the surface directed outward 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 Fig 1.2, so that no part of the wall W is within S.

Similarly the moment of force, $\vec{G}$, on the particle P about a reference point O may be obtained in terms of the dimensionless moment, $\vec{\tilde{G}}$, defined by

$$\vec{G} = \eta L^2 V \vec{\tilde{G}} \tag{1.3.16}$$

as

$$\tilde{G}_i = \int_{S_P} \varepsilon_{ijk} \tilde{r}_j \tilde{\sigma}_{kl} n_l d\tilde{S} = \int_{S} \varepsilon_{ijk} \tilde{r}_j \tilde{\sigma}_{kl} n_l d\tilde{S} \tag{1.3.17a}$$

in which ε_{ijk} is the alternating tensor defined by

$$\varepsilon_{ijk} = \begin{cases} +1 & \text{if i, j, k is an even permutation,} \quad \text{e.g., 2,3,1} \\ -1 & \text{if i, j, k is an odd permutation,} \quad \text{e.g., 1,3,2} \\ 0 & \text{if two or more indices are the same,} \quad \text{e.g., 1,2,2} \end{cases} \tag{1.3.17b}$$

and $\vec{\tilde{r}}$ is the position of the surface element relative to the reference point O (c.f., Fig. 1.2).

1.3.2 - Inner and Outer Region

In solving Eq.s (1.3.3a-f) with B.C.s (1.3.8a-h) for the limit as $\in \rightarrow 0$, the dependent dimensionless (tilde) variables should be expanded in terms of the parameter $\in$. In this manner one obtains an outer region solution. Then for the inner region solution an inner region expansion in $\in$ is required for each point on the solid surfaces S_p and S_w. Therefore, at a completely general point Q at position $\vec{\tilde{r}}_Q$ on the surface S_p (or on the surface S_w), Cox defined locally a set of orthogonal coordinates $(\tilde{\xi}, \tilde{\eta})$ lying within the solid surface (c.f., Fig 1.3) with unit metric tensor in terms of the outer variables. He also employed a local outer region Cartesian coordinates $(\tilde{x}, \tilde{y}, \tilde{z})$ with origin at Q, $\tilde{z}$ being normal to the solid surface (S_p or S_w) and directed into the liquid and with the $\tilde{z}$ and $\tilde{y}$ axes tangent to $\tilde{\xi}$ and $\tilde{\eta}$ coordinate lines at Q, respectively, (c.f., Fig 1.3).

Inner region variables (denoted as barred variables) at Q are then defined by

$$\tilde{x} = \in^{1/2} \bar{x}, \qquad \tilde{y} = \in^{1/2} \bar{y}, \qquad \tilde{z} = \in \bar{z}, \qquad \tilde{t} = \bar{t} \tag{1.3.18}$$

$$\vec{\tilde{v}} = \vec{\tilde{U}} + \vec{\tilde{\Omega}} \times \vec{\tilde{r}} + \vec{\bar{v}}, \qquad \tilde{p} = \bar{p}, \qquad \tilde{\psi} = \bar{\psi}, \quad \tilde{c}_i = \bar{c}_i, \quad \tilde{\rho} = \bar{\rho} \tag{1.3.19}$$

where $\vec{\tilde{U}}$ here is the dimensionless velocity of the surface under consideration at Q (equal to either $\vec{\tilde{U}}_P$ or $\vec{\tilde{U}}_W$ at Q), $\vec{\tilde{\Omega}}$ is the dimensionless angular velocity of the solid surface defined by

$$\vec{\Omega} = \frac{V}{L}\vec{\tilde{\Omega}} \tag{1.3.20a}$$

($\vec{\Omega}$ being the dimensional angular velocity of either the particle or the wall relative to a fixed point) and $\vec{\tilde{r}}$ here is the position vector relative to the point Q, the original of the local Cartesian coordinate system $(\tilde{x}, \tilde{y}, \tilde{z})$, in outer variables. Therefore, noting that

$$\vec{\tilde{\Omega}} \times \vec{\tilde{r}} = \begin{vmatrix} \vec{i}_x & \vec{i}_y & \vec{i}_z \\ \tilde{\Omega}_x & \tilde{\Omega}_y & \tilde{\Omega}_z \\ \tilde{x} & \tilde{y} & \tilde{z} \end{vmatrix}$$

$$= \left(\tilde{\Omega}_y \tilde{z} - \tilde{\Omega}_z \tilde{y}\right)\vec{i}_x - \left(\tilde{\Omega}_x \tilde{z} - \tilde{\Omega}_z \tilde{x}\right)\vec{i}_y + \left(\tilde{\Omega}_x \tilde{y} - \tilde{\Omega}_y \tilde{x}\right)\vec{i}_z$$

the three components of the velocity in Eq. (1.3.19), by the use of (1.3.18), may be written as

$$\begin{aligned} \tilde{v}_x &= \tilde{U}_x + \bar{v}_x - \epsilon^{1/2}\,\tilde{\Omega}_z \bar{y} + \epsilon \tilde{\Omega}_y \bar{z} \\ \tilde{v}_y &= \tilde{U}_y + \bar{v}_y + \epsilon^{1/2}\,\tilde{\Omega}_z \bar{x} - \epsilon \tilde{\Omega}_x \bar{z} \\ \tilde{v}_z &= \tilde{U}_z + \bar{v}_z + \epsilon^{1/2}\left(\tilde{\Omega}_x \bar{y} - \tilde{\Omega}_y \bar{x}\right) \end{aligned} \tag{1.3.20b}$$

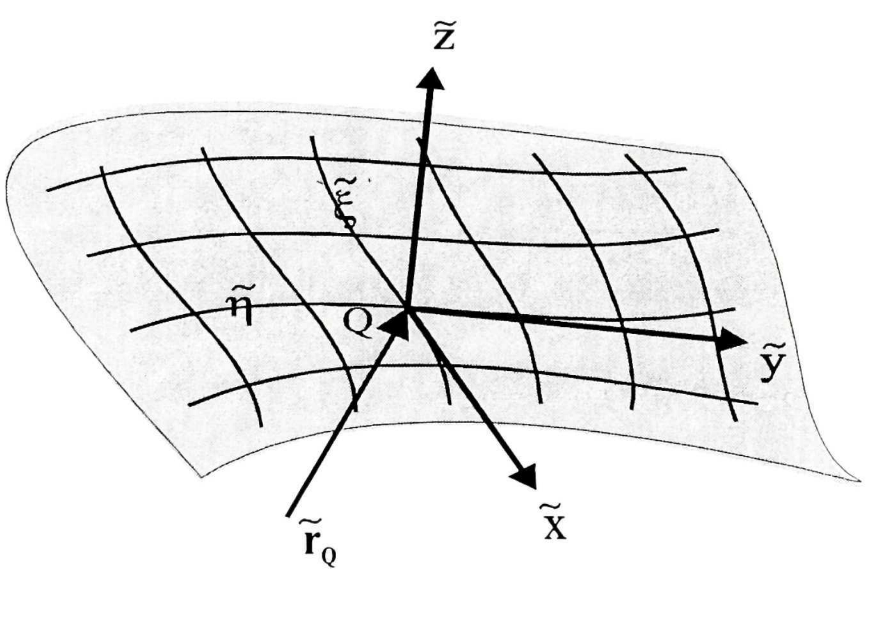

Fig. 1.3 - Local orthogonal curvature coordinates (ξ, η̃) lying on the solid surface showing the local Cartesian coordinates (x̃, ỹ, z̃) at the general point Q.

The solution procedure would be to solve Eq.s (1.3.3a-f) together with B.C.s (1.3.8a-c) at infinity in an expansion in $\in$, as for the outer region solution. Then at each point Q on the surfaces S_p and S_w an inner region expansion in $\in$, is made by solving Eq.s (1.3.3a-f) with B.C.s (1.3.8d-h) (the boundary conditions on the solid surfaces) 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 general shape of the particle surface S_p (or the 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

$$\tilde{z} = a_{11}\tilde{x}^2 + 2a_{12}\tilde{x}\tilde{y} + a_{22}\tilde{y}^2 + (\text{cubic terms in } \tilde{x}, \tilde{y}) + \cdots \qquad (1.3.21a)$$

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 $\tilde{\xi}$ and $\tilde{\eta}$ coordinates). For example, for a surface geometry as symmetry as an arch surface of a sphere with the dimensionless curvature radius $\tilde{R} = 1$, the equation of particle shape, in the local Cartesian coordinates $(\tilde{x}, \tilde{y}, \tilde{z})$ is defined by

$$\tilde{z} + 1 = (1 - \tilde{x}^2 - \tilde{y}^2)^{1/2},$$

which, upon the use of the binomial theorem,

$$(a+b)^n = a^n + \frac{n}{1!}a^{n-1}b + \frac{n(n-1)}{2!}a^{n-2}b^2 + \frac{n(n-1)(n-2)}{3!}a^{n-3}b^3 + \cdots, \qquad (1.3.21b)$$

may be expressed as

$$\tilde{z} = -\frac{1}{2}(\tilde{x}^2 + \tilde{y}^2) - \frac{1}{8}(\tilde{x}^2 + \tilde{y}^2)^2 + \cdots \qquad (1.3.21c)$$

Within the inner region, for simplicity, Cox solved 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 $\bar{z}$ of 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 are completely determined.

1.3.3 - Electrical Problem

1.3.3.1 - Outer Region Solution

A special case of the problem discussed in §1.3.2 in which the fluid velocity $\vec{\tilde{v}}$ is zero everywhere is considered in this section. This implies that the velocity $\vec{\tilde{U}}$ of the surfaces S_p and S_w of particle and wall must also be zero and that $\vec{\tilde{v}} \to 0$ at infinity, so that the problem would reduce to a steady state of a purely electrical nature. A subscript E is used to denote all dependent variables for this case (i.e., $\tilde{c}_{1E}$, $\tilde{c}_{2E}$, $\tilde{\rho}_E$, $\tilde{\psi}_E$ and $\tilde{p}_E$). Thus, letting $\vec{\tilde{v}} = 0$ and $\partial \tilde{c}_1 / \partial \tilde{t} = \partial \tilde{c}_2 / \partial \tilde{t} = 0$, Eq.s (1.3.3a-e) [with (1.3.3f) automatically satisfied], for steady state, may be expressed as

$$\tilde{\nabla}^2 \tilde{c}_{1E} + \tilde{\nabla} \cdot \left(\tilde{c}_{1E} \tilde{\nabla} \tilde{\psi}_E \right) = 0 \qquad (1.3.22a)$$

$$\tilde{\nabla}^2 \tilde{c}_{2E} - \tilde{\nabla} \cdot \left(\tilde{c}_{2E} \tilde{\nabla} \tilde{\psi}_E \right) = 0 \qquad (1.3.22b)$$

$$\epsilon^2 \tilde{\nabla}^2 \tilde{\psi}_E = -\tilde{\rho}_E \qquad (1.3.22c)$$

$$\tilde{\rho}_E = \frac{1}{2} \left(\tilde{c}_{1E} - \tilde{c}_{2E} \right) \qquad (1.3.22d)$$

$$\tilde{\nabla} \tilde{p}_E = -\lambda \tilde{\rho}_E \tilde{\nabla} \tilde{\psi}_E \qquad (1.3.22e)$$

Then B.C.s (1.3.8a-h) [with (1.3.8c, d) automatically satisfied] may be written as

$$\tilde{c}_{1E} \to 1 \qquad \tilde{c}_{2E} \to 1 \qquad (1.3.23a)$$

$$\tilde{\psi}_E \to 0 \qquad (1.3.23b)$$

as $|\vec{\tilde{r}}| \to \infty$, with

$$\vec{n} \cdot \left[\tilde{\nabla} \tilde{c}_{1E} + \tilde{c}_{1E} \tilde{\nabla} \tilde{\psi}_E \right] = 0 \qquad \text{on } S_P \text{ and } S_W \qquad (1.3.23c)$$

$$\vec{n} \cdot \left[\tilde{\nabla} \tilde{c}_{2E} - \tilde{c}_{2E} \tilde{\nabla} \tilde{\psi}_E \right] = 0 \qquad \text{on } S_P \text{ and } S_W \qquad (1.3.23d)$$

$$\tilde{\psi}_E = \tilde{\psi}_P \qquad \text{on } S_P \qquad (1.3.23e)$$

$$\tilde{\psi}_E = \tilde{\psi}_W \qquad \text{on } S_W \tag{1.3.23f}$$

The dimensionless flux of the ions of species 1 denoted by $\vec{\tilde{q}}_{1E}$ is defined by

$$\vec{\tilde{q}}_{1E} = \tilde{\nabla}\tilde{c}_{1E} + \tilde{c}_{1E}\tilde{\nabla}\tilde{\psi} \tag{1.3.24a}$$

which may be written in Cartesian coordinates $(\tilde{x}, \tilde{y}, \tilde{z})$ with unit vectors $(\vec{i}_x, \vec{i}_y, \vec{i}_z)$ as

$$\begin{aligned}\tilde{q}_{1Ex}\vec{i}_x + \tilde{q}_{1Ey}\vec{i}_y + \tilde{q}_{1Ez}\vec{i}_z = &\left(\frac{\partial\tilde{c}_{1E}}{\partial\tilde{x}} + \tilde{c}_{1E}\frac{\partial\tilde{\psi}_E}{\partial\tilde{x}}\right)\vec{i}_x + \left(\frac{\partial\tilde{c}_{1E}}{\partial\tilde{y}} + \tilde{c}_{1E}\frac{\partial\tilde{\psi}_E}{\partial\tilde{y}}\right)\vec{i}_y \\ &+ \left(\frac{\partial\tilde{c}_{1E}}{\partial\tilde{z}} + \tilde{c}_{1E}\frac{\partial\tilde{\psi}_E}{\partial\tilde{z}}\right)\vec{i}_z\end{aligned} \tag{1.3.24b}$$

Then Eq. (1.3.22a) becomes

$$\tilde{\nabla}\cdot\vec{\tilde{q}}_{1E} = 0 \tag{1.3.25}$$

Upon multiplying it by $\tilde{\psi}_E$ and integrating that over the liquid volume V contained with a large sphere S_R of radius R (V is bounded by S_p, S_w and S_R with $R \to \infty$) the energy equation for the ions of species 1, by using the divergence theorem,

$$\int_V \nabla\cdot\vec{A}\,dV = \int_S \vec{A}\cdot\vec{n}\,dS, \tag{1.3.26a}$$

may be written as

$$\int_V \tilde{\nabla}\cdot\left(\tilde{\psi}_E\vec{\tilde{q}}_{1E}\right)d\tilde{V} = -\int_{S_P+S_W+S_R} \tilde{\psi}_E\vec{\tilde{q}}_{1E}\cdot\vec{n}\,d\tilde{S} \tag{1.3.26b}$$

where $d\tilde{S}$ and $d\tilde{V}$ are dimensionless elements of surface area and volume and $\vec{n}$ is the unit vector normal to the surface (S_p, S_w or S_R) drawn into the liquid. Using the relationship

$$\nabla\cdot\left(c\vec{A}\right) = \nabla c\cdot\vec{A} + c\nabla\cdot\vec{A} \tag{1.3.26c}$$

the integral over the volume may be expressed as

$$\int_V \tilde{\nabla}\cdot\left(\tilde{\psi}_E\vec{\tilde{q}}_{1E}\right)d\tilde{V} = \int_V \left(\tilde{\nabla}\tilde{\psi}_E\right)\cdot\vec{\tilde{q}}_{1E}d\tilde{V} + \int_V \tilde{\psi}_E\left(\tilde{\nabla}\cdot\vec{\tilde{q}}_{1E}\right)d\tilde{V} \tag{1.3.27a}$$

and, by the aid of (1.3.23c, e, f, 24a), the surface integral may be evaluated as

$$\begin{aligned}\int_S \tilde{\psi}_E\vec{\tilde{q}}_{1E}\cdot\vec{n}\,d\tilde{S} &= \int_{S_P} \tilde{\psi}_P\vec{\tilde{q}}_{1E}\cdot\vec{n}\,d\tilde{S} + \int_{S_W} \tilde{\psi}_W\vec{\tilde{q}}_{1E}\cdot\vec{n}\,d\tilde{S} + \int_{S_R} \tilde{\psi}_E\vec{\tilde{q}}_{1E}\cdot\vec{n}\,d\tilde{S} \\ &= \int_{S_R} \tilde{\psi}_E\vec{\tilde{q}}_{1E}\cdot\vec{n}\,d\tilde{S}\end{aligned} \tag{1.3.27b}$$

But, B.C.s (1.3.23a,b) and Eq. (1.3.25) show that (so long as $\tilde{c}_{1E}$, $\tilde{c}_{2E}$, and $\tilde{\psi}_E$ tend to their limits sufficiently rapidly as $|\vec{\tilde{r}}| \to \infty$) the last integral in (1.3.27a) and also the integral on the right-hand side of (1.3.27b) vanishes giving [c.f., Eq. (1.3.26b, 27a)]

$$\int_V \vec{\tilde{q}}_{1E} \cdot \tilde{\nabla} \tilde{\psi}_E d\tilde{V} = 0 \tag{1.3.27c}$$

Since the quantity $-\tilde{q}_{1E} \cdot \tilde{\nabla} \tilde{\psi}_E$ 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. If the summation (integral) of strictly positive quantities is equal to zero, the only possible evaluation of them is that all individual quantities must be zero, from which it follows that

$$\vec{\tilde{q}}_{1E} \cdot \tilde{\nabla} \tilde{\psi} = 0 \tag{1.3.28a}$$

everywhere. This may also expressed in the Cartesian coordinate system as

$$\tilde{q}_{1Ex} \frac{\partial \tilde{\psi}_E}{\partial \tilde{x}} + \tilde{q}_{1Ey} \frac{\partial \tilde{\psi}_E}{\partial \tilde{y}} + \tilde{q}_{1Ez} \frac{\partial \tilde{\psi}_E}{\partial \tilde{z}} = 0 \qquad (1.3.28b$$

Consider now any equipotential surface Σ given by $\tilde{\psi}_E$ = constant (c.f., Fig. 1.4). If the coordinate system is chosen such that its origin lays on the surface Σ with the $\tilde{z}$ -axis being normal to the surface, because of equipotential, $\partial \tilde{\psi}_E / \partial \tilde{x}$ and also $\partial \tilde{\psi}_E / \partial \tilde{y}$ in Eq. (1.3.28) vanish, giving $\tilde{q}_{1Ez} = 0$ (zero component normal to Σ). Therefore, for the plane Σ, Eq. (1.3.24) may be expressed as

$$\vec{\tilde{q}}_{1E} = \tilde{\nabla}_2 \tilde{c}_{1E} \tag{1.3.29}$$

where $\tilde{\nabla}_2$ is the two dimensional gradient operator on the surface Σ. From this Eq.(1.3.25) reduces to

$$\tilde{\nabla}_2 \cdot \tilde{\nabla}_2 \tilde{c}_{1E} = 0 \qquad \text{or} \qquad \tilde{\nabla}_2^2 \tilde{c}_{1E} = 0 \tag{1.3.30}$$

on the surface Σ. Multiplying this by $\tilde{c}_{1E}$ and integrating over that part Σ^* of the surface Σ d externally by a closed line L^* drawn on Σ, as shown in Fig. 1.4, one obtains, upon using the divergence theorem,

$$\int_{L^*} \tilde{c}_{1E} \tilde{\nabla}_2 \tilde{c}_{1E} \cdot \vec{n}^* d\tilde{l} = \int_{\Sigma^*} |\tilde{\nabla}_2 \tilde{c}_{1E}|^2 d\tilde{S} \tag{1.3.31}$$

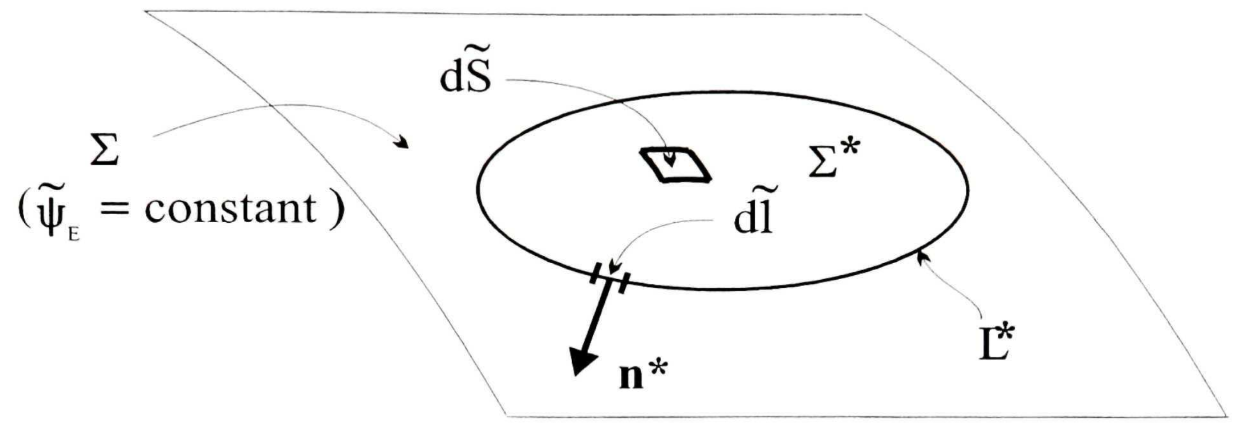

Fig. 1.4 - An area Σ^* bounded by the closed line L^* on equipotential surface Σ.

in which $d\tilde{S}$ is an element area of Σ^*, $d\tilde{l}$ an element of length of L^* and $\vec{n}^*$ 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 $\tilde{c}_{1E}$ on Σ tending to a constant value sufficiently rapidly at infinity, by the use of (1.3.23a), we see that the integral on the left hand side of (1.3.31) tends to zero giving

$$\int_{\Sigma^*} |\tilde{\nabla}_2 \tilde{c}_{1E}|^2 \, d\tilde{S} = 0 \tag{1.3.32}$$

Since the integrand in Eq. (1.3.32) is strictly non-negative, it follows that

$$\tilde{\nabla}_2 \tilde{c}_{1E} = 0 \tag{1.3.33}$$

so that $\tilde{c}_{1E}$ is equal to a constant on an equipotential surface Σ. Thus, the ion flux $\vec{\tilde{q}}_{1E}$ (and by a similar argument the ion flux $\vec{\tilde{q}}_{2E}$) is zero everywhere. From this, Eq.s (1.3.22a, b) may be replaced by

$$\tilde{\nabla} \tilde{c}_{1E} + \tilde{c}_{1E} \tilde{\nabla} \tilde{\psi}_E = 0 \tag{1.3.34a}$$

$$\tilde{\nabla} \tilde{c}_{2E} - \tilde{c}_{2E} \tilde{\nabla} \tilde{\psi}_E = 0 \tag{1.3.34b}$$

Then, with B.C.s (1.3.23c, d) being automatically satisfied, Eq.s (1.3.34a, b) may be expressed as

$$\frac{\tilde{\nabla} \tilde{c}_{1E}}{\tilde{c}_{1E}} = -\tilde{\nabla} \tilde{\psi}_E, \qquad \frac{\tilde{\nabla} \tilde{c}_{2E}}{\tilde{c}_{2E}} = +\tilde{\nabla} \tilde{\psi}_E$$

Its solution is

$$\ln \tilde{c}_{1E} = -\tilde{\psi}_E + c, \qquad \ln \tilde{c}_{2E} = +\tilde{\psi}_E + c$$

Imposing B.C.s (1.3.23a, b) results in

$$\tilde{c}_{1E} = e^{-\tilde{\psi}_E}, \qquad \tilde{c}_{2E} = e^{+\tilde{\psi}_E} \tag{1.3.35}$$

Eq.s (1.3.22d, e) then give

$$\tilde{\rho}_E = \frac{1}{2}\left(e^{-\tilde{\psi}_E} - e^{+\tilde{\psi}_E}\right) = -\sinh \tilde{\psi}_E \tag{1.3.36}$$

and

$$\int \left(\tilde{\nabla}\tilde{p}_E\right) \cdot d\vec{\tilde{r}} = \lambda \int \sinh \tilde{\psi}_E \left(\tilde{\nabla}\tilde{\psi}_E\right) \cdot d\vec{\tilde{r}}$$

the integration of which is

$$\tilde{p}_E = \lambda \cosh \tilde{\psi}_E + c$$

But, it is assumed, without loss of generality, that $\tilde{p}_E \to 0$ as $|\vec{\tilde{r}}| \to \infty$, or equivalently as $\tilde{\psi}_E \to 0$. Thus, the pressure $\tilde{p}_E$ is determined by

$$\tilde{p}_E = \lambda \left(\cosh \tilde{\psi}_E - 1\right) \tag{1.3.37}$$

which is a well known result first derived by Langmuir (1938) and independently by Derjaguin (1940). It should be noted that since $\tilde{\rho}_E$ is a function of $\tilde{\psi}_E$ the electrical body force $\lambda \tilde{\rho}_E \tilde{\nabla} \tilde{\psi}_E$ acting on the liquid [c.f., Eq.(1.3.22e)], is conservative, so that no fluid flow is produced (like the gravitation force acting on a liquid). The remaining equation, Eq.(1.3.22c), with B.C.s (1.3.23b, e, f) gives $\tilde{\psi}_E$ being determined by

$$\epsilon^2 \tilde{\nabla}^2 \tilde{\psi}_E = \sinh \tilde{\psi}_E \tag{1.3.38}$$

with

$$\tilde{\psi} \to 0 \qquad \text{as} \left|\vec{\tilde{r}}\right| \to \infty \tag{1.3.39a}$$

$$\tilde{\psi}_E = \tilde{\psi}_P \qquad \text{on } S_P \tag{1.3.39b}$$

$$\tilde{\psi}_E = \tilde{\psi}_W \qquad \text{on } S_W \tag{1.3.39c}$$

Although the solution (1.3.35-39) to the electrical problem considered here is valid even if $\in$ is large, Cox was interested in this solution in the limit as $\in \to 0$ in the inner and outer regions of expansion (see § 1.3.2).

In the outer region where the above (tilde) variables are used, Eq. (1.3.38) with B.C. (1.3.39a) at infinity may be solved by expanding $\widetilde{\psi}_E$ in a power series of $\in$ as[1]

$$\widetilde{\psi}_E = \widetilde{\psi}_{E0} + \in \widetilde{\psi}_{E1} + \in^2 \widetilde{\psi}_{E2} + \cdots$$

Thus, Eq. (1.3.38) may be written as

$$\in^2 \widetilde{\nabla}^2\left(\widetilde{\psi}_{E0} + \in\widetilde{\psi}_{E1} + \cdots\right) = \frac{e^{\left(\widetilde{\psi}_{E0} + \in\widetilde{\psi}_{E1} + \cdots\right)} - e^{-\left(\widetilde{\psi}_{E0} + \in\widetilde{\psi}_{E1} + \cdots\right)}}{2}$$
$$= \left(\widetilde{\psi}_{E0} + \in\widetilde{\psi}_{E1} + \cdots\right) + \frac{1}{3!}\left(\widetilde{\psi}_{E0} + \in\widetilde{\psi}_{E1} + \cdots\right)^3 + \cdots$$

which indicates that

$$\widetilde{\psi}_E = 0 \qquad (1.3.40a)$$

correct to all orders in $\in$. Consequently, by the aid of Eq.s (1.3.35-37) one may obtain

$$\widetilde{c}_{1E} = 1 \qquad \widetilde{c}_{2E} = 1 \qquad (1.3.40b)$$

$$\widetilde{\rho}_E = 0 \qquad (1.3.40c)$$

and

$$\widetilde{p}_E = 0 \qquad (1.3.40d)$$

everywhere in the outer region correct to all orders in $\in$.

1.3.3.2 - Inner Region Solution Procedure

By the aid of definition (1.3.18, 19), Eq. (1.3.38) may be written in terms of inner variables as

$$\in^2 \left[\frac{\partial^2 \overline{\psi}_E}{\partial\left(\sqrt{\in}\overline{x}\right)^2} + \frac{\partial^2 \overline{\psi}_E}{\partial\left(\sqrt{\in}\overline{y}\right)^2} + \frac{\partial^2 \overline{\psi}_E}{\partial\left(\in \overline{z}\right)^2}\right] = \sinh \overline{\psi}_E$$

Thus, in the inner region at a point Q on the particle surface S_p, one observes that $\overline{\psi}_E$ on the

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[1]The last subscript of any dependent variable denotes the order of that variable in $\in$.

$\bar{z}$ -axis (i.e. where $\bar{x} = \bar{y} = 0$) satisfies

$$\frac{\partial^2 \bar{\psi}_E}{\partial \bar{z}^2} + \in \left(\frac{\partial^2 \bar{\psi}_E}{\partial \bar{x}^2} + \frac{\partial^2 \bar{\psi}_E}{\partial \bar{y}^2} \right) = \sinh \bar{\psi}_E \tag{1.3.41}$$

with boundary condition, given by (1.3.39b), as

$$\bar{\psi}_E = \tilde{\psi}_P \qquad \text{at } \bar{z} = 0 \tag{1.3.42}$$

whilst matching onto the outer solution, given by (1.3.40a), requires

$$\bar{\psi}_E \to 0 \qquad \text{as } \bar{z} \to \infty \tag{1.3.43}$$

Letting $\bar{\psi}_E = \bar{\psi}_{E0} + \in \bar{\psi}_{E1} + \in^2 \bar{\psi}_{E2} + \cdots$ Eq. (1.3.41) may be expressed as

$$\left[\frac{\partial^2}{\partial \bar{z}^2} + \in \left(\frac{\partial^2}{\partial \bar{x}^2} + \frac{\partial^2}{\partial \bar{y}^2} \right) \right] \left(\bar{\psi}_{E0} + \in \bar{\psi}_{E1} + \cdots \right) = \frac{1}{2} \left[e^{\left(\bar{\psi}_{E0} + \in \bar{\psi}_{E1} + \cdots \right)} - e^{-\left(\bar{\psi}_{E0} + \in \bar{\psi}_{E1} + \cdots \right)} \right]$$

$$= \frac{1}{2} \left[\left(1 + \in \bar{\psi}_{E1} + \cdots \right) e^{\bar{\psi}_{E0}} - \left(1 - \in \bar{\psi}_{E1} + \cdots \right) e^{-\bar{\psi}_{E0}} \right] = \sinh \bar{\psi}_{E0} + \in \bar{\psi}_{E1} \cosh \bar{\psi}_{E0} + O\left(\in^2 \right) \tag{1.3.44}$$

Thus, collecting terms of order unity gives

$$\frac{\partial^2 \bar{\psi}_{E0}}{\partial \bar{z}^2} = \sinh \bar{\psi}_{E0} \tag{1.3.45a}$$

with boundary conditions

$$\bar{\psi}_{E0} = \tilde{\psi}_P \qquad \text{at } \bar{z} = 0 \tag{1.3.45b}$$

$$\bar{\psi}_{E0} \to 0 \qquad \text{as } \bar{z} \to \infty \tag{1.3.45c}$$

Terms of order $\in$ satisfy

$$\frac{\partial^2 \bar{\psi}_{E1}}{\partial \bar{z}^2} - \left(\cosh \bar{\psi}_{E0} \right) \bar{\psi}_{E1} = - \left(\frac{\partial^2 \bar{\psi}_{E0}}{\partial \bar{x}^2} + \frac{\partial^2 \bar{\psi}_{E0}}{\partial \bar{y}^2} \right) \tag{1.3.46a}$$

with boundary conditions

$$\bar{\psi}_{E1} = 0 \qquad \text{at } \bar{z} = 0 \tag{1.3.46b}$$

$$\bar{\psi}_{E1} \to 0 \qquad \text{as } \bar{z} \to \infty \tag{1.3.46c}$$

Upon substitution the expansion of the quantities, $\bar{c}_{1E}$, $\bar{c}_{2E}$, $\bar{\rho}_E$ and $\bar{p}_E$ expressed as

$$\bar{c}_{1E} = \bar{c}_{1E0} + \in \bar{c}_{1E1} + \cdots, \qquad \bar{c}_{2E} = \bar{c}_{2E0} + \in \bar{c}_{2E1} + \cdots$$
$$\bar{\rho}_E = \bar{\rho}_{E0} + \in \bar{\rho}_{E1} + \cdots, \qquad \bar{p}_E = \bar{p}_{E0} + \in \bar{p}_{E1} + \cdots \qquad (1.3.47)$$

into Eq.s (1.3.22a-e) and B.C.s (1.3.23c-f), written entirely in terms of inner variables, equations and boundary conditions for $\left(\bar{c}_{1E0}, \bar{c}_{2E0}, \bar{\rho}_{E0}, \bar{p}_{E0}\right)$ and for $\left(\bar{c}_{1E1}, \bar{c}_{2E1}, \bar{\rho}_{E1}, \bar{p}_{E1}\right)$, etc... are so obtained by collecting the terms of the same order in $\in$. This has been done by Cox and reported explicitly in his paper [Cox (1997)].

1.3.4 - Hydrodynamic Problem

A purely hydrodynamic problem would be another special case of the problem discussed in §1.3.1in which the liquid is flowing as a result of the motion of the particle P and/or the wall W as well as the prescribed flow at infinity. For this case the ion concentrations are taken to be zero with no electric field present. This implies that the electric potentials of the particle and of the wall are zero. Variables with a subscript H are used for this case (i.e., $\tilde{\vec{v}}_H$, $\tilde{p}_H$). Then Eq. (1.3.3) [with (1.3.3a-d) being automatically satisfied] and B.C.s (1.3.8c, d) [with (1.3.8a, b, e, f) being automatically satisfied] may be expressed as

$$\tilde{\nabla}^2 \tilde{\vec{v}}_H - \tilde{\nabla} \tilde{p}_H = 0 \qquad (1.3.48a)$$

$$\tilde{\nabla} \cdot \tilde{\vec{v}}_H = 0 \qquad (1.3.48b)$$

and

$$\tilde{\vec{v}}_H \rightarrow \left(\text{given flow at infinity}\right) \qquad \text{as} \quad |\tilde{\vec{r}}| \rightarrow \infty \qquad (1.3.49a)$$

$$\left.\begin{aligned} \tilde{\vec{v}}_H &= \tilde{\vec{U}}_P && \text{on} \quad S_P \\ \tilde{\vec{v}}_H &= \tilde{\vec{U}}_W && \text{on} \quad S_W \end{aligned}\right\} \qquad (1.3.49b)$$

Thus, the flow field $\left(\tilde{\vec{v}}_H, \tilde{p}_H\right)$ is the creeping flow solution to the problem, and does not depend on the parameter $\in$. In order to obtain an expansion in $\in$ 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) Cox expanded $\left(\vec{\tilde{v}}_H, \tilde{p}_H\right)$ as a Taylor series about Q in the $\tilde{x}$, $\tilde{y}$, $\tilde{z}$ coordinates. If the inner region hydrodynamic variables $\vec{\bar{v}}_H$ and $\bar{p}_H$ are defined as in (1.3.19), then one obtains

$$\begin{aligned}
\bar{v}_{Hx} &= \frac{\partial \tilde{v}_{Hx}}{\partial \tilde{x}}|_Q\, \tilde{x} + \left(\frac{\partial \tilde{v}_{Hx}}{\partial \tilde{y}}|_Q + \tilde{\Omega}_z\right)\tilde{y} + \left(\frac{\partial \tilde{v}_{Hx}}{\partial \tilde{z}}|_Q - \tilde{\Omega}_y\right)\tilde{z} + \frac{1}{2}\frac{\partial^2 \tilde{v}_{Hx}}{\partial \tilde{x}^2}|_Q\, \tilde{x}^2 + \cdots \\
\bar{v}_{Hy} &= \left(\frac{\partial \tilde{v}_{Hy}}{\partial \tilde{x}}|_Q - \tilde{\Omega}_z\right)\tilde{x} + \frac{\partial \tilde{v}_{Hy}}{\partial \tilde{y}}|_Q\, \tilde{y} + \left(\frac{\partial \tilde{v}_{Hy}}{\partial \tilde{z}}|_Q + \tilde{\Omega}_x\right)\tilde{z} + \frac{1}{2}\frac{\partial^2 \tilde{v}_{Hy}}{\partial \tilde{x}^2}|_Q\, \tilde{x}^2 + \cdots \\
\bar{v}_{Hz} &= \left(\frac{\partial \tilde{v}_{Hz}}{\partial \tilde{x}}|_Q + \tilde{\Omega}_y\right)\tilde{x} + \left(\frac{\partial \tilde{v}_{Hz}}{\partial \tilde{y}}|_Q - \tilde{\Omega}_x\right)\tilde{y} + \frac{\partial \tilde{v}_{Hz}}{\partial \tilde{z}}|_Q\, \tilde{z} + \frac{1}{2}\frac{\partial^2 \tilde{v}_{Hz}}{\partial \tilde{x}^2}|_Q\, \tilde{x}^2 + \cdots
\end{aligned} \tag{1.3.50a}$$

$$\bar{p}_H = \tilde{p}_H|_Q + \frac{\partial \tilde{p}_H}{\partial \tilde{x}}|_Q\, \tilde{x} + \frac{\partial \tilde{p}_H}{\partial \tilde{y}}|_Q\, \tilde{y} + \frac{\partial \tilde{p}_H}{\partial \tilde{z}}|_Q\, \tilde{z} + \frac{1}{2}\frac{\partial^2 \tilde{p}_H}{\partial \tilde{x}^2}|_Q\, \tilde{x}^2 + \cdots \tag{1.3.50b}$$

in which $|_Q$ denotes evaluation at the point Q. From the no-slip boundary condition on the solid surface and from the definition of $\vec{\bar{v}}_H$ in (1.3.19), it follows that

$$\vec{\bar{v}} = 0 \qquad \text{on} \quad \tilde{z} = a_{11}\tilde{x}^2 + 2a_{12}\tilde{x}\tilde{y} + a_{22}\tilde{y}^2 + \cdots \tag{1.3.51}$$

for all $(\tilde{x}, \tilde{y})$. This, when introducing to (1.3.50a), gives restrictions on the values of the derivatives of $\vec{\tilde{v}}_H$ at Q. In addition, further restrictions are obtained from Eq.s (1.3.50a, b) and from their derivatives with respect to $\tilde{x}$, $\tilde{y}$ and $\tilde{z}$ by evaluating them at Q. By writing Eq.s (1.3.50a, b) in terms of the inner variables $(\bar{x}, \bar{y}, \bar{z})$, defined by (1.3.18), and using the above restrictions on the derivatives of $\vec{\tilde{v}}_H$ at Q, Cox obtained the values of $\vec{\bar{v}}_H$ and $\bar{p}_H$ and their $\bar{x}$ and $\bar{y}$ derivatives evaluated on the $\bar{z}$ -axis as expansions in ϵ .

1.3.5 - Electroviscous Equations

The solution of the general electrohydrodynamic problem [given by Eq.s (1.3.3.a-h) and B.C.s (1.3.8a-h)] may be considered as the sum of the solution of the purely electrical problem (discussed in §1.3.3), the solution of the purely hydrodynamic problem (discussed in §1.3.4) and a new set of electroviscous dependent variables denoted by an asterisk as a coupling between the electrical and hydrodynamic equations. Thus, upon introducing

$$\begin{aligned}
&\vec{\tilde{v}} = \vec{\tilde{v}}_H + \vec{\tilde{v}}^* \qquad && \tilde{p} = \tilde{p}_H + \tilde{p}_E + \tilde{p}^* \qquad && \tilde{\psi} = \tilde{\psi}_E + \tilde{\psi}^* \\
&\tilde{c}_1 = \tilde{c}_{1E} + \tilde{c}_1^* && \tilde{c}_2 = \tilde{c}_{2E} + \tilde{c}_2^* && \tilde{\rho} = \tilde{\rho}_E + \tilde{\rho}^*
\end{aligned} \tag{1.3.52}$$

to Eq.s (1.3.3a-f) and B.C.s (1.3.8a-h), and noting that $\tilde{c}_{1E}$, $\tilde{c}_{2E}$, $\tilde{\psi}$ $\cdots$ satisfy Eq.s (1.3.22a-e) with B.C.s (1.3.23a-f) and $\vec{\tilde{v}}_H$, $\tilde{p}_H$ satisfy Eq.s (1.3.48a,b) with B.C.s (1.3.49a,b), the remaining terms including the elctroviscous variables $\vec{\tilde{v}}^*$, $\tilde{p}^*$, $\tilde{c}_1^*$ $\cdots$ must satisfy

$$\tilde{\nabla}^2\tilde{c}_1^* + \tilde{\nabla}\cdot\left(\tilde{c}_{1E}\tilde{\nabla}\tilde{\psi}^* + \tilde{c}_1^*\tilde{\nabla}\tilde{\psi}_E + \tilde{c}_1^*\tilde{\nabla}\tilde{\psi}^*\right) =$$
$$\mathrm{Pe}\left(\vec{\tilde{v}}_H\cdot\tilde{\nabla}\tilde{c}_{1E} + \vec{\tilde{v}}_H\cdot\tilde{\nabla}\tilde{c}_1^* + \vec{\tilde{v}}^*\cdot\tilde{\nabla}\tilde{c}_{1E} + \vec{\tilde{v}}^*\cdot\tilde{\nabla}\tilde{c}_1^* + \frac{\partial\tilde{c}_{1E}}{\partial\tilde{t}} + \frac{\partial\tilde{c}_1^*}{\partial\tilde{t}}\right) = 0 \tag{1.3.53a}$$

$$\tilde{\nabla}^2\tilde{c}_2^* - \tilde{\nabla}\cdot\left(\tilde{c}_{2E}\tilde{\nabla}\tilde{\psi}^* + \tilde{c}_2^*\tilde{\nabla}\tilde{\psi}_E + \tilde{c}_2^*\tilde{\nabla}\tilde{\psi}^*\right) =$$
$$\mathrm{Pe}\left(\frac{D_1}{D_2}\right)\left(\vec{\tilde{v}}_H\cdot\tilde{\nabla}\tilde{c}_{2E} + \vec{\tilde{v}}_H\cdot\tilde{\nabla}\tilde{c}_2^* + \vec{\tilde{v}}^*\cdot\tilde{\nabla}\tilde{c}_{2E} + \vec{\tilde{v}}^*\cdot\tilde{\nabla}\tilde{c}_2^* + \frac{\partial\tilde{c}_{2E}}{\partial\tilde{t}} + \frac{\partial\tilde{c}_2^*}{\partial\tilde{t}}\right) = 0 \tag{1.3.53b}$$

$$\epsilon^2\,\tilde{\nabla}^2\tilde{\psi}^* = -\tilde{\rho}^* \tag{1.3.53c}$$

$$\tilde{\rho}^* = \frac{1}{2}\left(\tilde{c}_1^* - \tilde{c}_2^*\right) \tag{1.3.53d}$$

$$\tilde{\nabla}^2\vec{\tilde{v}}^* - \tilde{\nabla}\tilde{p}^* = \lambda\left(\tilde{\rho}^*\tilde{\nabla}\tilde{\psi}_E + \tilde{\rho}_E\tilde{\nabla}\tilde{\psi}^* + \tilde{\rho}^*\tilde{\nabla}\tilde{\psi}^*\right) \tag{1.3.53e}$$

$$\tilde{\nabla}\cdot\vec{\tilde{v}}^* = 0 \tag{1.3.53f}$$

with boundary conditions

$$\tilde{c}_1^* \to 0 \qquad\qquad \tilde{c}_2^* \to 0 \tag{1.3.54a}$$

$$\tilde{\psi}^* \to 0 \tag{1.3.54b}$$

$$\vec{\tilde{v}}^* \to 0 \tag{1.3.54c}$$

as $\left|\vec{\tilde{r}}\right| \to \infty$ and

$$\vec{\tilde{v}}^* = 0 \tag{1.3.54d}$$

$$\vec{n}\cdot\left[\tilde{\nabla}\tilde{c}_1^* + \tilde{c}_{1E}\tilde{\nabla}\tilde{\psi}^* + \tilde{c}_1^*\tilde{\nabla}\tilde{\psi}_E + \tilde{c}_1^*\tilde{\nabla}\tilde{\psi}^*\right] = 0 \tag{1.3.54e}$$

$$\vec{n}\cdot\left[\tilde{\nabla}\tilde{c}_2^* - \tilde{c}_{2E}\tilde{\nabla}\tilde{\psi}^* - \tilde{c}_2^*\tilde{\nabla}\tilde{\psi}_E - \tilde{c}_2^*\tilde{\nabla}\tilde{\psi}^*\right] = 0 \tag{1.3.54f}$$

$$\widetilde{\psi}^* = 0 \tag{1.3.54g}$$

on S_p and on S_w. In deriving (1.3.53a, b) it should be noted that, in general, $\partial \widetilde{c}_1 / \partial \widetilde{t}$ and $\partial \widetilde{c}_2 / \partial \widetilde{t}$ are non-zero and must be included, since the boundaries S_p and S_w move and thus the time-independent solutions for $\widetilde{c}_{1E}$ and $\widetilde{c}_{2E}$ as calculated in § 1.3.3, must be considered as functions of $\widetilde{t}$.

As for the outer region of the expansion, the solution of the purely electrical problem is given by (1.3.40) by applying boundary conditions only at infinity (and match onto the inner region expansions as the surfaces S_p or S_w are approached). Thus, upon the substitution of this solution into Eq.s (1.3.53a-f) and B.C.s (1.3.54 a-g), we see that in this outer region, the electroviscous variables $\widetilde{\vec{v}}^*$, $\widetilde{p}^*$, $\widetilde{c}_1^*$ $\cdots$ satisfy

$$\widetilde{\nabla}^2\widetilde{c}_1^* + \widetilde{\nabla}^2\widetilde{\psi}^* + \widetilde{\nabla}\cdot\left(\widetilde{c}_1^*\widetilde{\nabla}\widetilde{\psi}^*\right) - \mathrm{Pe}\left(\widetilde{\vec{v}}_H + \widetilde{\vec{v}}^*\right)\cdot\widetilde{\nabla}\widetilde{c}_1^* - \mathrm{Pe}\frac{\partial \widetilde{c}_1^*}{\partial \widetilde{t}} = 0 \tag{1.3.55a}$$

$$\widetilde{\nabla}^2\widetilde{c}_2^* - \widetilde{\nabla}^2\widetilde{\psi}^* - \widetilde{\nabla}\cdot\left(\widetilde{c}_2^*\widetilde{\nabla}\widetilde{\psi}^*\right) - \mathrm{Pe}\left(\frac{D_1}{D_2}\right)\left(\widetilde{\vec{v}}_H + \widetilde{\vec{v}}^*\right)\cdot\widetilde{\nabla}\widetilde{c}_2^* - \mathrm{Pe}\frac{\partial \widetilde{c}_2^*}{\partial \widetilde{t}} = 0 \tag{1.3.55b}$$

$$\epsilon^2\,\widetilde{\nabla}^2\widetilde{\psi}^* = -\widetilde{\rho}^* \tag{1.3.55c}$$

$$\widetilde{\rho}^* = \frac{1}{2}\left(\widetilde{c}_1^* - \widetilde{c}_2^*\right) \tag{1.3.55d}$$

$$\widetilde{\nabla}^2\widetilde{\vec{v}}^* - \widetilde{\nabla}\widetilde{p}^* = \lambda\,\widetilde{\rho}^*\widetilde{\nabla}\widetilde{\psi}^* \tag{1.3.55e}$$

$$\widetilde{\nabla}\cdot\widetilde{\vec{v}}^* = 0 \tag{1.3.55f}$$

with boundary conditions

$$\widetilde{c}_1^* \to 0 \qquad\qquad \widetilde{c}_2^* \to 0 \tag{1.3.56a}$$

$$\widetilde{\psi}^* \to 0 \tag{1.3.56b}$$

$$\widetilde{\vec{v}}^* \to 0 \tag{1.3.56c}$$

as $\widetilde{\vec{r}} \to \infty$. The equations and boundary conditions for $\widetilde{\vec{v}}^*$, $\widetilde{p}^*$, $\widetilde{c}_1^*$, $\cdots$ in the inner region of expansion at a point Q (on either surface S_p or S_w) may be obtained by writing Eq.s (1.3.53) and B.C.s (1.3.54) in terms of the inner variables using (1.3.18, 19) and then substituting the known expansions for the purely hydrodynamic problem variables (which are obtained by solving the equations and corresponding boundary conditions given in § 1.3.4.) and the expansions for the electrical problem variables given in § 1.3.3. However, in the inner region, boundary conditions are applied only at the solid boundary (i.e. at $\bar{z} = 0$)and match onto the outer region (at Q) as $\bar{z} \to \infty$. This is so obtained by Cox by applying the rigorous procedure of a matched asymptotic expansion of inner and outer expansions up to order ϵ^5. As a consequence of a logical process, he pointed out that the lowest order correction due to the electrohydrodynamic effects on the velocity and pressure fields appear at order ϵ^4, on the ion concentration of either specie and potential at the order ϵ^2 and on the charge density at order ϵ^4. Therefore, the electroviscous velocity, pressure, ion concentrations, potential and charge density may be written, in terms of outer variables, respectively, as

$$\vec{\tilde{v}}^* = \epsilon^4 \vec{\tilde{v}}_4^* + \cdots \tag{1.3.57a}$$

$$\tilde{p}^* = \epsilon^4 \tilde{p}_4^* + \cdots \tag{1.3.57b}$$

$$\tilde{c}_1^* = \epsilon^2 \tilde{c}_{12}^* + \cdots \qquad \tilde{c}_2^* = \epsilon^2 \tilde{c}_{22}^* + \cdots \tag{1.3.58a}$$

$$\tilde{\psi}^* = \epsilon^2 \tilde{\psi}_2^* + \cdots \tag{1.3.58b}$$

$$\tilde{\rho}^* = \epsilon^4 \tilde{\rho}_4^* \tag{1.3.58c}$$

Upon substituting these quantities in Eq.s (1.3.55e, f) and B.C. (1.3.56c), it follows that the electroviscous flow field satisfy a creeping flow equation

$$\tilde{\nabla}^2 \vec{\tilde{v}}_4^* - \tilde{\nabla} \tilde{p}_4^* = 0 \tag{1.3.59a}$$

$$\tilde{\nabla} \cdot \vec{\tilde{v}}_4^* = 0 \tag{1.3.59b}$$

with boundary condition

$$\vec{\tilde{v}}_4^* \to 0 \qquad \text{as} \quad \left| \vec{\tilde{r}} \right| \to \infty \tag{1.3.59c}$$

It can be concluded that this flow field resulting from the tangential movement of the ions in the diffuse double layer and hence it has the components on the solid surfaces (just outside the double layer) only parallel to the plane tangent to the solid surface (i.e. normal to the $\tilde{z}$ -axis). Therefore, $\vec{\tilde{v}}_4^*$ at the point Q (i.e., at $\tilde{z} = 0$) may be written as

$$\vec{\tilde{v}}_4^* = \tilde{B}_x \vec{i}_x + \tilde{B}_y \vec{i}_y \tag{1.3.59d}$$

where $\vec{i}_x$ and $\vec{i}_y$ are unit vectors in the $\tilde{x}$ and $\tilde{y}$ directions in the tangent plane to the surface and where $\tilde{B}_x$ and $\tilde{B}_y$ are the components of velocity which, in general, are function of electroviscous parameters and position on the solid surfaces. They are determined by Cox upon evaluating $\vec{\tilde{v}}_4^*$ at point Q (i.e., by matching $\vec{\tilde{v}}_4^*$ as the solid boundary is approached onto $\vec{\tilde{v}}_4^*$ as $|\vec{\tilde{r}}| \to \infty$) as

$$\tilde{B}_{Jx} = \lambda\left\{-4\ln\left[\cosh\left(\frac{\tilde{\psi}_J}{4}\right)\right]\frac{\partial \beta_{J1}}{\partial \tilde{x}} + \tilde{\psi}_J \frac{\partial \beta_{J2}}{\partial \tilde{x}}\right\} \qquad J = W, P \tag{1.3.59e}$$

$$\tilde{B}_{Jy} = \lambda\left\{-4\ln\left[\cosh\left(\frac{\tilde{\psi}_J}{4}\right)\right]\frac{\partial \beta_{J1}}{\partial \tilde{y}} + \tilde{\psi}_J \frac{\partial \beta_{J2}}{\partial \tilde{y}}\right\} \tag{1.3.59f}$$

in which parameters (β_{J1}, β_{J2}) are the value of the electroviscous ion concentrations and potential on the solid surfaces J, just outside the double layer, that is

$$\beta_{J1} = \tilde{c}_{12}^*, \qquad \beta_{J2} = \tilde{\psi}_2^* \qquad \text{on} \quad S_J \tag{1.3.59h}$$

The perturbation of ion concentrations at the lowest order [i.e. at O($\in^2$)] of counter-ions, $\tilde{c}_{12}^*$, and co-ions, $\tilde{c}_{22}^*$, satisfies the same equation which is obtained by Cox as

$$\tilde{\nabla}^2 \tilde{c}_{i2}^* = \mathrm{Pe}\left(\frac{D_1 + D_2}{2D_2}\right)\left(\vec{\tilde{v}}_H \cdot \tilde{\nabla}\tilde{c}_{i2}^* + \frac{\partial \tilde{c}_{12}^*}{\partial \tilde{t}}\right) \tag{1.3.60a}$$

with boundary conditions

$$\vec{n}\cdot\tilde{\nabla}\tilde{c}_{i2}^* = \mathrm{Pe}\, F_{cP}\,(\vec{n}\cdot\tilde{\nabla})(\vec{n}\cdot\tilde{\nabla})(\vec{n}\cdot\vec{\tilde{v}}_H) \qquad \text{on } S_P \tag{1.3.60b}$$

$$\vec{n}\cdot\tilde{\nabla}\tilde{c}_{i2}^* = \mathrm{Pe}\, F_{cW}\,(\vec{n}\cdot\tilde{\nabla})(\vec{n}\cdot\tilde{\nabla})(\vec{n}\cdot\vec{\tilde{v}}_H) \qquad \text{on } S_W \tag{1.3.60c}$$

$$\tilde{c}_{i2}^* \to 0 \qquad \text{as } |\vec{\tilde{r}}| \to \infty \tag{1.3.60d}$$

in which F_{cP} and F_{cW} are functions of the diffusivity of ions and surface potential defined by

$$F_{cJ} = \frac{1}{2D_2}\left[(D_2 - D_1)\tilde{\psi}_J - 4(D_2 + D_1)\ln\left(\cosh\frac{\tilde{\psi}_J}{4}\right)\right] \qquad J = (P, W) \tag{1.3.60e}$$

The perturbation in potential at $O(\epsilon^2)$, $\widetilde{\psi}_2^*$, satisfies

$$\widetilde{\psi}_2^* = \left(\frac{D_2 - D_1}{D_2 + D_1}\right)\widetilde{c}_{i2}^* + \widetilde{\phi} \qquad (1.3.61a)$$

in which $\widetilde{\phi}$ satisfies Laplace's equation

$$\widetilde{\nabla}^2\widetilde{\phi} = 0 \qquad (1.3.61b)$$

together with boundary conditions

$$\vec{n}\cdot\widetilde{\nabla}\widetilde{\phi} = \mathrm{Pe}\ F_{\phi P}\left(\vec{n}\cdot\widetilde{\nabla}\right)\left(\vec{n}\cdot\widetilde{\nabla}\right)\left(\vec{n}\cdot\vec{\widetilde{v}}_H\right) \qquad \text{on } S_P \qquad (1.3.61c)$$

$$\vec{n}\cdot\widetilde{\nabla}\widetilde{\phi} = \mathrm{Pe}\ F_{\phi W}\left(\vec{n}\cdot\widetilde{\nabla}\right)\left(\vec{n}\cdot\widetilde{\nabla}\right)\left(\vec{n}\cdot\vec{\widetilde{v}}_H\right) \qquad \text{on } S_W \qquad (1.3.61d)$$

$$\widetilde{\phi} \rightarrow 0 \qquad \text{as } \left|\vec{\widetilde{r}}\right| \rightarrow \infty \qquad (1.3.61e)$$

where we have written

$$F_{\phi P} = \left(\frac{2D_1}{D_1 + D_2}\right)\widetilde{\psi}_P, \qquad F_{\phi W} = \left(\frac{2D_1}{D_1 + D_2}\right)\widetilde{\psi}_W \qquad (1.3.61f)$$

1.3.6 - Force and Torque on Particle

The dimensionless force, $\vec{\widetilde{F}}$, [defined by (1.3.15)] and moment of force, $\vec{\widetilde{G}}$, [defined by (1.3.16)] experienced by the particle P could be calculated by the integrals (1.3.14, 17) in § 1.3.1 taken over any chosen surface S completely enclosing the particle. The simplest surface would be the particle surface S_p in the outer region (i.e. it is taken to be just outside of the double layer surrounding the particle), so that in the integrands (1.3.14,17a) the stress tensor $\widetilde{\sigma}_{ij}$ is used in terms of outer variables, defined by (1.3.11, 12). In the outer region, by the aid of Eq.s (1.3.57a, b) and Eq. (1.3.58b), $\vec{\widetilde{v}}$, $\widetilde{p}$ and $\widetilde{\psi}$, given by (1.3.52), may be written as

$$\vec{\widetilde{v}} = \vec{\widetilde{v}}_H + \epsilon^4\ \vec{\widetilde{v}}_4^* \qquad (1.3.62a)$$

$$\widetilde{p} = \widetilde{p}_H + \epsilon^4\ \widetilde{p}_4^* \qquad (1.3.62b)$$

$$\widetilde{\psi} = \epsilon^2\ \widetilde{\psi}_2^* \qquad (1.3.62c)$$

Here $\vec{\widetilde{v}}_H$ and $\widetilde{p}_H$ are the pure hydrodynamic velocity and pressure discussed in § 1.3.4. In writing Eq.s (1.3.62b, c) it is noted that by the aid of (1.3.40a, d) $\widetilde{\psi}_E = 0$ and $\widetilde{p}_E = 0$ throughout the outer region. By introducing the expansion (1.3.62) to the stress tensor (1.3.12), the dimensionless force on the particle $\widetilde{F}$ is determined by

$$\widetilde{F} = \widetilde{F}_H + \epsilon^4 \widetilde{F}_4^* + \cdots \tag{1.3.63}$$

The hydrodynamic force, $\widetilde{F}_H$ may be easily determined by solving the purely hydrodynamic problem discuss in § 1.3.4 and then using the relationship (1.3.14). But, as for the electroviscous force, the required solution for the electroviscous flow field given by (1.3.59) is not an easy task due to imposing the complex boundary conditions on the solid surfaces. Fortunately, for a stationary wall there is an alternative way to calculate the force by employing the Lorentz reciprocal theorem, which states that instead of solving a complex flow field, solve an easier one and from that find the force for the former.

If we define a disturbance flow field $\left(\vec{\widetilde{v}}_{Tk}, \widetilde{P}_{Tk}\right)$ due to a translation (indices T denotes translation without rotation) of the particle P with unit velocity in the k^{th} direction (k = 1, 2, 3) in a semi-infinite quiescent fluid bounded by an infinite plane wall (c.f., Fig. 1.5), the flow field, for each direction k, satisfies Stokes equation, that is

$$\widetilde{\nabla}^2 \vec{\widetilde{v}}_{Tk} - \widetilde{\nabla} P_{Tk} = 0 \qquad \text{and} \qquad \widetilde{\nabla} \cdot \vec{\widetilde{v}}_{Tk} = 0$$

or in indices notation as

$$\frac{\partial^2 \widetilde{v}_{Tki}}{\partial \widetilde{r}_j \partial \widetilde{r}_j} - \frac{\partial \widetilde{P}_{Tk}}{\partial \widetilde{r}_i} = 0 \qquad (i, j = 1, 2, 3) \tag{1.3.64a}$$

$$\frac{\partial \widetilde{v}_{Tki}}{\partial \widetilde{r}_i} = 0 \tag{1.3.64b}$$

together with the corresponding boundary conditions, that is [c.f., definition (1.3.12c)]

$$\widetilde{v}_{Tki} = \delta_{ik} \qquad \text{on } S_p \tag{1.3.65a}$$

$$\widetilde{v}_{Tki} = 0 \qquad \text{on } S_W \tag{1.3.65b}$$

$$\widetilde{v}_{Tki} = 0 \qquad \text{as } |\vec{\widetilde{r}}| \to 0 \tag{1.3.65c}$$

The first boundary condition shows that the velocity of the fluid is equal to unity only in the

the direction of the translation of the particle, i.e. when i = k (c.f., Fig.1.5), which is the no-slip boundary condition. The first boundary condition shows that the velocity of the fluid is equal to unity only in the direction of the translation of the particle, i.e. when i = k (c.f., Fig.1.5), which is the no slip boundary condition on the particle surface.

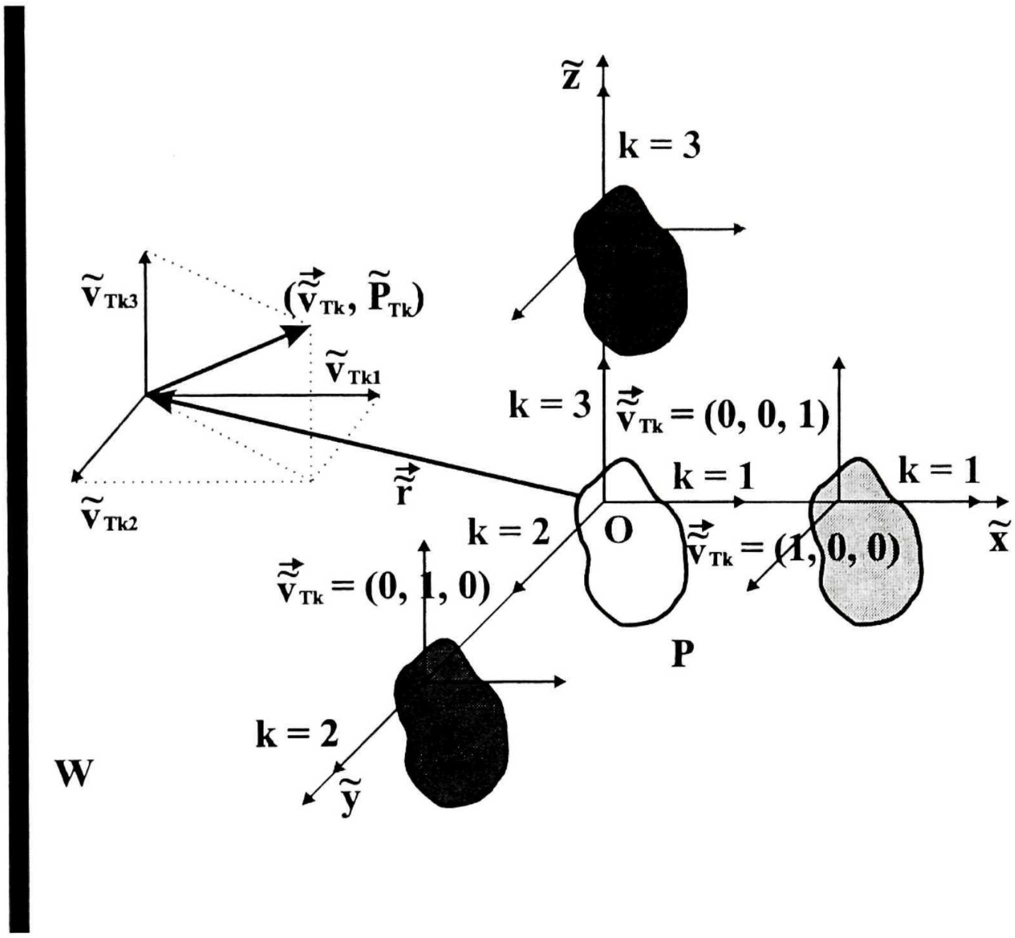

Fig. 1.5 - Flow field $\left(\vec{\tilde{v}}_{Tk}, \tilde{p}_{Tk}\right)$ produced at position $\vec{\tilde{r}}$ of a general point of the fluid due to the pure translation of particle P with unit velocity in the direction of either $\tilde{x}$, $\tilde{y}$ or $\tilde{z}$ -axis corresponding to k = 1, 2 or 3, respectively.

Then Lorentz reciprocal theorem may be written as [Happel & Brenner (1965)]

$$\int_S \tilde{v}_{Tki}\sigma^*_{4ij} n_j d\tilde{S} = \int_S \tilde{v}^*_{4i}\sigma_{Tkij} n_j d\tilde{S} \tag{1.3.66}$$

in which $\tilde{\sigma}_{Tkij}$ is the stress tensor for the flow field $\left(\vec{\tilde{v}}_{Tk}, \tilde{P}_{Tk}\right)$, n_j is the unit vector normal and outward to a closed surface S bounded any fluid volume. Surface S may consist of a number of distinct surfaces. Let S include the particle surface S_P, the wall surface S_W, and an imaginary surface of a semi-sphere drawn into fluid with an infinite radius R, S_R, (c.f., Fig 1.6). Thus, the first integral in the Lorentz reciprocal theorem may be expressed as

$$\int_S \tilde{v}_{Tki}\tilde{\sigma}^*_{4ij}n_j d\tilde{S} = \int_{S_P} \tilde{v}_{Tki}\tilde{\sigma}^*_{4ij}n_j d\tilde{S} + \int_{S_W} \tilde{v}_{Tki}\tilde{\sigma}^*_{4ij}n_j d\tilde{S} + \int_{S_R} \tilde{v}_{Tki}\tilde{\sigma}^*_{4ij}n_j d\tilde{S} \qquad (1.3.67a)$$

The velocity $\tilde{v}_{Tki}$ is due to particle translation, and hence it is induced by a point force application of the Oseen technique (assuming the force exerted on the fluid, by the particle, can be considered as a point force), so that it should be of order $\tilde{R}^{-1}$ [Happel & Brenner (1965), p. 83)]. Like pressure, the stress tensor (force per unit area), noting that the magnitude of the force is finite, is of order $\tilde{R}^{-2}$ and the surface of a sphere is equal to $4\pi\tilde{R},^2$ so that $d\tilde{S}$ is of order $\tilde{R}^2$. Therefore, the integrand of the third integral of the right hand side of (1.3.67a) is of order $\tilde{R}^{-1}$, and hence it tends to zero as $\tilde{R} \to \infty$, from which it follows that

$$\int_{S_R} \tilde{v}_{Tki}\tilde{\sigma}^*_{4ij}n_j d\tilde{S} \to 0 \qquad \text{as } \tilde{R} \to \infty \qquad (1.3.67b)$$

The second term in (1.3.67a) is obviously equal to zero, since by B.C. (1.3.65b) the velocity on the wall is equal to zero and the electroviscous stress tensor on the wall is of order unity (i.e. it is not too large), resulting in

$$\int_{S_W} \tilde{v}_{Tki}\tilde{\sigma}^*_{4ij}n_j d\tilde{S} = 0 \qquad (1.3.67c)$$

But, the first integral is exactly what we are looking for, the electroviscous force. By the aid of B.C. (1.3.65a) the velocity on the particle surface S_P is only non-zero and equal to unity when i = k [c.f., definition (1.3.12c)]. Thus, letting $\tilde{v}_{Tki} = 1$ and $i = k$, the first integral in the right hand side of Eq. (1.3.67a) becomes

$$\int_{S_P} 1 \times \tilde{\sigma}^*_{4kj}n_j d\tilde{S}$$

which represents the electroviscous force $\tilde{F}^*_{4k}$ [c.f., Eq (1.3.14)]. Therefore, by the aid of (1.3.67), the Lorentz reciprocal theorem, given by (1.3.66), may be expressed as

$$\tilde{F}^*_{4k} = \int_{S_P} \tilde{v}^*_{4i}\tilde{\sigma}_{Tkij}n_j d\tilde{S} + \int_{S_W} \tilde{v}^*_{4i}\tilde{\sigma}_{Tkij}n_j d\tilde{S} + \int_{S_R} \tilde{v}^*_{4i}\tilde{\sigma}_{Tkij}n_j d\tilde{S} \qquad (1.3.68)$$

By the same argument as for integral (1.3.67b) the third integral of the right hand side of (1.3.68) vanishes. Therefore, in view of the definition (1.3.59d), the remaining integrals may be expressed as

$$\tilde{F}^{*}_{4k} = \int_{S_P} \tilde{B}_i \tilde{\sigma}_{Tkij} n_j d\tilde{S} + \int_{S_W} \tilde{B}_i \tilde{\sigma}_{Tkij} n_j d\tilde{S} \qquad (1.3.69)$$

The above analysis is illustrated in Fig. 1.6.

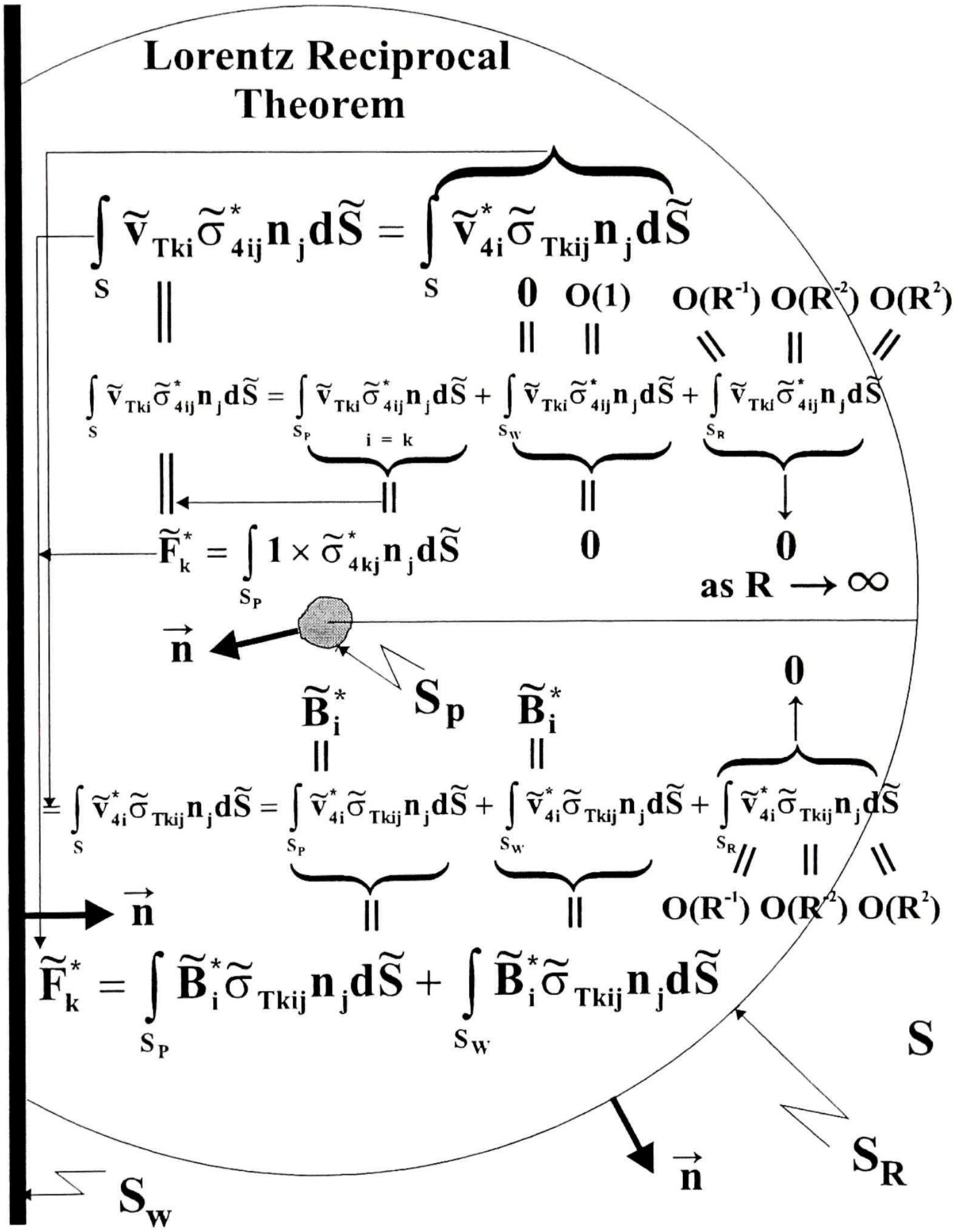

Fig. 1.6 - Surface S consist of S_p, S_W and S_R bounded a volume of fluid showing calculation of electroviscous forces upon application of the Lorentz reciprocal theorem.

Thus, the advantages of the application of the Lorentz reciprocal theorem is that, in order to know the force we require only to obtain the stress tensor corresponding to the flow field $\left(\vec{\tilde{v}}_{Tk}, \tilde{P}_{Tk}\right)$, multiplying it by the known boundary conditions of the electroviscous flow field and integrating it over the solid surfaces. Whereas, to obtain the force in a direct fashion we need to solve the whole electroviscius flow field to obtain the required electroviscous stress tensor.

Similarly, the torque experienced by the particle around a reference point O may be expressed as

$$\vec{\tilde{G}} = \vec{\tilde{G}}_H + \epsilon^4 \vec{\tilde{G}}_4^* \tag{1.3.70}$$

The hydrodynamic torque may be determined upon using Eq. (1.3.17) for the purely hydrodynamic problem. The electroviscous torque is so obtained upon applying the Lorentz reciprocal theorem as

$$\tilde{G}_{4k}^* = \int_{S_P} \tilde{B}_j \tilde{\sigma}_{Rkij} n_i d\tilde{S} + \int_{S_W} \tilde{B}_j \tilde{\sigma}_{Rkij} n_i d\tilde{S} \tag{1.3.71}$$

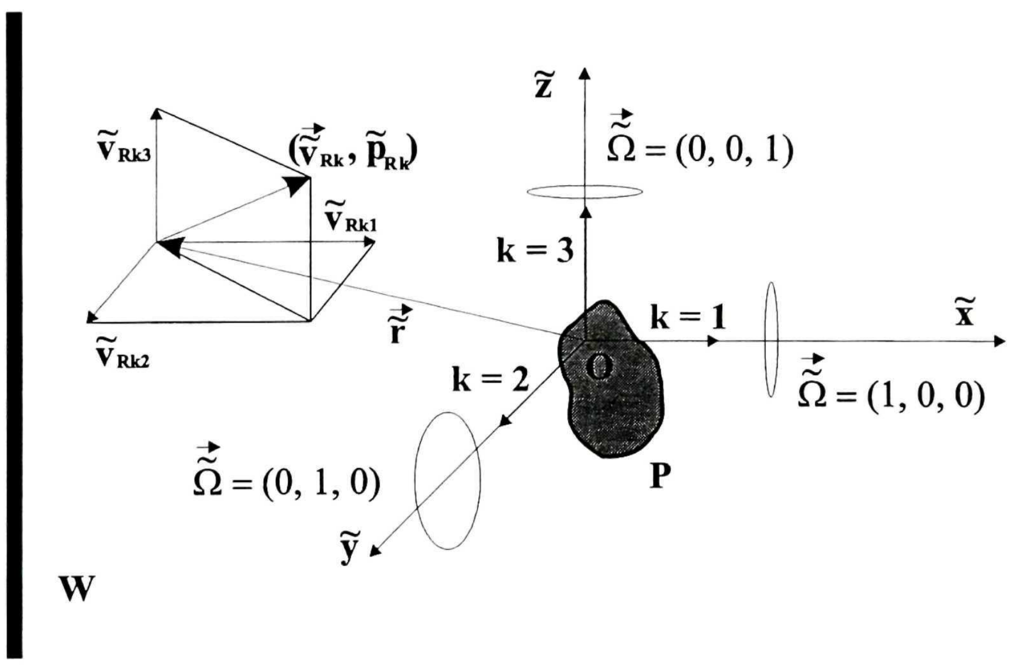

Fig. 1.7 - Flow field $\left(\vec{\tilde{v}}_{Rk}, \tilde{p}_{Rk}\right)$ produced at position $\vec{\tilde{r}}$ of a general point of the fluid due to the pure rotation of the particle P with unit angular velocity around either $\tilde{x}$, $\tilde{y}$ or $\tilde{z}$ -axis corresponding to k = 1, 2 or 3, respectively.

in which $\widetilde{B}_j$ is given by (1.3.59e, f) and $\widetilde{\sigma}_{Rkij}$ is the stress tensor for the flow field $\left(\vec{\widetilde{v}}_{Rk}, \widetilde{p}_{Rk}\right)$ satisfying the creeping flow equations

$$\frac{\partial^2 \widetilde{v}_{Rki}}{\partial \widetilde{r}_j \partial \widetilde{r}_j} - \frac{\partial \widetilde{p}_{Rk}}{\partial \widetilde{r}_i} = 0 \qquad (1.3.72a)$$

$$\frac{\partial \widetilde{v}_{Rki}}{\partial \widetilde{r}_i} = 0 \qquad (1.3.72b)$$

due to the rotation of the particle with unit angular velocity about an axis in the k-direction passing from point O in the quiescent fluid with the wall W being at rest (c.f., Fig 1.7). Therefore, it satisfies the following boundary conditions

$$\widetilde{v}_{Rki} = \varepsilon_{kij}\widetilde{r}_j \qquad \text{on } S_P \qquad (1.3.73a)$$

$$\widetilde{v}_{Rki} = 0 \qquad \text{on } S_W \qquad (1.3.73b)$$

$$\widetilde{v}_{Rik} \rightarrow 0 \qquad \text{as } \left|\vec{\widetilde{r}}\right| \rightarrow \infty \qquad (1.3.73c)$$

where $\widetilde{r}_j$ is the position vector relative to the reference point O and ε_{kij} is the alternating tensor, defined by (1.3.17b).

1.3.7 - Force on Sedimenting Sphere

Cox applied his general theory to the sedimentation of a charged sphere in an unbounded electrolyte and derived the total force experienced by the particle, for low Peclet numbers, as

$$F = -\left[6\pi\eta a + \frac{24\pi\varepsilon_m^2 (kT)^3}{\left(z_1 e\right)^4 c_\infty a}\left(\frac{G^2}{D_1} + \frac{H^2}{D_2}\right)\right] U_{SED}^{ST} \qquad (1.3.74)$$

in which ε_m is the permitivity of the medium, defined by (1.2.1b), (kT) the thermal energy, $\left(z_1 e\right)$ the charge of an ion of type of counter-ions, c_∞ the number ion bulk concentrations, (D_1, D_2) the diffusivity of (counter-ions, co-ions), and the surface potential is involved via parameters G and H, defined by (1.2.32c). The first term in the formula (1.3.74) is the well known Stokes drag formula for the sedimentation of uncharged sphere with velocity U_{SED}^{ST} and radius a, given by (1.2.17). The perturbation in the force (electroviscous force), the second term, was obtained by applying the Lorentz reciprocal theorem. Comparisons with the result of Oshima *et al.* (1984) is given in the next section.

1.4 - Results and Conclusions

Electroviscous phenomena for a thin diffuse double layer surrounding charged solid surfaces under a motion in a symmetric electrolyte are analysed by *Cox general theory (1997)*. The flow field, described by Stokes equations, perturbs the electric field induced by a charged solid surface. This is because the flow disturbs the ions in the diffuse double layer resulting in a perturbation in the charged density which causes the perturbation in the potential, described by the Poisson equation, given by (1.3.3c). The perturbation potential known as the streaming potential, in turns, causes a tangential motion of the ions in the diffuse double layer [by exerting an electrostatic force on them, described by the Lorentz-Stokes-Einstein equation, given by (1.3.1b)], resulting in a perturbation in the flow field. Or mathematically stated, there is a coupling between the electrical and hydrodynamic equations describing the system. Ions are also subject to a motion induced by the Brownian motion as a consequence of the difference in their concentrations (the concentration gradients), depending on their diffusion coefficients, described by the Fick's second law, given by (1.2.9), appearing as the first term in the convective diffusion equation (1.3.1a). Therefore, the electroviscous effects arise from the interaction among the flow field, Brownian motion, and the electric field originating from the charged boundaries and producing the diffuse double layer surrounding charged solid surfaces.

The streaming potential, with a magnitude of order ϵ^2 (ϵ is the ratio of the double layer thickness to the length scale of the problem assumed to be small), is a function of the perturbation in ion concentration as can be observed by Eq. (1.3.61a, b), in addition to the flow field appearing in its boundary conditions, given by (1.3.61c-f). It is observed from this equation that for identical diffusivities of counter-ions and co-ions the streaming potential is independent of the perturbation of ion concentration, as it is supposed to be.

The electroviscous ion concentrations of either species at the leading order, $O(\epsilon^2)$, satisfy the same equations and boundary conditions, determined by the relations (1.3.60). At the second approximation, $O(\epsilon^3)$, the perturbation in concentration of counter-ions and co-ions are also the same, resulting in a perturbation of the charge density appearing at the higher order, $O(\epsilon^4)$, [c.f., (1.3.58c]. In addition to the flow, the diffusivity of ions appears in both the equation and their boundary conditions. The electroviscous ion concentrations also depend on the ζ-potentials of the solid surfaces appearing on their boundary conditions, as it is supposed to be.

The electroviscous flow field satisfying the creeping flow equations, given by (1.3.59a, b), is of order (ϵ^4). Because of assumptions of the no-penetration of ions on the solid surfaces (non-conducting solid surfaces, and the absence of any chemical reactions) and especially the thin double layer thickness assumption, this perturbed flow has only a tangential component on the solid surfaces just outside the double layer. These boundary conditions, determined by (1.3.59c- h), depend not only on the steaming potential and ζ-potentials of the solid surfaces, but also on the electroviscous ion concentrations and the diffusivity of counter-ions and co-ions. Though electroviscous flow field is two orders of magnitude smaller than the steaming potential, it exerts a force and torque on the particle (electroviscous force and torque), which is two orders of magnitude greater than the one exerted by the streaming potential, as can be observed from the Maxwell stress tensor, given by (1.3.12). The tangential and normal component of the force as well as the torque, experienced by the particles are determined upon applying the Lorentz reciprocal theorem, outlined in § 3.6. The contribution to the force from this perturbed flow has been neglected in a number of publications in favor of the Maxwell stress tensor resulting from the streaming potential.

Ohshima, *et al.* (1984) derived the electroviscous velocity for the sedimentation of a charged sphere which is sufficiently far from other solid surfaces for interactionns to be absent, or mathematically stated in unbounded electrolyte, given by (1.2.28). Cox applied his general theory to obtain the drag force experienced by such a particle, given by (1.3.74). The Peclet number in both theories is assumed to be much smaller than unity. For the interaction of two solid surfaces, Wu, Warszynski & van de Ven (1996) calculated numerically the normal component of the force per unit length experienced by a long charged cylinder under translation near and parallel to a charged plane wall, for arbitrary Peclet numbers. Cox obtained an analytical expression for normal component of the force [presented in Wu, *et al.* (1996)'s paper] and also the tangential component of the force experienced by a charged cylinder under both translation and rotation parallel and near to a charged wall, for low Peclet numbers, given by (1.2.32). Warszynski & van de Ven (2000) reconsidered the translation problem of the cylinder-wall to obtain an analytical expression for the normal component of the force, given by (1.2.33).

To compare Cox's theory with the Oshima, Healy, White & O'Brien (1984)'s theory, the molar conductivity (A_i) which is related to the ion diffusion coefficient (D_i) via the mobility of the ions (ν_i) [upon using the *Nernst-Einstein equation* ($D_i = N_A kT\ \nu_i$)] may be written as

$$A_i = F_r^2 z_i^2 \upsilon_i = \left(N_A e\right)^2 z_i^{\,2} \upsilon_i = \frac{N_A\left(z_i e\right)^2}{kT} D_i \qquad (1.4.1a)$$

Thus, m_i, defined by relationships (1.2.28b, c), may be expressed in terms of ion diffusion coefficients as

$$m_i = \frac{2\varepsilon_m kT}{3\eta\left(z_i e\right)^2}\cdot\frac{N_A e^2 kT}{D_i N_A\left(z_i e\right)^2} = \frac{2\varepsilon_m (kT)^2}{3\eta\left(z_i e\right)^2 z_i^{\,2} D_i} \qquad (1.4.1b)$$

which is similar but different from that defined by (1.2.16b) by a factor z_i^2. From this and from the definition of the reciprocal double layer thickness, κ, given by (1.2.2b), the Oshima *et al.*'s theory (1984) for the sedimentation velocity may be written as

$$U_{SED} = \left\{1 + \frac{8\varepsilon_m^2 (kT)^3}{\eta e^4\left(c_1 z_1^2 + c_2 z_2^2\right)a^2}\left[\frac{G^2}{z_1^2 D_1} + \frac{H^2}{z_2^2 D_2 (1+I)}\right] + \right\} U_{SED}^{ST} \qquad (1.4.2)$$

Using Stokes' law, given by (1.2.17), the force, F, the fluid exerts on the particle P may be determined from it as

$$F = -\left\{6\pi\eta a + \frac{48\pi\varepsilon_m^2 (kT)^3}{e^4\left(c_1 z_1^2 + c_2 z_2^2\right)a}\left[\frac{G^2}{z_1^2 D_1} + \frac{H^2}{z_2^2 D_2 (1+I)}\right]\right\} U_{SED}^{ST} \qquad (1.4.3.a)$$

But, in view of the definition (1.2.2b) (noting that the length scale L here is taken to be identical to the sphere radius a), the parameter I, appearing in the dominator of (1.4.3a), defined by the relationship (1.2.28d), may be evaluated in a general form as

$$I = O(\in) + O(\in^3) \tag{1.4.3.b}$$

Thus, upon applying the binomial theorem, given by (1.3.21b), Oshima *et al.*'s theory may be expressed as

$$F = -\left\{ 6\pi\eta a + \frac{48\pi\varepsilon_m^2 (kT)^3}{e^4\left(c_1 z_1^2 + c_2 z_2^2\right)a} \left\{ \frac{G^2}{z_1^2 D_1} + \frac{H^2}{z_2^2 D_2} \left[1 - O(\varepsilon) - O(\varepsilon^3) + \cdots\right] \right\} \right\} U_{SED}^{ST} \tag{1.4.3c}$$

from which it follows that the electroviscous force at the first approximation for a symmetric electrolyte considered in the Cox theory ($z_1 = z_2$ and hence $c_1 = c_2 = c_\infty$) is exactly the same as that obtained by Oshima *et al.* Although the formula (1.4.3c) has terms of order $\in^5$ and those of order $\in^6 \cdots$, it is not obvious to determine its order [c.f., formula (1.2.28a)], whilst Cox's theory is valid up to order $\in^5$, the order considered in his general theory. Since Cox obtained the force for low Peclet numbers, he concluded that the Oshima *et al.*'s theory is valid for low Peclet numbers, though it is not mentioned by the authors in their paper.

As for the cylinder-wall problem, Cox's theory, given by (1.2.32a), for identical particle and wall potentials predicts

$$F_z = \frac{\sqrt{2}\pi}{2} \frac{\varepsilon_m^2 (kT)^3}{(z_1 e)^4 c_\infty} \frac{a\sqrt{a}}{h^2\sqrt{h}} \left[5U^2 + 4Ua\Omega - (a\Omega)^2\right] \left(\frac{G}{D_1} + \frac{H}{D_2}\right)^2 \tag{1.4.4}$$

Whereas, Warszynski & van de Ven's theory (2000), given by (1.2.33), for the identical ζ potential predicts

$$F_z = \frac{5\sqrt{2}\pi}{4} \frac{\varepsilon_m^2 (kT)^3}{(z_1 e)^4 c_\infty} \frac{a\sqrt{a}}{h^2\sqrt{h}} \left(\frac{G}{D_1} + \frac{H}{D_2}\right)^2 U^2 + \frac{3\sqrt{2}\pi}{4} \frac{\varepsilon_m^3 (kT)^4}{(z_1 e)^6 c_\infty^2} \frac{\sqrt{a}}{h^3\sqrt{h}} \left(\frac{G}{D_1} - \frac{H}{D_2}\right)^2 U^2 \tag{1.4.5}$$

From this it follows that for the translation of the cylinder the magnitude of the force obtained from Cox's theory is two times larger than that predicted by Warszynski & van de Ven 's theory (2000). For translation of a particle, both Cox's formula and Warszynski & van de Ven's predict a positive, zero or negative value for the normal component of the force, depending on the magnitude of the particle and wall ζ-potentials and the ratio of diffusivity of ions. Warszynski & van de Ven's theory (2000) also predicts the second approximation term due to the contribution of the tangential electric field resulting from the streaming potential appeared at O (ϵ^6), which agrees with that obtained by Bike and Prieve (1987). Bike and Prieve considered only this term to calculate the force which obviously is not the dominant contribution to it. The tangential component of the force is of order Pe and the normal component of O (Pe^2). Thus, because of the proportionality to U^2 the change in the direction of the flow does not reverse the direction of the normal component of the force.

Therefore, it is concluded that for a sedimentation of an spherical charged particle in an unbounded electrolyte, the electroviscous drag force, arising from the interaction among viscous, Brownian and electrical forces, obtained by Cox (1997) is in complete agreement with the Oshima *et al.*'s theory (1984). Whereas, Cox's theory [presented in Wu *et al.*'s paper (1996)] and Warszynski & van de Ven's theory (2000) for the motion of a charged cylinder near and parallel to a charged wall, obtained for low Peclet numbers, predict different values for the magnitude of the force and by a factor of two for identical ζ-potentials of the wall and cylinder surfaces. Warszynski & van de Ven (2000)'s results agree with Wu *et al.*'s numerical solution (1996) for arbitrary Peclet numbers. The authors speak of a lift force, presumably not realizing that under certain conditions the normal force can be negative.

Chapter Two

Electroviscous Cylinder-Wall Interactions

2.1 - Introduction

The problem of a long charged cylinder moving parallel to a charged plane wall for translation and rotation of the particle has been solved analytically by Raymond Cox and reported in a paper by Wu, Warszynski & van de Ven (1996) and for the translation of a cylinder by Warszynski & van de Ven (2000). In both theories the Peclet number and the clearance between the cylinder and wall are assumed to be small. Cox obtained the electroviscous force by applying the Lorentz reciprocal theorem as outlined in his general theory. Warszynski & van de Ven (2000) assumed the same orders for the perturbation in ion concentrations and potential as those given in Cox's general theory (1997), but obtained the force directly from stress tensors resulting from the perturbation in both hydrodynamic and electrical fields. Cox obtained both tangential and normal components of the force analytically. Warszynski & van de Ven (2000) obtained the lift component of the force analytically, but derived an analytical expression for the tangential component of the force containing an integral which is evaluated numerically. These only two available theories, given by (1.2.32, 33), predict different values for the magnitude of the force. It is the purpose of this chapter to reconsider the problem with the above assumptions to investigate the validity of either solution.

The analytical approach to the problem is based on the matched asymptotic expansion technique, which is a powerful technique to solve partial differential equations involving a small parameter. The idea is that the domain of interest is divided into two regions, the so-called inner and outer regions. The inner region is taken to be a small portion of the domain in the neighbourhood of the nearby contact point, and the outer region is the region everywhere outside the gap. For the inner region, variables are expanded in terms of the small parameter in a way that only dominant terms are being considered in the equations, so to simplify them for an easier solution. Moreover, a solution which is valid for the outer region, known as the outer solution, is required. At the boundary of the inner and outer regions these two solutions must predict the same value for those variables. Thus, the outer solution as it approaches the gap, should match smoothly to the inner solution as it approaches to the outer region. This is called the matching condition. With this procedure, one obtains the solution (inner plus outer solution) for the problem which is valid for all the domain of interest. Here, we are concerned with the inner solution, bearing in mind that the matching condition must be satisfied.

Thus, following the problem statement, the inner solution of the purely hydrodynamic problem, in an expansion of the normalized clearance, δ, (for $\delta << 1$) is presented in § 2.3. The perturbation of ion concentrations, in an expansion of the Peclet number, Pe, (for Pe << 1) is given in § 2.4. It contains outer and inner regions with inner region solutions of orders Pe and Pe^2, respectively. The perturbation of the potential is determined in § 2.5. The electroviscous force is obtained in § 2.6. It includes the tangential derivative of the electroviscous ion concentrations and potential, the determination of the stress tensor for translation of the particle parallel and normal to the wall and applying them to obtain the tangential and normal components of the force, upon the use of the Lorentz reciprocal theorem. The matching condition and the existence of the outer solution are discussed in § 2.7. Finally, results and conclusions are given in § 2.8.

2.2 - Problem Statement

Consider an electrically charged smooth cylindrical particle P moving in an electrolyte solution with a stationary charged plane wall W being present. The liquid is assumed to contain a symmetric electrolyte with two species of ions with charges $+z_1e$ and $-z_1e$. For the sake of simplicity we consider a long cylinder parallel to the wall in order to reduce the problem to a two dimensional one. The radius of the cylinder is denoted by a and the gap width between cylinder and wall by h.

The double layer thickness (Debye length), denoted by κ^{-1}, is assumed to be much smaller than the gap width, and the gap width is much smaller than the radius of the cylinder. Thus, $\epsilon << \delta << 1$ where

$$\delta = \frac{h}{a}, \qquad \epsilon = \frac{1}{\kappa a} \tag{2.2.1}$$

This condition fulfills the thin double layer condition considered in *Cox's general theory (1997)*. It is further assumed that the Peclet number, Pe, entering the electroviscous equations, defined by relationship (1.3.4), is much smaller than unity.

A right-handed Cartesian coordinate system (x, y, z) is chosen such that the center of the circular cross section of the cylinder coincides with the point ($x = 0$, $z = h + a$) with the y coordinate being parallel to its axis (c.f., Fig 2.1).

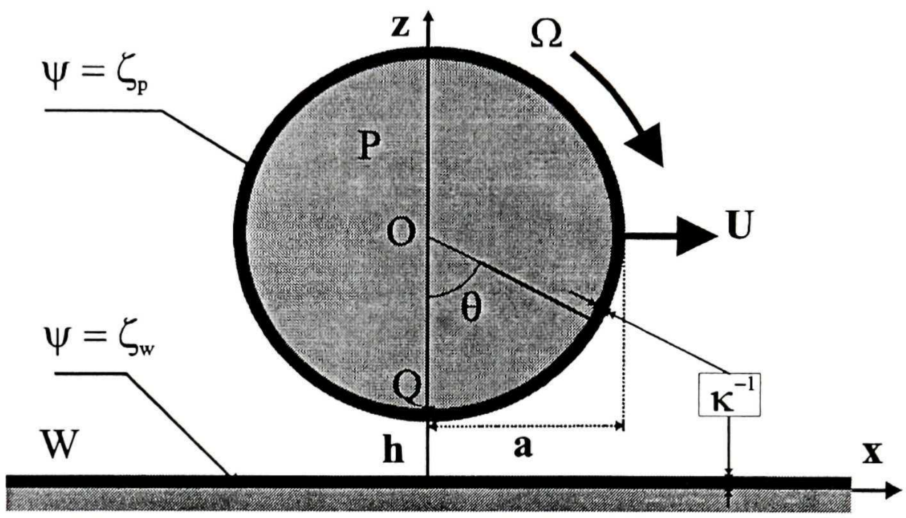

Fig. 2.1 - A charged cylinder translates and rotates parallel to a charged wall.

The cylinder is assumed to be translating perpendicular to its axis with velocity $\vec{u} = (U, 0, 0)$ and rotating around it with angular velocity $\vec{\Omega} = (0, \Omega, 0)$ in a fluid at rest. By taking the coordinate system to translate along with the cylinder, the problem reduces to a steady state one. That is, the flow field $(\vec{u}, p)$, the ion concentrations of either species and the electric potential at position $\vec{r}$ relative to the moving coordinate system (x, z) remain unchanged during the motion of the particle. As a consequence, since the electroviscous ion concentrations and potential arise from the coupling between electrical and hydrodynamic equations (hereafter denoted by c_2 and ψ_2)[1], would be time independent. The problem is equivalent to the one in which the particle is only rotating with angular velocity Ω in a fluid in which both wall and liquid are under translation with velocity $\vec{u} = (-U, 0, 0)$ for the wall and the fluid at infinity. Thus, the velocity $\vec{u}$ of the liquid on the cylinder surface in this

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[1]For simplicity we use the notation c_2 and ψ_2 instead of c_{i2}^* and ψ_2^* in Cox's general theory (1997), with the indices 2 denoting their orders in ϵ.

coordinate system is determined by

$$\vec{\Omega} \times \vec{r} = \begin{vmatrix} \vec{i}_x & \vec{i}_y & \vec{i}_z \\ 0 & \Omega & 0 \\ x & y & z-a-h \end{vmatrix} = \Omega(z-h-a)\vec{i}_x - \Omega x \vec{i}_z \tag{2.2.2}$$

where $\vec{i}_k(k = x, y, z)$ are the unit base vectors coinciding with the (x, y, z) coordinates. The surface of the wall, denoted by S_W, and that of the cylinder, S_P, may be written as

$$z = 0, \qquad \text{on } S_W, \qquad \left.\begin{aligned} x &= a\sin\theta \\ z &= h + a - a\cos\theta \end{aligned}\right\} \qquad \text{on } S_P \tag{2.2.3}$$

where θ is the polar angle associated with the cylinder cross section measured from the point Q (the nearest point of the cylinder to the wall) in the counter clockwise sense, as shown in Fig 2.1.

For the outer region we use variables made dimensionless by the length scale a, characteristic velocity U and the characteristic ion concentrations c_∞. Thus, the outer variables denoted by a tilde are defined by the relationship (1.3.2) in which L is taken to be a and V to be U. From this it follows that [c.f., (1.3.9, 20a, 4, 7, 15, 6, 5)]

$$\tilde{U} = 1, \quad \tilde{\Omega} = \frac{a\Omega}{U}, \quad Pe = \frac{aU}{D_1}, \quad \lambda = \frac{2c_\infty akT}{\eta U}, \quad \vec{F} = \eta U \tilde{\vec{F}}, \quad \epsilon = \left[\frac{\varepsilon_r \varepsilon_0 kT}{2(az_1e)^2 c_\infty}\right]^{1/2}$$

(2.2.4a)

Here, $\vec{F}$ is the force per unit length of the cylinder. The ζ-potential of the solid surfaces denoted by (ζ_P, ζ_W), are made dimensionless by relation (1.3.10) as

$$\tilde{\psi}_P = \left(\frac{z_1e}{kT}\right)\zeta_P \qquad \tilde{\psi}_W = \left(\frac{z_1e}{kT}\right)\zeta_W \tag{2.2.4b}$$

By eliminating the azimuth angle θ in (2.2.3), the solid surfaces, S_P and S_W, may be expressed in terms of the outer variables as

$$\tilde{z} = 0 \qquad \text{on } S_W, \qquad \tilde{z} = 1 + \delta \pm (1 - \tilde{x}^2)^{1/2} \qquad \text{on } S_P \tag{2.2.5}$$

(where the ± signs account for the upper and lower parts of the cylinder, respectively), and the normal unit vectors outward to them, denoted by $\vec{n}_P$ and $\vec{n}_W$, as

$$\vec{n}_W = \vec{i}_z, \qquad \vec{n}_P = \sin\theta\,\vec{i}_x - \cos\theta\,\vec{i}_z = \tilde{x}\vec{i}_x + (\tilde{z} - 1 - \delta)\vec{i}_z \tag{2.2.6}$$

2.3 - Hydrodynamics

2.3.1 - Flow in Outer Region

It is assumed that the liquid is incompressible, that is the fluid density, ρ, is constant everywhere. In addition, the Reynolds number, Re, based on the cylinder radius defined by $Re = a\rho U/\eta$ which is characteristic of the hydrodynamics in the outer region, is assumed to be small enough so that inertia effects can be negligible. As its definition indicates, this condition is achieved when either the kinematic viscosity, ν, ($\nu = \eta/\rho$) of the liquid is high (highly viscous liquid), the particle size is small or the characteristic velocity is small. The second and third condition (for the size of colloidal particles and its velocity close to the wall) are certainly fulfilled in experiments. Thus, the purely hydrodynamic flow satisfies the creeping flow equations (Stokes equations)

$$\tilde{\nabla}^2\vec{\tilde{u}} - \tilde{\nabla}\tilde{p} = 0 \tag{2.3.1}$$

$$\tilde{\nabla}\cdot\vec{\tilde{u}} = 0 \tag{2.3.2}$$

with boundary conditions on the solid surfaces [c.f., (2.2.2, 5)]

$$\tilde{u}_x = -1, \qquad \tilde{u}_z = 0 \qquad \text{on } \tilde{z} = 0 \tag{2.3.3}$$

$$\tilde{u}_x = \tilde{\Omega}(\tilde{z} - 1 - \delta), \qquad \tilde{u}_z = -\tilde{\Omega}\tilde{x} \qquad \text{on } \tilde{z} = 1 + \delta \pm \sqrt{(1 - \tilde{x}^2)} \tag{2.3.4}$$

and at infinity

$$\tilde{u}_x = -1, \qquad \tilde{u}_z = 0 \qquad \text{as} \left|\vec{r}\right| \to \infty \tag{2.3.5}$$

This produces a flow field which is bounded, or mathematically stated, it is of order unity (i.e. it is neither very small nor very large as observed from its boundary conditions). Since the small parameter δ appears in the boundary condition (2.3.4a) (as a consequence of the geometry of the problem) the outer solution can be constructed upon the expansion of the flow field in δ as[1]

$$\begin{aligned} \tilde{u}_x &= \tilde{u}_{x0} + \delta\, \tilde{u}_{x1} + \delta^2\, \tilde{u}_{x2} \cdots, \qquad \tilde{p} = \tilde{p}_0 + \delta\, \tilde{p}_1 + \delta^2\, \tilde{p}_2 \quad \cdots, \\ \tilde{u}_z &= \tilde{u}_{z0} + \delta\, \tilde{u}_{z1} + \delta^2\, \tilde{u}_{z2} \cdots \end{aligned} \tag{2.3.6}$$

---

[1] The last indices of any variable denotes the order of that variable in δ.

The leading term in the right-hand side of the expansion (2.3.6) is of order unity, $O(\delta^0)$, as it is supposed to be, the second term is much smaller than the first one, the third one is much smaller than the second one, and so on, since δ is assumed to be much smaller than unity. Thus, a solution of the problem up to two or three terms gives a very good approximation for the flow field when $\delta < 1$, even if δ is not very small.

To solve this problem at the first approximation, we neglect the terms beyond order unity. In other words, in the expansion (2.3.6) δ should be taken to be equal to zero. Thus, for this limiting case, the cylinder would be in contact with the wall since δ is the gap width between the cylinder and the wall. For this case, both B.C.s (2.3.3a, 4a) cannot simultaneously be satisfied at the origin. Thus, a first approximation to the flow for the outer region would be the solution of Eq.s (2.3.1, 2) with B.C.s (2.3.3-5) in which $\delta = 0$ which is valid throughout the fluid except in the neighbourhood of the origin, because of the singularity at this point. Thus, an individual solution must be constructed for the small portion of the domain around the neighbourhood of the nearby contact point (inner solution) which is valid for this region that is, the equations of motion as well as the boundary conditions on both solid surfaces bounding this region must be satisfied. By the way, for the inner region solution, the boundary condition at infinity, given by (2.3.5), is not imposed since this region only includes (and hence the solution of which is only valid for) a small portion of the neighbourhood of the nearby contact point. Instead, it has to satisfy the matching condition asymptote by requiring that the inner solution, as it approaches the outer edge of the inner region, being matched to the outer solution as it approaches the origin i.e. as $\tilde{x} \to 0$.

2.3.2 - Flow in Inner Region

Since the clearance between the particle and wall is assumed to be very small, it is justified to apply lubrication theory to analyze the flow field within the gap. Thus, to solve the flow field for this region we expand the independent variables (the two dimensions, $\widetilde{X}$ and $\tilde{z}$) and the dependent variables ($\tilde{u}_x$, $\tilde{u}_z$, $\tilde{p}$) in terms of the parameter δ according to their magnitudes in order to consider only the dominant terms (at each order in δ) in the equations of the motion to be solved for either order in δ. It is obvious that in the inner region the $\widetilde{Z}$ dimension has a lower magnitude than the $\widetilde{X}$ dimension and hence the space in this direction is too tight for the fluid to manoeuver, so that the lower magnitude of the velocity would be the velocity in this direction, $\tilde{u}_z$. In the gap the flow is subject to the strong shear. This is because in the gap the velocity field falls from its maximum value (on the particle surface) to its minimum value (zero on the wall) in a shorter distance than in any other part of the medium. In other words the derivative of the velocity field with respect to the $\hat{z}$-axis reaches its highest value in the gap. Thus, the derivative of the pressure with respect to $\hat{z}$ reaches its lowest value in the gap, according to Bernoulli's law. Therefore, we may define the inner variables denoted by a hat (ˆ) as

$$\begin{aligned} &\tilde{x} = \delta^{1/2}\hat{x}, \qquad &&\tilde{z} = \delta\,\hat{z} && \\ &\tilde{u}_x = \hat{u}_x, \qquad &&\tilde{u}_z = \delta^{1/2}\hat{u}_z, \qquad &&\tilde{p} = \delta^{-3/2}\hat{p} \end{aligned} \tag{2.3.7}$$

Thus, the cylinder shape for the gap, (i.e., the lowest part of the cylinder) may be expressed in terms of the inner variables as (c.f., Fig. 2.2)

$$\delta(1-\hat{z}) = -1 + \left(1-\delta\hat{x}^2\right)^{\frac{1}{2}} \tag{2.3.8}$$

or upon expansion of the bracket by the binomial theorem as

$$\hat{z} = 1 + \frac{1}{2}\hat{x}^2 + \delta\frac{\hat{x}^4}{8} + \cdots \tag{2.3.9}$$

Then, upon introducing the expansion (2.3.7) in (2.3.1-4), the equations of motion for the inner region are determined by

$$\frac{\partial^2\hat{u}_x}{\partial\hat{z}^2} - \frac{\partial\hat{p}}{\partial\hat{x}} + \delta\frac{\partial^2\hat{u}_x}{\partial\hat{x}^2} = 0 \tag{2.3.10}$$

$$-\frac{\partial\hat{p}}{\partial\hat{z}} + \delta\frac{\partial^2\hat{u}_z}{\partial\hat{z}^2} + \delta^2\frac{\partial^2\hat{u}_z}{\partial\hat{x}^2} = 0 \tag{2.3.11}$$

$$\frac{\partial\hat{u}_x}{\partial\hat{x}} + \frac{\partial\hat{u}_z}{\partial\hat{z}} = 0 \tag{2.3.12}$$

The boundary conditions are [c.f., B.C.s (2.3.3, 4)]

$$\hat{u}_x = -1, \qquad \hat{u}_z = 0 \qquad \text{on } \hat{z} = 0 \tag{2.3.13}$$

$$\hat{u}_x = -\tilde{\Omega} + \delta\tilde{\Omega}(\hat{z}-1), \quad \hat{u}_z = -\tilde{\Omega}\hat{x} \quad \text{on } \hat{z} = 1 + \frac{\hat{x}^2}{2} + \delta\frac{\hat{x}^4}{8} + O\left(\delta^2\right) \tag{2.3.14}$$

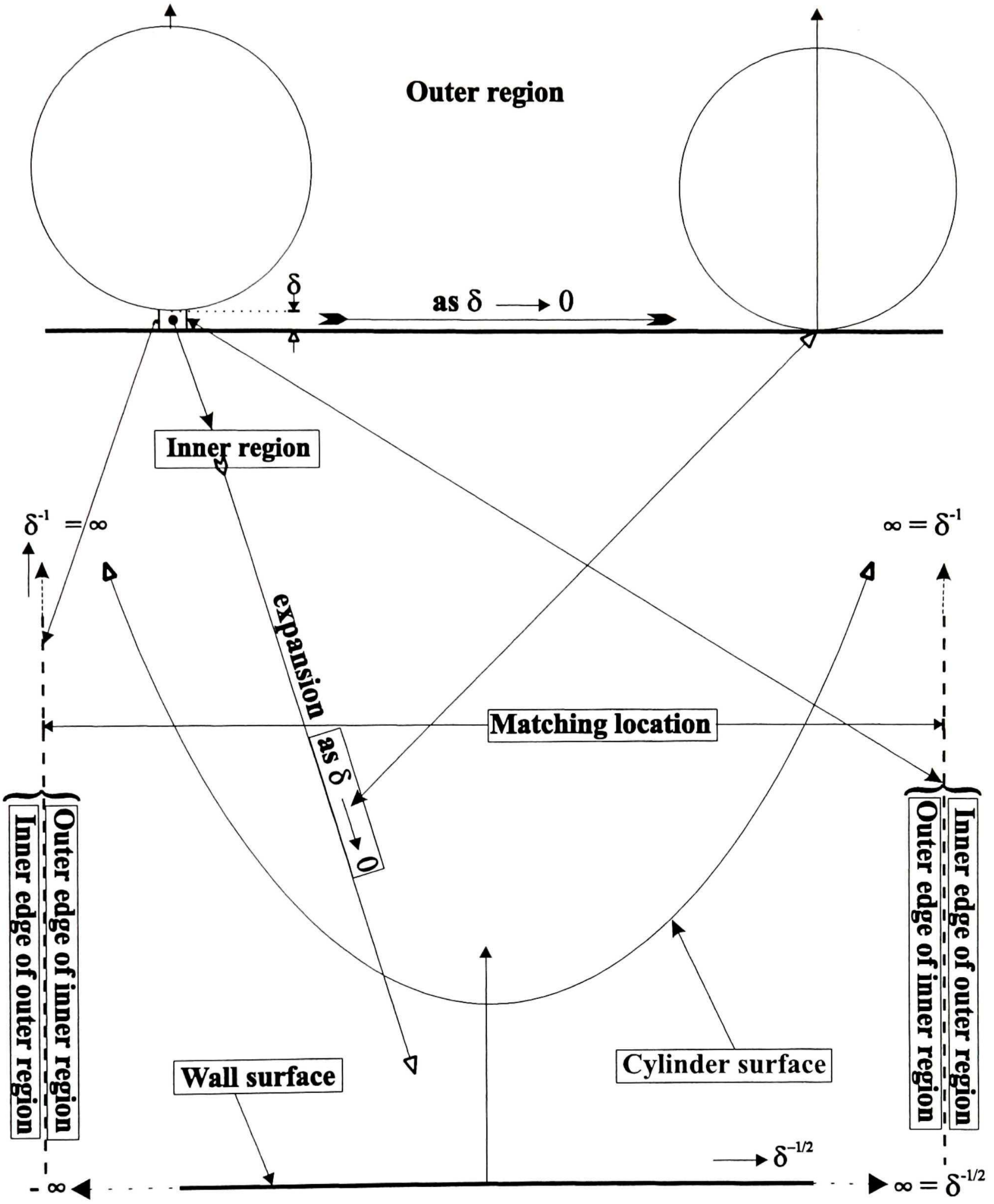

Fig. 2.2-Inner and outer regions - Inner region expansion.

Since δ is very small, the expansion $\tilde{x} = \delta^{1/2}\hat{x}$ in (2.3.7) indicates that, for $\tilde{x}$ of order unity, $\hat{x}$ has to be large enough to satisfy this matching location asymptote (i.e., as $\delta \to 0$, $\hat{x} \to \pm\infty$, c.f., Fig. 2.2) . Because the flow field in the outer region is of order unity, the dependent inner variables at the first approximation has also to match onto the outer variables at order δ^0 that is,

$$\vec{\hat{u}}_0\Big|_{\hat{x}\to\pm\infty} = \vec{\tilde{u}}_0\Big|_{\tilde{x}\to 0}, \qquad \hat{p}_0\Big|_{\hat{x}\to\pm\infty} = \tilde{p}_0\Big|_{\tilde{x}\to 0} \qquad (2.3.15)$$

in which ∞ for the inner dimension means the location of the outer edge of the inner region, as shown in Fig. 2.2. Thus, the expansion of the independent variables in (2.3.7) indicates that for the solution to satisfy the matching condition (2.3.15), we require

$$\hat{u}_x = O(\hat{x}^0), \qquad \hat{u}_z = O(\hat{x}^{+1}), \qquad \hat{p} = O(\hat{x}^{-3}) \qquad \text{as } \hat{x}\to \pm\infty \qquad (2.3.16)$$

2.3.2.1- Inner Solution at Lowest Order in δ

The inner solution may be constructed upon introducing an expansion of the flow field as

$$\hat{u}_x = \hat{u}_{x0} + \delta\,\hat{u}_{x1} + \cdots, \qquad \hat{u}_z = \hat{u}_{z0} + \delta\,\hat{u}_{z1} + \cdots, \qquad \hat{p} = \hat{p}_0 + \delta\,\hat{p}_1 + \cdots \qquad (2.3.17)$$

to the equations of motion given by (2.3.10-16). Doing so, and collecting the terms of the same order in δ, at order unity they satisfy

$$\frac{\partial^2 \hat{u}_{x0}}{\partial \hat{z}^2} = \frac{\partial \hat{p}_0}{\partial \hat{x}} \qquad (2.3.18)$$

$$\frac{\partial \hat{p}_0}{\partial \hat{z}} = 0 \qquad (2.3.19)$$

$$\frac{\partial \hat{u}_{x0}}{\partial \hat{x}} + \frac{\partial \hat{u}_{z0}}{\partial \hat{z}} = 0 \qquad (2.3.20)$$

with boundary conditions

$$\hat{u}_{x0} = -1,, \qquad \hat{u}_{z0} = 0 \qquad \text{on } \hat{z} = 0 \qquad (2.3.21)$$

$$\hat{u}_{x0} = -\tilde{\Omega}, \qquad \hat{u}_{z0} = -\hat{x}\tilde{\Omega} \qquad \text{on } \hat{z} = 1 + \frac{1}{2}\hat{x}^2 \qquad (2.3.22)$$

and with matching condition

$$\hat{u}_{x0} = O(1), \qquad \hat{u}_{z0} = O(\hat{x}), \qquad \hat{p}_0 = O(\hat{x}^{-3}) \quad \text{as } \hat{x} \to \pm\infty \tag{2.3.23}$$

Eq. (2.3.19) indicates that to the leading term the pressure is independent of $\hat{z}$, so that Eq. (2.3.18) may easily be integrated twice with respect to $\hat{z}$ to give

$$\hat{u}_{x0} = \frac{1}{2}\frac{d\hat{p}_0}{d\hat{x}}\hat{z}^2 + A\hat{z} + B \tag{2.3.24}$$

Imposing B.C.s (2.3.21a, 22a) results in

$$B = -1, \qquad\qquad A = -\frac{1}{2}\frac{d\hat{p}_0}{d\hat{x}}\hat{H} + \left(1-\tilde{\Omega}\right)\hat{H}^{-1} \tag{2.3.25}$$

where we have written

$$\hat{H} = 1 + \frac{1}{2}\hat{x}^2 \tag{2.3.26}$$

The x-component of the velocity is obtained as

$$\hat{u}_{x0} = \frac{1}{2}\frac{d\hat{p}_0}{d\hat{x}}\left(\hat{z}^2 - \hat{H}\hat{z}\right) + \left(1-\tilde{\Omega}\right)\hat{H}^{-1}\hat{z} - 1 \tag{2.3.27}$$

Introducing its derivative with respect to $\hat{x}$ into the continuity equation (2.3.20) gives the equation for the z-component of the velocity:

$$\frac{\partial \hat{u}_{z0}}{\partial \hat{z}} = -\frac{1}{2}\frac{d^2\hat{p}_0}{d\hat{x}^2}\left(\hat{z}^2 - \hat{H}\hat{z}\right) + \frac{1}{2}\frac{d\hat{p}_0}{d\hat{x}}\hat{x}\hat{z} + \left(1-\tilde{\Omega}\right)\hat{x}\hat{z}\hat{H}^{-2} \tag{2.3.28}$$

Integrating it with respect to $\hat{z}$ and imposing B.C. (2.3.21b) results in

$$\hat{u}_{z0} = -\frac{1}{2}\frac{d^2\hat{p}_0}{d\hat{x}^2}\left[\frac{1}{3}\hat{z}^3 - \frac{1}{2}\hat{H}\hat{z}^2\right] + \frac{1}{4}\frac{d\hat{p}_0}{d\hat{x}}\hat{x}\hat{z}^2 + \frac{1}{2}\left(1-\tilde{\Omega}\right)\hat{x}\hat{H}^{-2}\hat{z}^2 \tag{2.3.29}$$

Imposing B.C. (2.3.22b) gives the equation for the pressure:

$$\frac{1}{12}\frac{d^2\hat{p}_0}{d\hat{x}^2}\hat{H}^3 + \frac{1}{4}\frac{d\hat{p}_0}{d\hat{x}}\hat{x}\hat{H}^2 + \frac{1}{2}\left(1+\tilde{\Omega}\right)\hat{x} = 0$$

or

$$\frac{d}{d\hat{x}}\left[\hat{H}^3\frac{d\hat{p}_0}{d\hat{x}}\right] = -6\left(1+\tilde{\Omega}\right)\hat{x} \tag{2.3.30}$$

which is equivalent to the Reynolds equation occurring in the classical lubrication theory. It may be integrated to give

$$\frac{d\hat{p}_0}{d\hat{x}} = -3\left(1+\tilde{\Omega}\right)\left(\hat{x}^2 + C\right)\hat{H}^{-3} \tag{2.3.31}$$

But the matching condition (2.3.23c) implies that the pressure tends to zero as both $\hat{x} \to +\infty$ and $\hat{x} \to -\infty$. Thus, the constant C is determined by

$$\hat{p}_0\Big|_{\hat{x}\to -\infty}^{\hat{x}\to \infty} = -3\left(1+\tilde{\Omega}\right)\int_{-\infty}^{\infty}\left(\hat{x}^2 + C\right)\hat{H}^{-3}d\hat{x} = 0 \tag{2.3.32}$$

By the use of [c.f., (2.3.26)]

$$\hat{x}^2 = 2\hat{H} - 2 \tag{2.3.33}$$

and the integrals

$$\int \hat{H}^{-2}d\hat{x} = \frac{1}{2}\frac{\hat{x}}{\hat{H}} + \frac{\sqrt{2}}{2}\tan^{-1}\left(\frac{\hat{x}}{\sqrt{2}}\right), \tag{2.3.34}$$

$$\int \hat{H}^{-3}d\hat{x} = \frac{\hat{x}}{4\hat{H}^2} + \frac{3\hat{x}}{8\hat{H}} + \frac{3\sqrt{2}}{8}\tan^{-1}\left(\frac{\hat{x}}{\sqrt{2}}\right) \tag{2.3.35}$$

Eq. (2.3.32) may be evaluated as

$$\left|\frac{\hat{x}}{\hat{H}} + \sqrt{2}\tan^{-1}\left(\frac{\hat{x}}{\sqrt{2}}\right) + (C-2)\left[\frac{\hat{x}}{4\hat{H}^2} + \frac{3\hat{x}}{8\hat{H}} + \frac{3\sqrt{2}}{8}\tan^{-1}\left(\frac{\hat{x}}{\sqrt{2}}\right)\right]\right|_{-\infty}^{\infty} = 0 \tag{2.3.36}$$

from which C is obtained to be equal to - 2/3. Thus, the pressure is determined by

$$\hat{p}_0 = -3\left(1+\tilde{\Omega}\right)\int_{-\infty}^{\hat{x}}\left(\hat{x}^2 - \frac{2}{3}\right)\hat{H}^{-3}d\hat{x} = 2\left(1+\tilde{\Omega}\right)\hat{x}\hat{H}^{-2} \tag{2.3.37}$$

To see how the matching condition is satisfied, for large value of $\hat{x}$, $\hat{H}^{-2}$ may be expressed as [c.f., (2.3.26)]

$$\hat{H}^{-2} = \left[\frac{1}{1+\frac{1}{2}\hat{x}^2}\right]^2 \to 4\hat{x}^{-4} \qquad \text{as } \hat{x} \to \pm\infty \tag{2.3.38}$$

Therefore, the pressure, determined by (2.3.37), for large distances from the origin (i.e. for the outer edges of the inner region, c.f., Fig. 2.2) may be written as

$$\hat{p} \to 8\left(1+\widetilde{\Omega}\right)\hat{x}^{-3} \qquad \text{as } \hat{x} \to \pm\infty \tag{2.3.39}$$

which satisfies the matching condition (2.3.23c). Now, from the first and second derivatives of the pressure, the x and z-components of the velocity, given by (2.3.27, 29), are obtained:

$$\hat{u}_{x0} = \left(1+\widetilde{\Omega}\right)\left[\left(4\hat{H}^{-3} - 3\hat{H}^{-2}\right)\left(\hat{z}^2 - \hat{H}\hat{z}\right) - \frac{1}{2}\right] + \left(1-\widetilde{\Omega}\right)\left[\hat{H}^{-1}\hat{z} - \frac{1}{2}\right] \tag{2.3.40}$$

$$\hat{u}_{z0} = \left(1+\widetilde{\Omega}\right)\hat{x}\left[\left(4\hat{H}^{-4} - 2\hat{H}^{-3}\right)\hat{z}^3 - \left(4\hat{H}^{-3} - \frac{3}{2}\hat{H}^{-2}\right)\hat{z}^2\right] + \frac{1}{2}\left(1-\widetilde{\Omega}\right)\hat{x}\hat{H}^{-2}\hat{z}^2 \tag{2.3.41}$$

In this manner, the inner solution of the flow field is determined by (2.3. 37, 40, 41), valid up to order δ [i.e. with an error term of $O(\delta)$], so that the smaller the gap width, the more accurate the result. If we are interested in improving the approximation of the flow field, we may solve the equations along with boundary conditions as well as matching conditions constructed at the second, third, ... order in δ for $\left(\hat{u}_{x1}, \hat{u}_{z1}, \hat{p}_1\right)$, $\left(\hat{u}_{x2}, \hat{u}_{z2}, \hat{p}_2\right), \ldots$ in the expansion (2.3.17), by the use of the solution at the lower order (for each order), i.e. by an iterative procedure.

2.4 - Electroviscous Ion Concentrations

2.4.1 - Outer Region

The perturbation in ion concentrations, here denoted by $\widetilde{c}_2$, for low Peclet numbers may be expanded in this parameter as[1]

$$\widetilde{c}_2 = Pe^0\widetilde{c}_{20} + Pe\,\widetilde{c}_{21} + Pe^2\frac{D_1 + D_2}{2D_2}\widetilde{c}_{22} + \cdots \tag{2.4.1}$$

This expansion may be introduced to the equation and boundary condition (1.3.60):

$$\nabla^2\left[\widetilde{c}_{20} + Pe\,\widetilde{c}_{21} + Pe^2\frac{D_1 + D_2}{2D_2}\widetilde{c}_{22} + \cdots\right] = Pe\frac{D_1 + D_2}{2D_2}\tilde{\bar{u}} \cdot \nabla\left[\widetilde{c}_{20} + Pe\,\widetilde{c}_{21} + \cdots\right]$$

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[1]The last indices of the electroviscous variables denote the order of those variables in Pe.

$$\vec{n}_J \cdot \nabla \left[\tilde{c}_{20} + Pe\tilde{c}_{21} + Pe^2 \frac{D_1 + D_2}{2D_2} \tilde{c}_{22} \right]_{S_J} = PeF_{cJ} \left(\vec{n}_J \cdot \nabla \right) \left(\vec{n}_J \cdot \nabla \right) \left(\vec{n}_J \cdot \tilde{\vec{u}} \right) \Big|_{S_J}$$

and

$$\left[\tilde{c}_{20} + Pe\tilde{c}_{21} + Pe^2 \frac{D_1 + D_2}{2D_2} \tilde{c}_{22} + \cdots \right] \to 0 \qquad \text{as } \tilde{\vec{r}} \to 0$$

in which F_{cJ} (J = P, W) is defined by (1.3.60e). Collecting terms, of the same order, in Pe results, at order Pe^0, in

$$\nabla^2 \tilde{c}_{20} = 0 \tag{2.4.2}$$

with boundary conditions

$$\vec{n}_J \cdot \nabla \tilde{c}_{20} \Big|_{S_J} = 0, \qquad \tilde{c}_{20} \to 0 \qquad \text{as } \tilde{\vec{r}} \to 0 \tag{2.4.3}$$

At order Pe:

$$\nabla^2 \tilde{c}_{21} = \frac{D_1 + D_2}{2D_2} \tilde{\vec{u}} \cdot \nabla c_{20} \qquad \text{or} \qquad \frac{\partial^2 \tilde{c}_{21}}{\partial \tilde{x}^2} + \frac{\partial^2 \tilde{c}_{21}}{\partial \tilde{z}^2} = 0 \tag{2.4.4}$$

with boundary conditions

$$\vec{n}_J \cdot \nabla \tilde{c}_{11} \Big|_{S_J} = F_{cJ} \left(\vec{n}_J \cdot \nabla \right) \left(\vec{n}_J \cdot \nabla \right) \left(\vec{n}_J \cdot \tilde{\vec{u}} \right) \Big|_{S_J} \qquad J = (P, W) \tag{2.4.5}$$

$$\tilde{c}_{21} \to 0 \qquad \text{as } \left| \tilde{\vec{r}} \right| \to \infty \tag{2.4.6}$$

The normal derivative and the normal component of the velocity may be written as [c.f., (2.2.6)]

$$\vec{n}_W \cdot \nabla = \vec{i}_z \cdot \left(\vec{i}_z \frac{\partial}{\partial \tilde{x}} + \vec{i}_y \frac{\partial}{\partial \tilde{y}} + \vec{i}_z \frac{\partial}{\partial \tilde{z}} \right) = \frac{\partial}{\partial \tilde{z}}, \tag{2.4.7}$$

$$\vec{n}_P \cdot \nabla = \tilde{x} \frac{\partial}{\partial \tilde{x}} + (\tilde{z} - 1 - \delta) \frac{\partial}{\partial \tilde{z}} \tag{2.4.8}$$

and

$$\vec{n}_W \cdot \tilde{\vec{u}} = \tilde{u}_z, \qquad \vec{n}_P \cdot \tilde{\vec{u}} = \tilde{x}\tilde{u}_x + (\tilde{z} - 1 - \delta)\tilde{u}_z \tag{2.4.9}$$

and at order Pe^2 :

$$\tilde{\nabla}^2 \tilde{c}_{22} = \vec{\tilde{u}} \cdot \nabla \tilde{c}_{21} = \left(\tilde{u}_x \frac{\partial}{\partial \tilde{x}} + \tilde{u}_z \frac{\partial}{\partial \tilde{z}} \right) \tilde{c}_{21} \qquad (2.4.10)$$

with boundary conditions

$$\vec{n}_W \cdot \nabla \tilde{c}_{22} \Big|_{S_W} = \frac{\partial \tilde{c}_{22}}{\partial \tilde{z}} \Big|_{S_W} = 0 \qquad (2.4.11)$$

$$\vec{n}_P \cdot \nabla \tilde{c}_{22} \Big|_{S_P} = \tilde{x} \frac{\partial \tilde{c}_{22}}{\partial \tilde{x}} + (\tilde{z} - 1 - \delta) \frac{\partial \tilde{c}_{22}}{\partial \tilde{z}} \Big|_{S_P} = 0 \qquad (2.4.12)$$

and

$$\tilde{c}_{22} \to 0 \qquad \text{as } \left| \vec{\tilde{r}} \right| \to \infty \qquad (2.4.13)$$

The equation and boundary condition (2.4.2, 3) guaranties that $\tilde{c}_{20} = 0$ everywhere. Since B.C. (2.4.3a) indicates that $\tilde{c}_{20}$ has no singularity at the origin and since it satisfies the homogenous Eq. (2.4.2) it follows that $\tilde{c}_{20}$ is bounded everywhere. By the aid of the divergence theorem, we may write

$$\int_{S_J} \tilde{c}_{20} \left(\vec{n}_J \cdot \nabla \tilde{c}_{20} \right) dS_J = \int_V \tilde{c}_{20} \nabla^2 \tilde{c}_{20} dV + \int_V \left| \nabla \tilde{c}_{20} \right|^2 dV$$

Since $\tilde{c}_{20}$ is bounded and $\vec{n}_J \cdot \nabla \tilde{c}_{20} = 0$ on all surfaces, it follows that the integral on the left-hand side is equal to zero and so is the first integral on the right-hand side. In addition, the integrand of the second integral on the right-hand side is always positive, so that the only possible value for $\nabla \tilde{c}_{20}$ is to be equal to zero, or equivalently $\tilde{c}_{20}$ is a constant. And since it has to satisfy B.C. (2.4.3b) too, it follows that $\tilde{c}_{20} = 0$ everywhere. Thus, it remains to determine $\tilde{c}_{21}$ and $\tilde{c}_{22}$, the perturbation of ion concentrations, at order Pe and Pe^2.

In order to solve the corresponding equations together with the boundary conditions, one should obtain a solution as an outer solution in the parameter δ at each order in Pe. But for the first approximation (at any order in Pe), the purely hydrodynamic velocity appears in the equation and boundary conditions, as mentioned in § 2.3, has a singularity at the origin. Therefore, for the electroviscous ion concentrations and equivalently for the electroviscous potential, a solution for the inner region is required. Because of this singularity (as we observed for the case of the purely hydrodynamic problem), the main contribution to the perturbation of ion concentrations comes from this region. By the way, for the inner region solution of the electroviscous effects (as for the case of the purely hydrodynamic), the boundary conditions at infinity given by (2.4.6, 13) are not imposed since this region only includes (and hence the solution of which is only valid for) a small portion of the neighbourhood of the nearby contact point. Instead, it has to satisfy the matching condition

$$\tilde{c}_2\Big|_{\tilde{x}\to 0} = \hat{c}_2\Big|_{\hat{x}\to\pm\infty} \tag{2.4.14}$$

2.4.2 - Inner Region

In view of expansion (2.3.7) and identities (2.4.7-9), the normal derivative of the normal derivative of the normal component of the purely hydrodynamic velocity appeared in B.C. (2.4.5) for the inner region are

$$(\vec{n}_P\cdot\nabla)(\vec{n}_P\cdot\nabla)(\vec{n}_P\cdot\vec{\tilde{u}}) = \left[\hat{x}\frac{\partial}{\partial\hat{x}} + (-\delta^{-1}+\hat{z}-1)\frac{\partial}{\partial\hat{z}}\right]\left[\hat{x}\frac{\partial}{\partial\hat{x}} + (-\delta^{-1}+\hat{z}-1)\frac{\partial}{\partial\hat{z}}\right]$$

$$\left[\delta^{\frac{1}{2}}(\hat{x}\hat{u}_x - \hat{u}_z) + \delta^{\frac{3}{2}}(\hat{z}-1)\hat{u}_z\right] = \delta^{-\frac{3}{2}}\frac{\partial^2}{\partial\hat{z}^2}(\hat{x}\hat{u}_x - \hat{u}_z) + O\left(\delta^{-\frac{1}{2}}\right)$$

$$(\vec{n}_W\cdot\nabla)(\vec{n}_W\cdot\nabla)(\vec{n}_W\cdot\vec{\tilde{u}}) = \left(\delta^{-1}\frac{\partial}{\partial\hat{z}}\right)\left(\delta^{-1}\frac{\partial}{\partial\hat{z}}\right)\left(\delta^{\frac{1}{2}}\hat{u}_z\right) = \delta^{-\frac{3}{2}}\frac{\partial^2\hat{u}_z}{\partial\hat{z}^2}$$

the second derivatives in which are obtained as [c.f.,(2.3.40, 41)]

$$\frac{\partial^2\hat{u}_z}{\partial\hat{z}^2} = (1+\tilde{\Omega})\hat{x}\left[12(2\hat{H}^{-4} - \hat{H}^{-3})\hat{z} - (8\hat{H}^{-3} - 3\hat{H}^{-2})\right] + (1-\tilde{\Omega})\hat{x}\hat{H}^{-2} \tag{2.4.15}$$

$$\frac{\partial^2}{\partial\hat{z}^2}(\hat{x}\hat{u}_{x0}) = (1+\tilde{\Omega})\hat{x}(8\hat{H}^{-3} - 6\hat{H}^{-2}) \tag{2.4.16}$$

Thus, if we expand the electroviscous ion concentrations for the inner region as

$$\tilde{c}_2 = \delta^{-3/2}\hat{c}_2 \tag{2.4.17}$$

for the inner region, at order Pe it satisfies [c.f., (2.4.4, 5)]:

$$\frac{\partial^2\hat{c}_{21}}{\partial\hat{z}^2} + \delta\frac{\partial^2\hat{c}_{21}}{\partial\hat{x}^2} = 0 \tag{2.4.18}$$

with boundary conditions

$$\frac{\partial \hat{c}_{21}}{\partial \hat{z}}\Big|_{\hat{z}=0} = \delta\ F_{cW}\left[\left(1+\widetilde{\Omega}\right)\hat{x}\left(-8\hat{H}^{-3}+3\hat{H}^{-2}\right)+\left(1-\widetilde{\Omega}\right)\hat{x}\hat{H}^{-2}\right] \tag{2.4.19}$$

$$-\frac{\partial \hat{c}_{21}}{\partial \hat{z}} + \delta\left[\hat{x}\frac{\partial \hat{c}_{21}}{\partial \hat{x}} + (\hat{z}-1)\frac{\partial \hat{c}_{21}}{\partial \hat{z}}\right]_{\hat{z}=\hat{H}} = \delta\ F_{cP}\left[\left(1+\widetilde{\Omega}\right)\hat{x}\left(-8\hat{H}^{-3}+3\hat{H}^{-2}\right)-\left(1+\widetilde{\Omega}\right)\hat{x}\hat{H}^{-2}\right] \tag{2.4.20}$$

and at order Pe^2 [c.f., (2.4.10-12)]:

$$\frac{\partial^2 \hat{c}_{22}}{\partial \hat{z}^2} + \delta\frac{\partial^2 \hat{c}_{22}}{\partial \hat{x}^2} = \delta^{3/2}\left(\hat{u}_{x0}\frac{\partial \hat{c}_{21}}{\partial \hat{x}} + \hat{u}_{z0}\frac{\partial \hat{c}_{21}}{\partial \hat{z}}\right) \tag{2.4.21}$$

with boundary condition

$$\frac{\partial \hat{c}_{22}}{\partial \hat{z}}\Big|_{\hat{z}=0} = 0, \qquad -\frac{\partial \hat{c}_{22}}{\partial \hat{z}} + \delta\left[\hat{x}\frac{\partial \hat{c}_{22}}{\partial \hat{x}} + (\hat{z}-1)\frac{\partial \hat{c}_{22}}{\partial \hat{z}}\right]\Big|_{\hat{z}=H} = 0 \tag{2.4.22}$$

2.4.2.1 - Inner Solution at Order Pe

The equation and boundary conditions at the first order in Pe, given by (2.4.18-20), suggest an expansion for $\hat{c}_{21}$ in δ as

$$\hat{c}_{21} = \hat{c}_m + \delta\ \hat{c}_n + \cdots \tag{2.4.23}$$

Upon substitution of this expansion in Eq. (3.4.18) and B.C.s (2.4.19, 20), it is observed that $\hat{c}_m$ satisfies

$$\frac{\partial^2 \hat{c}_m}{\partial \hat{z}^2} = 0 \tag{2.4.24}$$

with boundary conditions

$$\frac{\partial \hat{c}_m}{\partial \hat{z}}\Big|_{\hat{z}=0} = 0 \tag{2.4.25}$$

$$\frac{\partial \hat{c}_m}{\partial \hat{z}}\Big|_{\hat{z}=\hat{H}} = 0 \tag{2.4.26}$$

Whereas $\hat{c}_n$ satisfies

$$\frac{\partial^2 \hat{c}_n}{\partial \hat{z}^2} + \frac{\partial^2 \hat{c}_m}{\partial \hat{x}^2} = 0 \tag{2.4.27}$$

with boundary conditions

$$\frac{\partial \hat{c}_n}{\partial \hat{z}}\Big|_{\hat{z}=0} = F_{cW}\left[\left(1+\tilde{\Omega}\right)\hat{x}\left(-8\hat{H}^{-3}+3\hat{H}^{-2}\right)+\left(1-\tilde{\Omega}\right)\hat{x}\hat{H}^{-2}\right] \tag{2.4.28}$$

and

$$-\frac{\partial \hat{c}_n}{\partial \hat{z}}+\hat{x}\frac{\partial \hat{c}_m}{\partial \hat{x}}\Big|_{\hat{z}=\hat{H}} = F_{cP}\left[\left(1+\tilde{\Omega}\right)\hat{x}\left(-8\hat{H}^{-3}+3\hat{H}^{-2}\right)-\left(1+\tilde{\Omega}\right)\hat{x}\hat{H}^{-2}\right] \tag{2.4.29}$$

Eq. (2.4.24) together with B.C.s (2.4.25, 26) guaranties that

$$\hat{c}_m = \text{Func}\left(\hat{x}\right) \tag{2.4.30}$$

Thus, Eq. (2.4.27) may easily be integrated with respect to $\hat{z}$ to give

$$\frac{\partial \hat{c}_n}{\partial \hat{z}} = -\frac{d^2\hat{c}_m}{d\hat{x}^2}\hat{z}+A(\hat{x}) \tag{2.4.31}$$

Imposing B.C. (2.4.28) results in

$$A = F_{cW}\left[\left(1+\tilde{\Omega}\right)\hat{x}\left(-8\hat{H}^{-3}+3\hat{H}^{-2}\right)+\left(1-\tilde{\Omega}\right)\hat{x}\hat{H}^{-2}\right] \tag{2.4.32}$$

Imposing B.C. (2.4.29) leads to the following differential equation for $\hat{c}_m$:

$$\begin{aligned}-\frac{d^2\hat{c}_m}{d^2\hat{x}}+F_{cW}\left[\left(1+\tilde{\Omega}\right)\hat{x}\left(-8\hat{H}^{-3}+3\hat{H}^{-2}\right)+\left(1-\tilde{\Omega}\right)\hat{x}\hat{H}^{-2}\right]=\\ \frac{d\hat{c}_m}{d\hat{x}}-F_{cW}\left[\left(1+\tilde{\Omega}\right)\hat{x}\left(-8\hat{H}^{-3}+3\hat{H}^{-2}\right)-\left(1-\tilde{\Omega}\right)\hat{x}\hat{H}^{-2}\right]\end{aligned} \tag{2.4.33}$$

or

$$\frac{d}{d\hat{x}}\left(\hat{H}\frac{d\hat{c}_m}{d\hat{x}}\right) = \left(F_{cP}+F_{cW}\right)\left(1+\tilde{\Omega}\right)\hat{x}\left(-8\hat{H}^{-3}+3\hat{H}^{-2}\right)-\left(F_{cP}-F_{cW}\right)\left(1-\tilde{\Omega}\right)\hat{x}\hat{H}^{-2} \tag{2.4.34}$$

Integrating it once and then dividing it by $\hat{H}$ results in

$$\frac{d\hat{c}_m}{d\hat{x}} = \left(F_{cP}+F_{cW}\right)\left(1+\tilde{\Omega}\right)\left(4\hat{H}^{-3}-3\hat{H}^{-2}\right)+\left(F_{cP}-F_{cW}\right)\left(1-\tilde{\Omega}\right)\hat{H}^{-2}+C\hat{H}^{-1} \tag{2.4.35}$$

Now, in view of the integrals (2.3.34, 35) and

$$\int \hat{H}^{-1} = \sqrt{2}\tan^{-1}\frac{\hat{x}}{\sqrt{2}} \tag{2.4.36}$$

Eq. (2.3.35) may be integrated to give

$$\hat{c}_m = \left(F_{cP} + F_{cW}\right)\left(1+\tilde{\Omega}\right)\hat{x}\hat{H}^{-2} + C\sqrt{2}\tan^{-1}\frac{\hat{x}}{\sqrt{2}} + \left(F_{cP} - F_{cW}\right)\left(1-\tilde{\Omega}\right)\left[\frac{1}{2}\hat{x}\hat{H}^{-1} + \frac{\sqrt{2}}{2}\tan^{-1}\frac{\hat{x}}{\sqrt{2}}\right] + D \tag{2.4.37}$$

But, since

$$\tan^{-1}\frac{\hat{x}}{\sqrt{2}} = \pm\frac{\pi}{2} - \frac{1}{\hat{x}} + O\left(\frac{1}{\hat{x}^3}\right) \qquad \text{as } \hat{x} \to \pm\infty \tag{2.4.38}$$

and since for large value of $\hat{x}$ any constants do not satisfy the matching condition (2.4.17), $D = 0$, and C must be determined in a way that $\hat{c}_m$ does not include the term $\tan^{-1} \hat{x}/\sqrt{2}$, that is

$$C = -\frac{1}{2}\left(F_{cP} - F_{cW}\right)\left(1-\tilde{\Omega}\right)$$

From this it follows that

$$\hat{c}_m = \left(F_{cP} + F_{cW}\right)\left(1+\tilde{\Omega}\right)\hat{x}\hat{H}^{-2} + \frac{1}{2}\left(F_{cP} - F_{cW}\right)\left(1-\tilde{\Omega}\right)\hat{x}\hat{H}^{-1} \tag{2.4.39}$$

2.4.2.2 - Inner Solution at Order Pe^2

Equation (2.4.21) implies an expansion in δ for $\hat{c}_{22}$ in the form of

$$\hat{c}_{22} = \delta^{1/2}\hat{c}_p + \delta^{3/2}\hat{c}_q + \cdots \tag{2.4.40}$$

Upon substitution of this expansion in Eq. (2.4.21) and corresponding boundary conditions given by (2.4.22) we see that $\hat{c}_p$ satisfies the same equation and boundary conditions as those for $\hat{c}_m$ given by (2.4.24-26), so that $\hat{c}_p$ such as $\hat{c}_m$ is independent of $\hat{z}$. Whereas $\hat{c}_q$ has to satisfy

$$\frac{\partial^2\hat{c}_q}{\partial\hat{z}^2} + \frac{d^2\hat{c}_p}{d\hat{x}^2} = \hat{u}_{x0}\frac{d\hat{c}_m}{d\hat{x}} \tag{2.4.41}$$

with boundary conditions

$$\left.\frac{\partial\hat{c}_q}{\partial\hat{z}}\right|_{\hat{z}=0} = 0 \tag{2.4.42}$$

$$\left.\frac{\partial \hat{c}_q}{\partial \hat{z}}\right|_{\hat{z}=\hat{H}} - \hat{x}\frac{d\hat{c}_p}{d\hat{x}} = 0 \tag{2.4.43}$$

Integration of Eq. (2.4.41) with respect to $\hat{z}$ yields

$$\frac{\partial \hat{c}_q}{\partial \hat{z}} = -\frac{d^2\hat{c}_p}{d\hat{x}^2}\hat{z} + \frac{d\hat{c}_m}{d\hat{x}}\int \hat{u}_{x0} d\hat{z} + C(\hat{x}) \tag{2.4.44}$$

Imposing B.C. (2.4.42) gives the value of C as

$$C = -\frac{d\hat{c}_m}{d\hat{x}}\left.\int \hat{u}_{x0} d\hat{z}\right|_{\hat{z}=0} \tag{2.4.45}$$

Imposing B.C. (2.4.43) leads to

$$\frac{d}{d\hat{x}}\left(\hat{H}\frac{d\hat{c}_p}{d\hat{x}}\right) = \frac{d\hat{c}_m}{d\hat{x}}\int_0^{\hat{H}} \hat{u}_{x0} d\hat{z} \tag{2.4.46}$$

the integral in which is evaluated as [c.f., (2.3.40)]

$$\int_0^{\hat{H}} \hat{u}_{x0} d\hat{z} = \left(1+\tilde{\Omega}\right)\left[\left(-3\hat{H}^{-2} + 4\hat{H}^{-3}\right)\left(\frac{1}{3}\hat{z}^3 - \frac{1}{2}\hat{H}\hat{z}^2\right) - \frac{1}{2}\hat{z}\right] + \left(1-\tilde{\Omega}\right)\left(\frac{1}{2}\hat{H}^{-1}\hat{z}^2 - \frac{1}{2}\hat{z}\right)\Bigg|_0^{\hat{H}} = -\frac{2}{3}\left(1+\tilde{\Omega}\right) \tag{2.4.47}$$

Thus, by the use of (2.4.39), Eq. (2.4.46) is integrated as

$$\frac{d\hat{c}_p}{d\hat{x}} = -\frac{2}{3}\left(F_{cP} + F_{cW}\right)\left(1+\tilde{\Omega}\right)^2 \hat{x}\hat{H}^{-3} - \frac{1}{3}\left(F_{cP} - F_{cW}\right)\left(1-\tilde{\Omega}^2\right)\hat{x}\hat{H}^{-2} + C\hat{H}^{-1} \tag{2.4.48}$$

Its second integration is [c.f., (2.4.36)]

$$\hat{c}_p = \frac{1}{3}\left(F_{cP} + F_{cW}\right)\left(1+\tilde{\Omega}\right)^2 \hat{H}^{-2} + \frac{1}{3}\left(F_{cP} - F_{cW}\right)\left(1-\tilde{\Omega}^2\right)\hat{H}^{-1} + C\sqrt{2}\tan^{-1}\frac{\hat{x}}{\sqrt{2}} + D$$

But, electroviscous ion concentrations at $O(Pe^2)$ are symmetric with respect to the z-axis (i.e. since they are proportional to U^2 by reversing the direction of the flow from U to -U and the coordinate from $\hat{x}$ to $-\hat{x}$, we expect to have the same electroviscous effects) and hence an odd function of $\hat{x}$ cannot be included in the electroviscous ion concentration at this order, resulting in C = 0. The constant D is also taken to be zero since, in view of (2.4.17, 40), it does not satisfy the matching condition at order unity, either. Thus, $\hat{c}_p$ is reduced to

$$\hat{c}_p = \frac{1}{3}\left(F_{cP} + F_{cW}\right)\left(1+\tilde{\Omega}\right)^2 \hat{H}^{-2} + \frac{1}{3}\left(F_{cP} - F_{cW}\right)\left(1-\tilde{\Omega}^2\right)\hat{H}^{-1} \tag{2.4.49}$$

Therefore, in view of (2.4.1, 17, 23, 40, 39, 49), the electroviscous ion concentrations for the inner region at the lowest order in δ in the expansion (2.4.1) are determined by

$$\begin{aligned}\tilde{c}_2 &= \delta^{-\frac{3}{2}}\mathrm{Pe}\left[\left(F_{cP} + F_{cW}\right)\left(1+\tilde{\Omega}\right)\hat{x}\hat{H}^{-2} + \frac{1}{2}\left(F_{cP} - F_{cW}\right)\left(1-\tilde{\Omega}\right)\hat{x}\hat{H}^{-1}\right] \\ &+\delta^{-1}\frac{D_1 + D_2}{2D_2}\mathrm{Pe}^2\left[\frac{1}{3}\left(F_{cP} + F_{cW}\right)\left(1+\tilde{\Omega}\right)^2 \hat{H}^{-2} + \frac{1}{3}\left(F_{cP} - F_{cW}\right)\left(1-\tilde{\Omega}^2\right)\hat{H}^{-1}\right]\end{aligned} \tag{2.4.50}$$

in which F_{cP} and F_{cW} are defined by (1.3.60e) as

$$F_{cJ} = \frac{1}{2D_2}\left[\left(D_2 - D_1\right)\tilde{\psi}_J - 4\left(D_2 + D_1\right)\ln\left(\cosh\frac{\tilde{\psi}_J}{4}\right)\right] \qquad J = \left(P, W\right) \tag{2.4.51}$$

2.5 - Electroviscous Potential

The equation and boundary conditions for the electroviscous potential denoted here by $\tilde{\psi}_2$ are given by relationships (1.3.61). The perturbation in ion concentrations also present in this equation is already determined. The second term in this equation, ϕ, satisfies the same equation and boundary conditions as those for the electroviscous ion concentrations of order Pe, given by (2.4.4, 6), in which F_{cP} and F_{cW} are respectively replaced by $F_{\varphi P}$ and $F_{\varphi W}$, defined by (1.3.61f). Thus, as for the case of electroviscous ion concentrations, if we expand the electroviscous potential as

$$\tilde{\psi}_2 = \delta^{-\frac{3}{2}}\hat{\psi}_2 \tag{2.5.1}$$

by the aid of relationships (2.4.39, 50) for the inner region, it is determined by

$$\begin{aligned}\tilde{\psi}_2 &= \delta^{-\frac{3}{2}}\mathrm{Pe}\left[\left(F_{\psi P} + F_{\psi W}\right)\left(1+\tilde{\Omega}\right)\hat{x}\hat{H}^{-2} + \frac{1}{2}\left(F_{\psi P} - F_{\psi W}\right)\left(1-\tilde{\Omega}\right)\hat{x}\hat{H}^{-1}\right] \\ &+\delta^{-1}\mathrm{Pe}^2\frac{D_2 - D_1}{2D_2}\left[\frac{1}{3}\left(F_{cP} + F_{cW}\right)\left(1+\tilde{\Omega}\right)^2 \hat{H}^{-2} + \frac{1}{3}\left(F_{cP} - F_{cW}\right)\left(1-\tilde{\Omega}^2\right)\hat{H}^{-1}\right]\end{aligned} \tag{2.5.2}$$

in which, in view of relationships (1.3.60, 61), $F_{\psi P}$ and $F_{\psi W}$ are defined by

$$F_{\psi J} = \frac{D_2 - D_1}{D_2 + D_1} F_{cJ} + \frac{2D_1}{D_2 + D_1} \tilde{\psi}_J \qquad J = (P, W) \tag{2.5.3}$$

2.6 - Force on Cylinder

The force per unit length, $\vec{F}$ experienced by the particle is the sum of the purely hydrodynamic force, $\vec{F}_H$, of order unity and the electroviscous force, $\vec{F}_4^*$, of order ϵ^4, that is

$$F_x = F_{Hx} + \epsilon^4 F_{4x}^*, \qquad F_z = F_{Hz} + \varepsilon^4 F_{4z}^* \tag{2.6.1}$$

2.6.1 - Hydrodynamic Force

The hydrodynamic force is determined from the relationship (1.3.14). It may be expressed in vectorial form as

$$\vec{\tilde{F}}_H = \int_{S_P} \vec{\vec{\tilde{\sigma}}}.\vec{n}_P d\vec{\tilde{S}}_P \tag{2.6.2}$$

$\vec{n}_P$ is the unit vector normal and outward to the cylinder surface, given by (2.2.6), as

$$\vec{n}_P = \tilde{x}\vec{i}_x + (z - 1 - \delta)\vec{i}_z \tag{2.6.3}$$

In view of the expansion (2.3.7), it may be expressed in terms of the inner variables as

$$n_{Px} = \delta^{\frac{1}{2}}\hat{x}, \qquad n_{Pz} = [-1 + \delta(\hat{z} - 1)] \tag{2.6.4}$$

$\vec{\vec{\tilde{\sigma}}}$, the stress tensor, is defined by

$$\tilde{\sigma}_{xx} = -\tilde{p} + 2\frac{\partial \tilde{u}_x}{\partial \tilde{x}}, \quad \tilde{\sigma}_{xz} = \frac{\partial \tilde{u}_x}{\partial \tilde{z}} + \frac{\partial \tilde{u}_z}{\partial \tilde{x}}, \quad \tilde{\sigma}_{zz} = -\tilde{p} + 2\frac{\partial \tilde{u}_z}{\partial \tilde{z}} \tag{2.6.5}$$

For the inner region it is determined by [c.f., expansion (2.3.7)]

$$\tilde{\sigma}_{xx} = -\delta^{-\frac{3}{2}}\hat{p} + 2\delta^{-\frac{1}{2}}\frac{\partial \hat{u}_x}{\partial \hat{x}}, \tilde{\sigma}_{xz} = \delta^{-1}\frac{\partial \hat{u}_x}{\partial \hat{z}} + \delta^0\frac{\partial \hat{u}_z}{\partial \hat{x}}, \tilde{\sigma}_{zz} = -\delta^{-\frac{3}{2}}\hat{p} + 2\delta^{-\frac{1}{2}}\frac{\partial \hat{u}_z}{\partial \hat{z}} \tag{2.6.6}$$

Thus, at the lowest order in δ we may write

$$\vec{\vec{\tilde{\sigma}}} \cdot \vec{n}_P = -\delta^{-1}\left[\hat{x}\hat{p}_0 + \frac{\partial \hat{u}_{x0}}{\partial \hat{z}}\right]\vec{i}_x + \left[\delta^{-\frac{3}{2}}\hat{p}_0 + \delta^{-\frac{1}{2}}\hat{x}\frac{\partial \hat{u}_{x0}}{\partial \hat{z}}\right]\vec{i}_z + O(\delta^0) \tag{2.6.7}$$

where $\hat{p}_0$ and $\hat{u}_{x0}$ are given by (2.3.37, 40), from which

$$\frac{\partial \hat{u}_{x0}}{\partial \hat{z}} = \left(1+\tilde{\Omega}\right)\left(4\hat{H}^{-3} - 3\hat{H}^{-2}\right)\left(2\hat{z} - \hat{H}\right) + \left(1-\tilde{\Omega}\right)\hat{H}^{-1} \tag{2.6.8}$$

and

$$\hat{x}\hat{p}_0 = 2\left(1+\tilde{\Omega}\right)\left(2\hat{H} - 2\right)\hat{H}^{-2} = 4\left(1+\tilde{\Omega}\right)\left(-\hat{H}^{-2} + \hat{H}^{-1}\right) \tag{2.6.9}$$

Thus, the x-component of $\tilde{\bar{\bar{\sigma}}} \cdot \vec{n}_P$ may be evaluated on the cylinder surface as

$$-\delta^{-1}\left[\hat{x}\hat{p}_0 + \frac{\partial \hat{u}_{x0}}{\partial \hat{z}}\right]_{\hat{z}=\hat{H}} = -\delta^{-1}\left[\left(1+\tilde{\Omega}\right)\hat{H}^{-1} + \left(1-\tilde{\Omega}\right)\hat{H}^{-1}\right] = -2\delta^{-1}\hat{H}^{-1} \tag{2.6.10}$$

At the first approximation the cylinder surface bounding the inner region is parallel to the wall, and hence $d\tilde{S}_P = d\tilde{S}_W = d\tilde{x} = \delta^{1/2} d\hat{x}$. Therefore, the contribution to the force from the inner region is obtained, upon the integration of the integrand and evaluating it from left to the right edge of inner region (-∞, +∞) as

$$\tilde{F}_{Hx} = -2\delta^{-1}\int_{-\infty}^{+\infty} \hat{H}^{-1}\delta^{\frac{1}{2}} d\hat{x} = -2\delta^{-\frac{1}{2}}\left|\sqrt{2}\tan^{-1}\frac{\hat{x}}{\sqrt{2}}\right|_{x=-\infty}^{x=+\infty} = -2\sqrt{2}\pi\delta^{-\frac{1}{2}} \tag{2.6.11}$$

Thus, in view of (2.2.1, 4) the dimensional x-component of the force is determined by

$$F_{Hx} = -2\sqrt{2}\pi\eta\sqrt{\frac{a}{h}}U \tag{2.6.12}$$

But, as for the z-component of the force, upon the comparison of the x and z-components of $\tilde{\bar{\bar{\sigma}}} \cdot \vec{n}_P$, it follows that the z-component contains terms of an odd function of $\hat{x}$ so that its integration with respect to $\hat{x}$ would be an even function of $\hat{x}$ and hence its evaluation between - ∞ and + ∞ vanishes, resulting in

$$F_{Hz} = 0 \tag{2.6.13}$$

The flow field in the outer region is bounded, and hence $\tilde{\bar{\bar{\sigma}}} \cdot \vec{n}_P$ is of order unity. Therefore, the contribution to the force from the outer region is of order unity and hence should be added to the force. But even though it is not small by itself it is much smaller than that of the inner region (which is of order $\delta^{-1/2}$, as $\delta \to 0$) and hence can be neglected in comparison with the leading term.

2.6.2 - Electroviscous Force

The electroviscous force, $\vec{\tilde{F}}_4^*$ is determined by applying the Lorentz reciprocal theorem, given by Eq.(1.3.69), which may be written in a vectorial form

$$\vec{\tilde{F}}_4^* = \int_{S_P} \vec{\tilde{B}}_P \cdot \vec{\vec{\tilde{\sigma}}}_P \cdot d\vec{\tilde{S}}_P + \int_{S_W} \vec{\tilde{B}}_W \cdot \vec{\vec{\tilde{\sigma}}}_W \cdot d\vec{\tilde{S}}_W \tag{2.6.14}$$

in which $\vec{\tilde{B}}_J$, given by (1.3.59), can be expressed as

$$\vec{\tilde{B}}_J = \lambda\left[\nabla - \vec{n}_J\left(\vec{n}_J \cdot \nabla\right)\right]\left\{-4\ln\left[\cosh\left(\frac{\tilde{\psi}_J}{4}\right)\right]\left(\tilde{c}_2\big|_J\right) + \tilde{\psi}_J\left(\tilde{\psi}_2\big|_J\right)\right\}, \; J = P, W \tag{2.6.15}$$

which represent the tangential derivatives [i.e. the total derivative, ∇, minus the normal derivative, $\vec{n}_J(\vec{n}_J \cdot \nabla)$] of the electroviscous ion concentrations and potential (times physicochemical properties of the system) evaluated on the solid surfaces J. $\vec{\vec{\tilde{\sigma}}}_J$ is the stress tensor due to the translation of a particle with unit velocity in the direction of force under determination evaluated on the surfaces J.

The integrand of the integrals of the force in (2.6.2) may be expressed as

$$\vec{\tilde{B}}_J \cdot \vec{\vec{\tilde{\sigma}}}_J \cdot d\vec{\tilde{S}}_J = \left[\tilde{B}_{Jx}\left(\tilde{\sigma}_{Jxx}n_{Jx} + \tilde{\sigma}_{Jxz}n_{Jz}\right) + \tilde{B}_{Jz}\left(\tilde{\sigma}_{Jzx}n_{Jx} + \tilde{\sigma}_{Jzz}n_{Jz}\right)\right]d\tilde{S}_J \tag{2.6.16}$$

The unit vector normal to the wall is $\vec{i}_z$ and that of the cylinder is given by (2.6.3), from which the integrand (2.6.16) evaluated on each solid surfaces is determined by

$$\vec{\tilde{B}}_W \cdot \vec{\vec{\tilde{\sigma}}}_W \cdot d\vec{\tilde{S}}_W = \left(\tilde{B}_{Wx}\tilde{\sigma}_{Wxz} + \tilde{B}_{Wz}\tilde{\sigma}_{Wzz}\right)d\tilde{S}_W \tag{2.6.17}$$

$$\vec{\tilde{B}}_P \cdot \vec{\vec{\tilde{\sigma}}}_P \cdot d\vec{\tilde{S}}_P = \left\{\tilde{B}_{Px}\left[\tilde{\sigma}_{Pxx}\tilde{x} + \tilde{\sigma}_{Pxz}(\tilde{z} - 1 - \delta)\right] + \tilde{B}_{Pz}\left[\tilde{\sigma}_{Pzx}\tilde{x} + \tilde{\sigma}_{Pzz}(\tilde{z} - 1 - \delta)\right]\right\}d\tilde{S}_P \tag{2.6.18}$$

2.6.2.1 - Determination of $\vec{\tilde{B}}_J$

The normal derivative involved in the relationship (2.6.15) is determined by

$$\vec{n}_W\left(\vec{n}_W \cdot \nabla\right) = \vec{i}_z\left[\vec{i}_z \cdot \left(\vec{i}_x \frac{\partial}{\partial \tilde{x}} + \vec{i}_z \frac{\partial}{\partial \tilde{z}}\right)\right] = \vec{i}_z \frac{\partial}{\partial \tilde{z}} = \delta^{-1}\vec{i}_z \frac{\partial}{\partial \hat{z}} \tag{2.6.19}$$

$$\vec{n}_p\left(\vec{n}_p\cdot\nabla\right)=\left[\widetilde{x}\vec{i}_x+(\widetilde{z}-1-\delta)\vec{i}_z\right]\left[\widetilde{x}\frac{\partial}{\partial\widetilde{x}}+(\widetilde{z}-1-\delta)\frac{\partial}{\partial\widetilde{z}}\right]$$

$$=\left\{\delta^{\frac{1}{2}}\hat{x}^2\frac{\partial}{\partial\hat{x}}+\delta^{\frac{1}{2}}\hat{x}\left[-\delta^{-1}+(\hat{z}-1)\right]\frac{\partial}{\partial\hat{z}}\right\}\vec{i}_x \tag{2.6.20}$$

$$+\left\{\hat{x}\left[-1+\delta(\hat{z}-1)\right]\frac{\partial}{\partial\hat{x}}+\delta^{-1}\left[-1+\delta(\hat{z}-1)\right]^2\frac{\partial}{\partial\hat{z}}\right\}\vec{i}_z$$

Introducing this in (2.6.15) and noting that $\widetilde{c}_2$ and $\widetilde{\psi}_2$ (c.f., 2.4.50, 5.2) are independent of $\hat{z}$ (and hence their values on the solid surfaces are the same and their derivatives with respect to $\hat{z}$ vanish) results in

$$\vec{\widetilde{B}}_W=\lambda\delta^{-\frac{1}{2}}\vec{i}_x\frac{\partial}{\partial\hat{x}}\left\{-4\ln\left[\cosh\left(\frac{\widetilde{\psi}_W}{4}\right)\right]\widetilde{c}_2+\widetilde{\psi}_W\widetilde{\psi}_2\right\} \tag{2.6.21}$$

$$\vec{\widetilde{B}}_P=\lambda\left[\delta^{-\frac{1}{2}}\vec{i}_x\frac{\partial}{\partial\hat{x}}+\vec{i}_z\hat{x}\frac{\partial}{\partial\hat{x}}\right]\left\{-4\ln\left[\cosh\left(\frac{\widetilde{\psi}_P}{4}\right)\right]\widetilde{c}_2+\widetilde{\psi}_P\widetilde{\psi}_2\right\} \tag{2.6.22}$$

Introducing $\widetilde{c}_2$, given by (2.4.50, 51), and $\widetilde{\psi}_2$, given by (2.5.2, 3), to (2.6.21, 22) results in

$$\widetilde{B}_{Wx}=\lambda\left\{\delta^{-2}Pe\left[L^1W_{P+W}\left(1+\widetilde{\Omega}\right)\left(-3\hat{H}^{-2}+4\hat{H}^{-3}\right)+L^1W_{P-W}\left(1-\widetilde{\Omega}\right)\left(-\frac{1}{2}\hat{H}^{-1}+\hat{H}^{-2}\right)\right]\right.$$
$$\left.+\delta^{-\frac{3}{2}}Pe^2\left[-\frac{2}{3}L^2W_{P+W}\left(1+\widetilde{\Omega}\right)^2\hat{x}\hat{H}^{-3}-\frac{1}{3}L^2W_{P-W}\left(1-\widetilde{\Omega}^2\right)\hat{x}\hat{H}^{-2}\right]\right\} \tag{2.6.23}$$

$$\widetilde{B}_{Px}=\lambda\left\{\delta^{-2}Pe\left[L^1P_{P+W}\left(1+\widetilde{\Omega}\right)\left(-3\hat{H}^{-2}+4\hat{H}^{-3}\right)+L^1P_{P-W}\left(1-\widetilde{\Omega}\right)\left(-\frac{1}{2}\hat{H}^{-1}+\hat{H}^{-2}\right)\right]\right.$$
$$\left.+\delta^{-\frac{3}{2}}Pe^2\left[-\frac{2}{3}L^2P_{P+W}\left(1+\widetilde{\Omega}\right)^2\hat{x}\hat{H}^{-3}-\frac{1}{3}L^2P_{P-W}\left(1-\widetilde{\Omega}^2\right)\hat{x}\hat{H}^{-2}\right]\right\} \tag{2.6.24}$$

$$\widetilde{B}_{Pz}=\lambda\left\{\delta^{-2}Pe\left[L^1P_{P+W}\left(1+\widetilde{\Omega}\right)\hat{x}\left(-3\hat{H}^{-2}+4\hat{H}^{-3}\right)+L^1P_{P-W}\left(1-\widetilde{\Omega}\right)\hat{x}\left(-\frac{1}{2}\hat{H}^{-1}+\hat{H}^{-2}\right)\right]\right.$$
$$\left.+\delta^{-\frac{3}{2}}Pe^2\left[-\frac{4}{3}L^2P_{P+W}\left(1+\widetilde{\Omega}\right)^2\left(\hat{H}^{-2}-\hat{H}^{-3}\right)-\frac{2}{3}L^2P_{P-W}\left(1-\widetilde{\Omega}^2\right)\left(\hat{H}^{-1}-\hat{H}^{-2}\right)\right]\right\}$$
$$\widetilde{B}_{Wz}=0 \tag{2.6.25}$$

Here $L^iJ_{P\pm W}$ [i = (1, 2) denote the order in Pe, and J = (P, W) denote the evaluation on the solid surfaces J] are defined by

$$L^1J_{P\pm W} = -4\ln\left[\cosh\left(\frac{\tilde{\psi}_J}{4}\right)\right]\left(F_{cP} \pm F_{cW}\right) + \tilde{\psi}_J\left(F_{\psi P} \pm F_{\psi W}\right), \quad (J = P, W) \qquad (2.6.26)$$

$$L^2J_{P\pm W} = \left\{-4\ln\left[\cosh\left(\frac{\tilde{\psi}_J}{4}\right)\right]\frac{D_2 + D_1}{2D_2} + \tilde{\psi}_J\frac{D_2 - D_1}{2D_2}\right\}\left(F_{cP} \pm F_{cW}\right) \qquad (2.6.27)$$

2.6.2.1.1 - Value of $L^iJ_{P\pm W}$

The constants $-4\ln\left(\cosh\tilde{\psi}_J/4\right)$ appearing in (2.6.26, 27) may be expressed as

$$-4\ln\left[\cosh\left(\frac{\tilde{\psi}_J}{4}\right)\right] = \begin{cases} -4\ln\left[\dfrac{e^{-\frac{\tilde{\psi}_J}{4}}\left(e^{+\frac{\tilde{\psi}_J}{2}} + 1\right)}{2}\right] = \tilde{\psi}_J - 4\ln\dfrac{1 + e^{\frac{\tilde{\psi}_J}{2}}}{2} \\[2ex] -4\ln\left[\dfrac{e^{+\frac{\tilde{\psi}_J}{4}}\left(1 + e^{-\frac{\tilde{\psi}_J}{2}}\right)}{2}\right] = -\tilde{\psi}_J - 4\ln\dfrac{1 + e^{-\frac{\tilde{\psi}_J}{2}}}{2} \end{cases} \qquad (2.6.29)$$

Subtracting and adding these two identities results in

$$\tilde{\psi}_J = -2\left(G_J - H_J\right), \qquad -4\ln\left[\cosh\left(\frac{\tilde{\psi}_J}{4}\right)\right] = -2\left(G_J + H_J\right) \qquad (2.6.30)$$

in which G_J and H_J are define by

$$G_J = \ln\frac{1 + e^{-\frac{\tilde{\psi}_J}{2}}}{2}, \qquad H_J = \ln\frac{1 + e^{+\frac{\tilde{\psi}_J}{2}}}{2} \qquad (2.6.31)$$

From this F_{cJ} and $F_{\psi J}$, defined by (2.4.51, 5.3), are determined by

$$F_{cJ} = \frac{-1}{D_2}\left[\left(D_2 - D_1\right)\left(G_J - H_J\right) + \left(D_2 + D_1\right)\left(G_J + H_J\right)\right] = \frac{-2}{D_2}\left[D_2G_J + D_1H_J\right]$$

(2.6.32)

$$F_{\psi J} = \frac{-2}{D_2(D_2 + D_1)}\left[D_2^2 G_J + D_2 D_1 G_J - D_2 D_1 H_J - D_1^2 H_J\right] = \frac{-2}{D_2}\left[D_2 G_J - D_1 H_J\right]$$

(2.6.33)

Thus, $L^1 J_{P\pm W}$ and $L^2 J_{P\pm W}$, given by (2.6.26, 27), may be expressed as

$$L^1 J_{P\pm W} = \frac{4}{D_2}\Big\{(G_J + H_J)\left[D_2(G_P \pm G_W) + D_1(H_P \pm H_W)\right] + (G_J - H_J)\times$$
$$\left[D_2(G_P \pm G_W) - D_1(H_P \pm H_W)\right]\Big\} = \frac{8}{D_2}\left[D_2 G_J(G_P \pm G_W) + D_1 H_J(H_P \pm H_W)\right]$$

(2.6.34)

$$L^2 J_{P\pm W} = -F_{cJ}(F_{cP} \pm F_{cW})$$
$$= \frac{4}{D_2^2}(D_2 G_J + D_1 H_J)\left[D_2(G_P \pm G_W) + D_1(H_P \pm H_W)\right] \qquad (2.6.35)$$

2.6.2.2 - Stress Tensor for Translation Parallel to Wall

The flow field for the translation of a particle with unit velocity parallel to a wall is determined by (2.3.37, 40, 41) in which $\widetilde{\Omega}$ is taken to be equal to zero. From them the components of the stress tensor, determined by (2.6.6), evaluated on the solid surface J, at the lowest order in δ are obtained as

$$\widetilde{\sigma}_{Jxx} = -\delta^{-\frac{3}{2}} 2\hat{x}\hat{H}^{-2} + O\left(\delta^{-\frac{1}{2}}\right)\Big|_{S_J}$$
$$\widetilde{\sigma}_{Jxz} = \widetilde{\sigma}_{zx} = \delta^{-1}\left(4\hat{H}^{-3} - 3\hat{H}^{-2}\right)\left(2\hat{z} - \hat{H}\right) + \hat{H}^{-1} + O(\delta^0)\Big|_{S_J} \qquad (2.6.360)$$
$$\widetilde{\sigma}_{Jzz} = -\delta^{-\frac{3}{2}} 2\hat{x}\hat{H}^{-2} + O\left(\delta^{-\frac{1}{2}}\right)\Big|_{S_J}$$

2.6.2.3 - Stress Tensor for Translation Normal to Wall

A suitable expansion of the variables for the flow field, produced by the translation of the particle with unit velocity normal to and away from wall, is

$$\widetilde{x} = \delta^{\frac{1}{2}}\hat{x}, \qquad \widetilde{z} = \delta\hat{z}$$
$$\widetilde{u}_x = \delta^{-\frac{1}{2}}\hat{u}_x, \qquad \widetilde{u}_z = \hat{u}_z, \qquad \widetilde{p} = \delta^{-2}\hat{p} \qquad (2.6.37)$$

Introducing this expansion to the Stokes equations, given by (2.3.1, 2), results in

$$\delta^{-\frac{3}{2}}\frac{\partial^2 \hat{u}_x}{\partial \hat{x}^2}+\delta^{-\frac{5}{2}}\frac{\partial^2 \hat{u}_x}{\partial \hat{z}^2}=\delta^{-\frac{5}{2}}\frac{\partial \hat{p}}{\partial \hat{x}} \tag{2.6.38}$$

$$\delta^{-1}\frac{\partial^2 \hat{u}_z}{\partial \hat{x}^2}+\delta^{-2}\frac{\partial^2 \hat{u}_z}{\partial \hat{z}^2}=\delta^{-3}\frac{\partial \hat{p}}{\partial \hat{z}} \tag{2.6.39}$$

$$\delta^{-1}\left(\frac{\partial \hat{u}_x}{\partial \hat{x}}+\frac{\partial \hat{u}_z}{\partial \hat{z}}\right)=0 \tag{2.6.40}$$

The boundary conditions are

$$\hat{u}_x=\hat{u}_z=0 \qquad \text{on } \hat{z}=0 \tag{2.6.41}$$

$$\hat{u}_x=0, \qquad \hat{u}_z=1 \qquad \text{on } \hat{z}=\hat{H} \tag{2.6.42}$$

Introducing the expansion (2.3.17) in this flow field leads to the same equations for the leading term as those obtained for the flow field for the translation of the particle parallel to the wall, given by (2.3.18-20), with boundary conditions

$$\hat{u}_{x0}=\hat{u}_{z0}=0 \qquad \text{on } \hat{z}=0 \tag{2.6.43}$$

$$\hat{u}_{x0}=0, \qquad \hat{u}_{z0}=1 \qquad \text{on } \hat{z}=\hat{H} \tag{2.6.44}$$

In view of equation (2.3.19), the pressure is independent of $\hat{z}$. Thus, integrating Eq. (2.3.18) twice with respect to $\hat{z}$ and imposing B.C.s (2.6.43a, 44a) results in

$$\hat{u}_{x0}=\frac{1}{2}\left(\hat{z}^2-\hat{H}\hat{z}\right)\frac{dp_0}{d\hat{x}} \tag{2.6.45}$$

Differentiating it with respect to $\hat{x}$ and introducing the result to the continuity equation (2.3.20), leads to the following differential equation for $\hat{u}_{z0}$:

$$\frac{\partial \hat{u}_{z0}}{\partial \hat{z}}=-\frac{1}{2}\left[\frac{d^2\hat{p}_0}{d\hat{x}^2}\left(\hat{z}^2-\hat{H}\hat{z}\right)-\hat{x}\frac{d\hat{p}_0}{d\hat{x}}\hat{z}\right] \tag{2.6.46}$$

Its integration is

$$\hat{u}_{z0}=-\frac{1}{2}\left[\frac{d^2\hat{p}_0}{d\hat{x}^2}\left(\frac{1}{3}\hat{z}^3-\frac{1}{2}\hat{H}\hat{z}^2\right)-\frac{1}{2}\hat{x}\frac{d\hat{p}_0}{d\hat{x}}\hat{z}^2\right]+C \tag{2.6.47}$$

Imposing B.C.s (2.6.43b, 44b) results in the following differential equation for the pressure:

$$\frac{d}{\partial\hat{x}}\left(\hat{H}^3\frac{d\hat{p}_0}{d\hat{x}}\right) = 12 \qquad (2.6.48)$$

Its integration is

$$\frac{d\hat{p}_0}{d\hat{x}} = 12\hat{x}\hat{H}^{-3} + C\hat{H}^{-3} \qquad (2.6.49)$$

The flow field is symmetric with respect to the $\hat{z}$-axis. Thus, the pressure must be an even function of $\hat{x}$ which indicates that $C = 0$. In view of the expansion (2.6.37e), any constants can not be included in the pressure either to satisfy the matching condition. In this way, upon integration of (2.6.49), the pressure is obtained as

$$\hat{p}_0 = -6\hat{H}^{-2} \qquad (2.6.50)$$

Now, introducing (2.6.49) and its derivative in (2.4.45, 47) and noting that the constant C in either of the equations is equal to zero, yields the components of the velocity as

$$\hat{u}_{x0} = 6\hat{x}\hat{H}^{-3}\left(\hat{z}^2 - \hat{H}\hat{z}\right) \qquad (2.6.51)$$

$$\hat{u}_{z0} = -2\left(6\hat{H}^{-4} - 5\hat{H}^{-3}\right)\hat{z}^3 + 3\left(4\hat{H}^{-3} - 3\hat{H}^{-2}\right)\hat{z}^2 \qquad (2.6.52)$$

Introducing the flow field (2.6.50-52), to the stress tensor, given by (2.6.5), written in terms of the inner variable [by the use of the expansion (2.6.37)], leads to

$$\begin{aligned}
\tilde{\sigma}_{Jxx} &= +\delta^{-2}6\hat{H}^{-2} + O\left(\delta^{-1}\right)\Big|_{S_J} \\
\tilde{\sigma}_{Jxz} = \tilde{\sigma}_{Jzx} &= \delta^{-\frac{3}{2}}6x\hat{H}^{-3}\left(2\hat{z} - \hat{H}\right) + O\left(\delta^{-½}\right)\Big|_{S_J} \\
\tilde{\sigma}_{Jzz} &= +\delta^{-2}6\hat{H}^{-2} + O\left(\delta^{-1}\right)O(\delta)\Big|_{S_J}
\end{aligned} \qquad (2.6.53)$$

2.6.2.4 - Force Parallel to Wall

The integrand of the force, given by (2.6.17, 18), for the tangential component of the force, is determined by the use of (2.6.23-25, 36). The stress tensor for the translation of a particle parallel to the wall, given by (2.6.36), is evaluated on the wall $(\hat{z} = 0)$ as

$$\tilde{\sigma}_{Wxx} = -\delta^{-\frac{3}{2}} 2\hat{x}\hat{H}^{-2} + O\left(\delta^{-\frac{1}{2}}\right)$$
$$\tilde{\sigma}_{Wxz} = \tilde{\sigma}_{Wzx} = \delta^{-1} 4\left(-\hat{H}^{-2} + \hat{H}^{-1}\right) + O\left(\delta^{0}\right) \qquad (2.6.54)$$
$$\tilde{\sigma}_{Wzz} = -\delta^{-\frac{3}{2}} 2\hat{x}\hat{H}^{-2} + O\left(\delta^{-\frac{1}{2}}\right)$$

and on the cylinder surface $\hat{z} = \hat{H}$ as

$$\tilde{\sigma}_{Pxx} = -\delta^{-\frac{3}{2}} 2\hat{x}\hat{H}^{-2} + O\left(\delta^{-\frac{1}{2}}\right)$$
$$\tilde{\sigma}_{Pxz} = \tilde{\sigma}_{Pzx} = \delta^{-1} 2\left(2\hat{H}^{-2} - \hat{H}^{-1}\right) + O\left(\delta^{0}\right) \qquad (2.6.55)$$
$$\tilde{\sigma}_{Pzz} = -\delta^{-\frac{3}{2}} 2\hat{x}\hat{H}^{-2} + O\left(\delta^{-\frac{1}{2}}\right)$$

The integrand of the force, given by (2.6.17,18), is obtained as [c.f., (2.6.23-25, 54, 55)]

$$\vec{\tilde{B}}_W \cdot \vec{\vec{\tilde{\sigma}}}_W \cdot d\vec{\tilde{S}}_W = \lambda\left\{\delta^{-\frac{5}{2}} Pe\left[L^1 W_{P+W}\left(1+\tilde{\Omega}\right)\left(-12\hat{H}^{-3} + 28\hat{H}^{-4} - 16\hat{H}^{-5}\right)\right.\right.$$
$$\left.\left. + L^1 W_{P-W}\left(1-\tilde{\Omega}\right)\left(-2\hat{H}^{-2} + 6\hat{H}^{-3} - 4\hat{H}^{-4}\right)\right] + \delta^{-2} Pe^2\left[\text{odd function of } \hat{x}\right]\right\} d\hat{x} \qquad (2.6.56)$$

$$\vec{\tilde{B}}_P \cdot \vec{\vec{\tilde{\sigma}}}_P \cdot d\vec{\tilde{S}}_P = \lambda\left\{\delta^{-\frac{5}{2}} Pe\left[L^1 P_{P+W}\left(1+\tilde{\Omega}\right)\left(-6\hat{H}^{-3} + 20\hat{H}^{-4} - 16\hat{H}^{-5}\right)\right.\right.$$
$$\left.\left. + L^1 P_{P-W}\left(1-\tilde{\Omega}\right)\left(-\hat{H}^{-2} + 4\hat{H}^{-3} - 4\hat{H}^{-4}\right)\right] + \delta^{-2} Pe^2\left[\text{odd function of } \hat{x}\right]\right\} d\hat{x} \qquad (2.6.57)$$

The force is obtained by the sum of the contribution from all individual points on the solid surfaces bounded the inner region, upon the integration from the left edge $(\hat{x} = -\infty)$ to the right edge $(\hat{x} = +\infty)$ of the inner region. Thus, in view of integrals (2.3.34, 35, 2.4.38),

$$\int_{-\infty}^{+\infty} \hat{H}^{-4} d\hat{x} = \frac{\hat{x}}{2}\left(\frac{1}{3}\hat{H}^{-3} + \frac{5}{12}\hat{H}^{-2} + \frac{1}{8}\hat{H}^{-1}\right) + \frac{5\sqrt{2}}{16}\tan^{-1}\left(\frac{\hat{x}}{\sqrt{2}}\right)\Bigg|_{-\infty}^{+\infty} = \frac{5\sqrt{2}\pi}{16} \qquad (2.6.58)$$

$$\int_{-\infty}^{+\infty} \hat{H}^{-5} d\hat{x} = \frac{\hat{x}}{8}\left(\hat{H}^{-4} + \frac{7}{6}\hat{H}^{-3} + \frac{35}{24}\hat{H}^{-2} + \frac{35}{16}\hat{H}^{-1}\right) + \frac{35\sqrt{2}}{128}\tan^{-1}\left(\frac{\hat{x}}{\sqrt{2}}\right)\Bigg|_{-\infty}^{+\infty} = \frac{35\sqrt{2}\pi}{128} \qquad (2.6.59)$$

$$\int_{-\infty}^{+\infty} \left[\text{odd functions of } \hat{x}\right] d\hat{x} = \left|\text{even functions of } \hat{x}\right|_{-\infty}^{+\infty} = 0 \qquad (2.6.60)$$

the x-component of the force, given by (2.6.14), is obtained as

$$\tilde{F}^*_{4x} = \lambda Pe\delta^{-\frac{5}{2}} \int_{-\infty}^{+\infty} \Big[L^1P_{P+W}\big(1+\tilde{\Omega}\big)\big(-6\hat{H}^{-3}+20\hat{H}^{-4}-16\hat{H}^{-5}\big)$$

$$+L^1P_{P-W}\big(1-\tilde{\Omega}\big)\big(-\hat{H}^{-2}+4\hat{H}^{-3}-4\hat{H}^{-4}\big)\Big]d\hat{x}$$

$$+\lambda Pe\delta^{-\frac{5}{2}} \int_{-\infty}^{+\infty} \Big[L^1W_{P+W}\big(1+\tilde{\Omega}\big)\big(-12\hat{H}^{-3}+28\hat{H}^{-4}-16\hat{H}^{-5}\big)$$

$$+L^1W_{P-W}\big(1-\tilde{\Omega}\big)\big(-2\hat{H}^{-2}+6\hat{H}^{-3}-4\hat{H}^{-4}\big)\Big]d\hat{x}$$

$$= \lambda Pe\delta^{-\frac{5}{2}}\left[L^1P_{P+W}\big(1+\tilde{\Omega}\big)\left(\frac{-9}{4}+\frac{25}{4}-\frac{35}{8}\right)+L^1P_{P-W}\big(1-\tilde{\Omega}\big)\left(\frac{-1}{2}+\frac{3}{2}-\frac{5}{4}\right)\right]\sqrt{2\pi}$$

$$+\lambda Pe\delta^{-\frac{5}{2}}\left[L^1W_{P+W}\big(1+\tilde{\Omega}\big)\left(\frac{-9}{2}+\frac{35}{4}-\frac{35}{8}\right)+L^1W_{P-W}\big(1-\tilde{\Omega}\big)\left(-1+\frac{9}{4}-\frac{5}{4}\right)\right]\sqrt{2\pi}$$

(2.6.61)

By the use of definition (2.2.5e, f), the dimensional force per unit length experienced by the particle, given by (2.6.1), is

$$\vec{F} = \vec{F}_H + \left(\frac{\varepsilon_r\varepsilon_0 kT}{2z^2{}_1e^2c_\infty a}\right)^2 \eta U\vec{\tilde{F}}^*_4 \qquad (2.6.62)$$

Thus, the x-component of the total force is determined by [c.f., (2.6.12, 61, 62, 2.2.1, 5)]

$$F_x = -2\sqrt{2}\pi\eta\sqrt{\frac{a}{h}}U - \sqrt{2}\pi\left[\frac{\varepsilon_r\varepsilon_0 kT}{2(az_1e)^2c_\infty}\right]^2 \eta U\frac{2c_\infty akT}{\eta U}\frac{aU}{D_1}\left(\frac{a}{h}\right)^{\frac{5}{2}} \times$$
$$\left[\frac{1}{8}\big(3L^1P_{P+W}+L^1W_{P+W}\big)\left(1+\frac{a\Omega}{U}\right)+\frac{1}{4}L^1P_{P-W}\left(1-\frac{a\Omega}{U}\right)\right] \qquad (2.6.63)$$

or, in view of (2.6.34), by

$$F_x = -2\sqrt{2}\pi\eta\sqrt{\frac{a}{h}}U - \frac{\sqrt{2}\pi}{2}\frac{(\varepsilon_r\varepsilon_0)^2(kT)^3}{(z_1e)^4c_\infty}\frac{\sqrt{a}}{h^2\sqrt{h}} \times$$
$$\left\{\left[\frac{(3G_P+G_W)}{D_1}(G_P+G_W)+\frac{(3H_P+H_W)}{D_2}(H_P+H_W)\right](U+a\Omega)\right. \qquad (2.6.64)$$
$$\left.+\left[\frac{2G_P}{D_1}(G_P-G_W)+\frac{2H_P}{D_2}(H_P-H_W)\right](U-a\Omega)\right\}$$

It is of interest to note that for small but equal surface potentials and equal ion mobilities (e.g. K^+ and Cl^-), the second term in square brackets on the right-hand side vanishes. The first term in square brackets, in view of the relation between the ion radius, a_i, and diffusion constant,

$$D = \frac{kT}{4\pi\eta a_i}, \qquad (2.6.65a)$$

reduces to

$$\frac{4\pi\eta(z_1 e)^2 a_i \zeta^2}{(kT)^3}, \qquad (2.6.65b)$$

In deriving (2.6.65b) the expansion (1.2.8e) and

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots \qquad (2.6.65c)$$

have been used. Thus, the electroviscous drag is proportional to ion size, similar to electroviscous drag on an isolated sphere, and scales with viscosity and ζ^2.

2.6.2.5 - Force Normal to Wall

The integrand of the force given by (2.6.17, 18), for the normal component of the force, is determined by the use of (2.6.23-25, 53). The stress tensor for translation of a particle normal to the wall, given by (2.6.53), is evaluated on the solid surfaces as

$$\begin{aligned}
\tilde{\sigma}_{Pxx} = \tilde{\sigma}_{Pzz} = \tilde{\sigma}_{Wxx} = \tilde{\sigma}_{Wzz} &= +\delta^{-2} 6\hat{H}^{-2} + O(\delta^{-1}) \\
\tilde{\sigma}_{Pxz} = \tilde{\sigma}_{Pzx} &= \delta^{-\frac{3}{2}} 6x\hat{H}^{-2} + O\left(\delta^{-\frac{1}{2}}\right) \\
\tilde{\sigma}_{Wxz} = \tilde{\sigma}_{Wzx} &= -\delta^{-\frac{3}{2}} 6x\hat{H}^{-2} + O\left(\delta^{-\frac{1}{2}}\right)
\end{aligned} \qquad (2.6.66)$$

From this, and (2.6.23-25) the integrand (2.6.17, 18) is evaluated on each solid surfaces with the result

$$\begin{aligned}
\vec{\tilde{B}}_W \cdot \vec{\vec{\tilde{\sigma}}}_W \cdot d\vec{\tilde{S}}_W = \lambda \Big\{ & \delta^{-3} Pe[\text{odd function of } \hat{x}] \\
& + \delta^{-\frac{5}{2}} Pe^2 \Big[8L^2 W_{P+W} (1+\tilde{\Omega})^2 (\hat{H}^{-4} - \hat{H}^{-5}) + 4L^2 W_{P-W} (1-\tilde{\Omega}^2)(\hat{H}^{-3} - \hat{H}^{-4}) \Big] \Big\} d\hat{x}
\end{aligned}$$

(2.6.67a)

$$\vec{\tilde{B}}_P \cdot \vec{\vec{\tilde{\sigma}}}_P \cdot d\vec{\tilde{S}}_P = \lambda\Big\{\delta^{-3}Pe\big[\text{odd function of } \hat{x}\big]$$

$$+\delta^{-\frac{5}{2}}Pe^2\Big[8L^2P_{P+W}\big(1+\tilde{\Omega}\big)^2\big(\hat{H}^{-4}-\hat{H}^{-5}\big)+4L^2P_{P-W}\big(1-\tilde{\Omega}^2\big)\big(\hat{H}^{-3}-\hat{H}^{-4}\big)\Big]\Big\}d\hat{x}$$

(2.6.67b)

Thus, the normal component of the force is determined by [c.f., (2.6.13, 62, 58-60]

$$F_z = \frac{\sqrt{2}\pi}{2}\frac{(\varepsilon_r\varepsilon_0)^2(kT)^3}{(z_1e)^4D_1^2c_\infty}\frac{a\sqrt{a}}{h^2\sqrt{h}}\times$$

$$\left\{\frac{5}{16}\big(L^2P_{P+W}+L^2W_{P+W}\big)(U+a\Omega)^2+\frac{1}{4}\big(L^2P_{P-W}+L^2W_{P-W}\big)\big(U^2-a^2\Omega^2\big)\right\}$$

(2.6.68)

or, in view of (2.6.35), by

$$F_z = \frac{\sqrt{2}\pi}{8}\frac{(\varepsilon_r\varepsilon_0)^2(kT)^3}{(z_1e)^4c_\infty}\frac{a\sqrt{a}}{h^2\sqrt{h}}\left\{5\left[\left(\frac{G_P}{D_1}+\frac{H_P}{D_2}\right)+\left(\frac{G_W}{D_1}+\frac{H_W}{D_2}\right)\right]^2(U+a\Omega)^2\right.$$

$$\left.+4\left[\left(\frac{G_P}{D_1}+\frac{H_P}{D_2}\right)^2-\left(\frac{G_W}{D_1}+\frac{H_W}{D_2}\right)^2\right]\big(U^2-a^2\Omega^2\big)\right\}$$

(2.6.69)

in which (G_P, G_W) and (H_P, H_W), given by (2.6.31), in view of definition (2.2.4b), may be expressed as

$$G_J = \ln\frac{1+e^{-\frac{z_1e\zeta_J}{2kT}}}{2}, \qquad H_J = \ln\frac{1+e^{\frac{z_1e\zeta_J}{2kT}}}{2} \qquad J=(P, W) \qquad (2.6.70)$$

In the formula (2.6.64, 69, 70), ε_r is the relative permitivity of the medium (dielectric constant), ε_0 the permitivity of the vacuum ($\varepsilon_r\varepsilon_0$ is the permitivity of the medium), η the viscosity of liquid, (kT) the thermal energy, z_1 the ion valency of either species, e the charge of a proton, c_∞ the number ion bulk concentrations, ζ_P and ζ_W the ζ-potentials of the particle and wall, D_1 and D_2 the diffusivity of counterions and coions, respectively; a is the cylinder radius, h the clearance between cylinder and wall; U is the translation velocity of the cylinder and Ω its angular velocity for its rotation in the clockwise direction.

It is of interest to note that for ions with the same mobility and for small but equal surface potentials of the wall and the particle, Eq. (2.6.69) reduces to

$$F_z = \frac{5\sqrt{2}\pi^3}{8} \frac{(\varepsilon_r \varepsilon_0)^2 \eta^2 a_i^2 \zeta^4}{c_\infty (kT)^3} \frac{a\sqrt{a}}{h^2\sqrt{h}} (U + a\Omega)^2 \tag{2.6.71}$$

It can be seen that the normal component force varies linearly with ion size squared $\left(a_i^2\right)$. It also varies linearly with η^2 and it proportional to the fourth power in ζ-potential.

2.7 - Discussion

2.7.1 - Matching Conditions

The inner solution of the perturbation of ion concentrations obtained in § 2.4 has to match to the outer solution by requiring that

$$\tilde{c}_2\Big|_{\tilde{x}\to 0} = \hat{c}_2\Big|_{\hat{x}\to\pm\infty} \tag{2.7.1}$$

To investigate how it works, for large values of $\hat{x}$, the perturbation of ion concentrations of order Pe, given by (2.4.23, 39,) and of order Pe^2, given by (2.4.40, 49), may be written as

$$\hat{c}_{21}\Big|_{\hat{x}\to\pm\infty} \to \left(F_{cP} - F_{cW}\right)\left(1 - \tilde{\Omega}\right)\hat{x}^{-1} \tag{2.7.2}$$

and

$$\hat{c}_{22}\Big|_{\hat{x}\to\pm\infty} \to \frac{2}{3}\left(F_{cP} - F_{cW}\right)\left(1 - \tilde{\Omega}^2\right)\hat{x}^{-2} \tag{2.7.3}$$

Thus, in view of (2.3.7, 4.17), the matching condition (2.7.1) gives

$$\tilde{c}_{21}\Big|_{\tilde{x}\to 0} \to \delta^{-1}\left(F_{cP} - F_{cW}\right)\left(1 - \tilde{\Omega}\right)\tilde{x}^{-1} \tag{2.7.4}$$

and

$$\tilde{c}_{22}\Big|_{\tilde{x}\to 0} \to \frac{2}{3}\delta^{0}\left(F_{cP} - F_{cW}\right)\left(1 - \tilde{\Omega}^2\right)\tilde{x}^{-2} \tag{2.7.5}$$

But, the electroviscous ion concentrations for both orders in Pe in the outer region must be of the same order in δ, since otherwise (noting that the flow field in the outer region is of order unity) Eq.s (2.4.10-13) for the perturbation in ion concentrations at order Pe^2 does not work anymore. In other words, the expansion (2.4.1) breaks down (i.e. it is not uniformly valid). From this it follows that for the matching condition to be satisfied at order δ^{-1}, in deriving Eq. (2.4.49), for $\hat{c}_p$, the constant of integration, D, must be included, resulting in

$$\tilde{c}_{22}\Big|_{\hat{x}\to 0} \to \delta^{-1}D \qquad (2.7.6)$$

By the way, evaluating this constant is not required, since in deriving the electroviscous force only the derivatives of the electroviscous ion concentrations [c.f., (2.6.21, 22)] are needed and hence the derivative of the constant D vanishes.

2.7.2 - Existence of Outer Solution

To investigate for the existence of an outer solution that satisfies the matching condition (2.7.4) we may use a tangent circle coordinate system (ζ, μ) which best describes the geometry of the problem for the outer region (c.f., Fig. A1). This coordinate system is discussed in Appendix A with the transformation

$$\tilde{x} = \frac{2\mu}{\zeta^2 + \mu^2}, \qquad \tilde{z} = \frac{2\zeta}{\zeta^2 + \mu^2}, \qquad 0 \le \zeta \le 1, \qquad -\infty < \mu < +\infty \qquad (2.7.7)$$

or equivalently,

$$\mu = \frac{2\tilde{x}}{\tilde{x}^2 + \tilde{z}^2}, \qquad \zeta = \frac{2\tilde{z}}{\tilde{x}^2 + \tilde{z}^2}, \qquad 0 \le \zeta \le 1, \quad -\infty < \mu < +\infty \qquad (2.7.8)$$

The cylinder surface is given by $\zeta = 1$ and the wall surface by $\zeta = 0$, the origin by $(\zeta = 0, \mu = \infty)$, and the far distances from the origin by $\zeta = \mu = 0$. The normal unit vector outward to the cylinder is $-\vec{i}_\zeta$ and that of the wall is $+\vec{i}_\zeta$. Thus, the electroviscous ion concentrations of order Pe, given by (2.4.4-6), may be written in this coordinate system as [c.f., (A.30)]

$$\frac{\partial^2 \tilde{c}_{21}}{\partial \zeta^2} + \frac{\partial^2 \tilde{c}_{21}}{\partial \mu^2} = 0 \qquad (2.7.9)$$

with boundary condition on the solid surfaces [c.f., (A.29)]

$$\frac{\partial \tilde{c}_{21}}{\partial \zeta} = 0 \quad \text{on } \zeta = 0, \qquad \frac{\partial \tilde{c}_{21}}{\partial \zeta} = 0 \quad \text{on } \zeta = 1 \qquad (2.7.10)$$

and at infinity

$$\tilde{c}_{21} \to 0 \qquad \text{as } (\zeta, \mu) \to 0 \qquad (2.7.11)$$

and with the matching condition [c.f., (2.7.4, 7)]

$$\tilde{c}_{21}\Big|_{\mu\to\infty} \to \frac{1}{2}\left(F_{cP}-F_{cW}\right)\left(1-\tilde{\Omega}\right)\mu \tag{2.7.12}$$

Its solution is

$$\tilde{c}_{21} = \frac{1}{2}\left(F_{cP}-F_{cW}\right)\left(1-\tilde{\Omega}\right)\mu \tag{2.7.13}$$

which may be expressed in Cartesian coordinates as [c.f., (2.7.8)]

$$\tilde{c}_2 = \delta^{-1}\left[\mathrm{Pe}\left(F_{cP}-F_{cW}\right)\left(1-\tilde{\Omega}\right)\frac{\tilde{x}}{\tilde{x}^2+\tilde{z}^2}+O\left(\mathrm{Pe}^2\right)\right] \tag{2.7.14}$$

To determine the outer solution at order Pe^2 the solution of the flow field for the outer region involved in Eq. (2.4.10) is required. It is easily observed that this solution satisfies the matching condition (2.7.4).

From the above discussion, it follows that the contribution from the outer region in electroviscous ion concentrations and equally the electroviscous potential is of order δ^{-1} for non-identical particle and wall surface potential, otherwise it is of order unity.

2.8 - Results and Conclusions

For a charged system, the cylinder experiences an electroviscous force of order ϵ^4 (ϵ is the ratio of the double layer thickness to the cylinder radius), resulting from the tangential movement of the ions in the diffuse double layers on the solid surfaces caused by perturbation of the electrical field. For an uncharged system, Stokes equations predict no force on the cylinder in the direction normal to the wall [c.f., (2.6.13)]. Whereas, for the charged system the cylinder experiences a normal component of the force, determined by the formula (2.6.69). The drag component of the purely hydrodynamic force for the inner region is of order $\delta^{-1/2}$ [c.f., (2.6.12)]. Because of symmetry, as a first approximation, it is independent of the rotation of the particle. For a charged system, the particle experiences an additional force (tangential component of electroviscous force) of order ϵ^4, determined by the formula (2.6.64). The tangential component of the electroviscous force is of order Pe (Pe is the Peclet number based on the radius and translation velocity of the cylinder, and diffusity of counter-ions), or linearly depends on the velocity, and it is of $O(\delta^{-5/2})$ in terms of the dimensionless clearance [i.e. $O(Pe\delta^{-5/2})$]. The normal component of the force is of order (Pe^2 $\delta^{-5/2}$).

The normal component of the force may be written in dimensionless form as

$$\widetilde{F}_z = \frac{\sqrt{2}\pi}{4} \in^4 \lambda Pe^2 \delta^{-5/2} f_z \tag{2.8.1a}$$

where f_z is a function of ζ-potentials, the ratio of diffusivity of ions, and the linear and angular velocity of the particle, defined by

$$\begin{aligned} f_z = 5\left[\left(G_P + \frac{D_1}{D_2}H_P\right) + \left(G_W + \frac{D_1}{D_2}H_W\right)\right]^2 \left(1+\widetilde{\Omega}\right)^2 \\ + 4\left[\left(G_P + \frac{D_1}{D_2}H_P\right)^2 - \left(G_W + \frac{D_1}{D_2}H_W\right)^2\right]\left(1-\widetilde{\Omega}^2\right) \end{aligned} \tag{2.8.1b}$$

The function f_z is plotted versus the ratio of the diffusivity of ions in Fig. 2.3 for the translation and in Fig. 2.4 for the rotation of the particle for three different ratios of ζ-potentials, $\zeta_p=0.5\zeta_w$, $\zeta_p=\zeta_w$, and $\zeta_p=2\zeta_w$. The valency of the ions is assumed to be one, the temperature of the medium is room temperature and ζ_w is taken to be -100 mV. Each curve has a minimum. The location of the minimum depends on the magnitudes of the ζ-potentials. The minimum can be either zero or negative. For identical ζ-potentials the minimum is zero for any combination of the linear and angular velocities, and for this example it occurred at $D_1/D_2=2.4791$. For the curve $\zeta_p=0.5\zeta_w$, $f_{zMin} = -0.1434$ for translation and $f_{zMin} = -0.1037$ for rotation of the particle and they correspond to $D_1/D_2=1.9344$ and $D_1/D_2=2.2788$ for the former and latter, respectively. For the curve $\zeta_p=2\zeta_w$ these values are ($f_{zMin}=-1.4846$, $D_1/D_2=4.1662$) for translation and ($f_{zMin}=-1.7199$, $D_1/D_2=3.2453$) for rotation of the particle. The tangential component of the force depends linearly on the ratio of the diffusivity of ions. For small ζ-potentials and for equal mobilities of ions, as a first approximation, the tangential component of the force, is linearly proportional to viscosity of medium, η, ion radius, a_i, and ζ^2, whereas the lift component is proportional to η^2, a_i^2 and ζ^4. For two special hydrodynamic cases, namely for $U = -a\Omega$ and $U = a\Omega$, for the normal component of the force, the present theory [c.f., (2.6. 69)] predicts no force for the former and four times the force (because of the

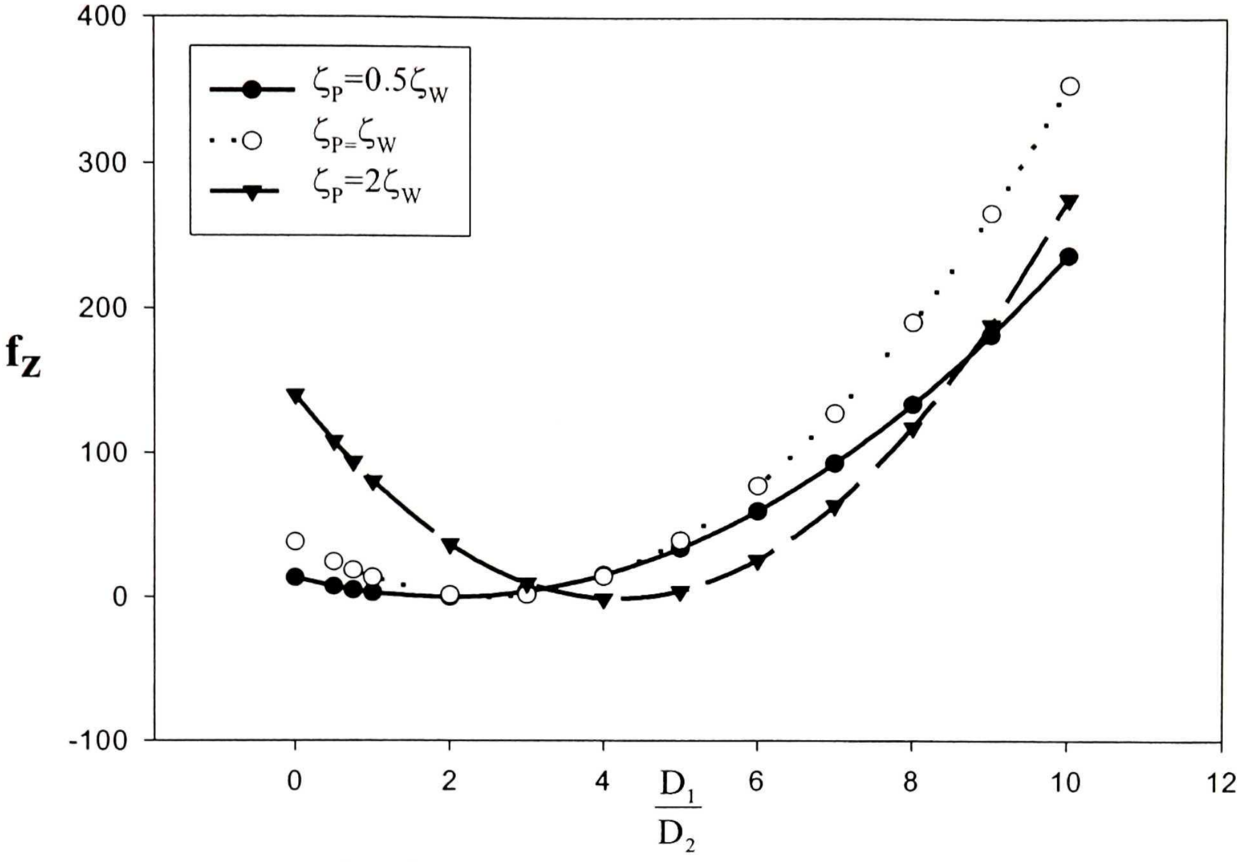


Fig. 2.3 - f_Z vs D_1/D_2 for translation of cylinder.

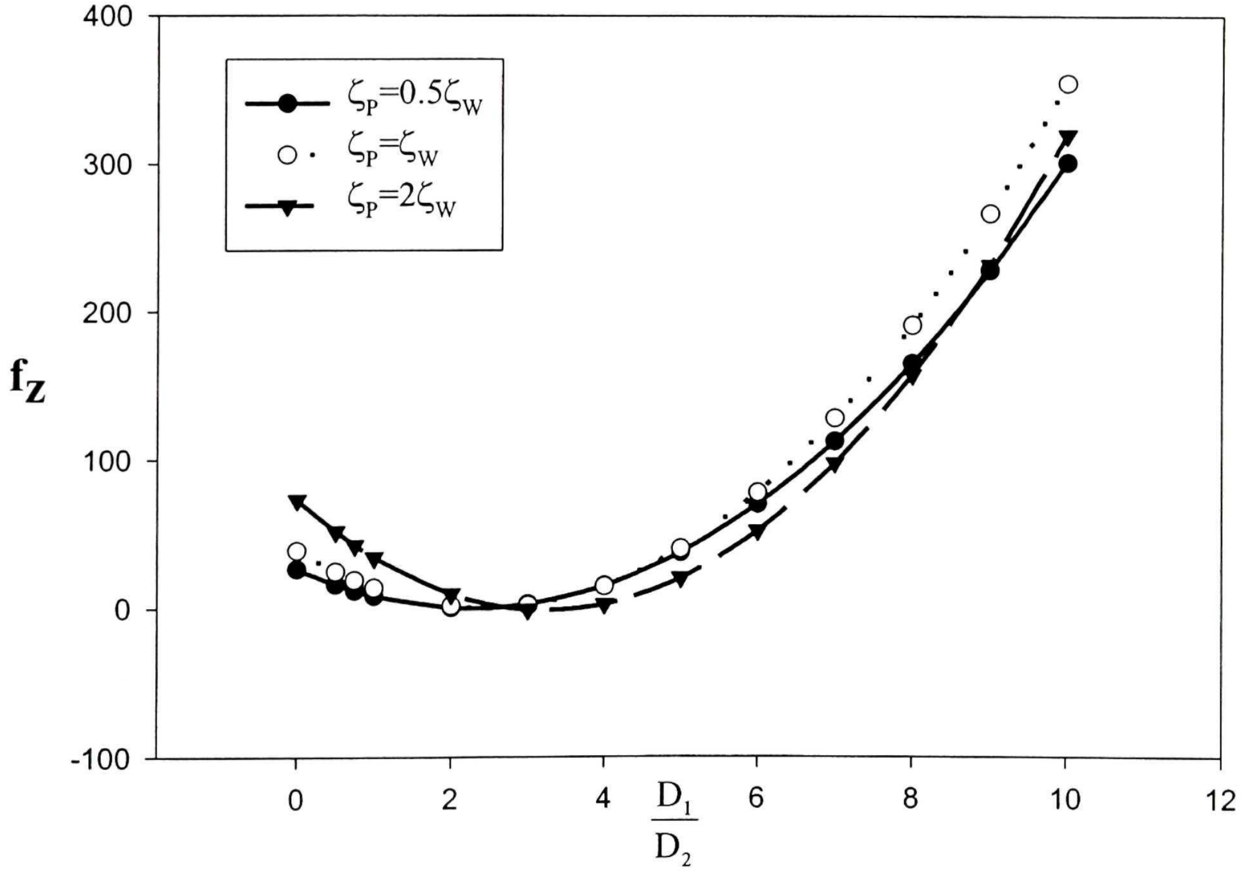


Fig. 2.4 - f_z vs D_1/D_2 for rotation of cylinder.

proportionality to the square of the velocity) produced by either the rotation or translation of the particle for the latter.

For identical particle and wall ζ-potentials, the present theory predicts the normal component of the electroviscous force of magnitude [c.f, (2.6.69)]

$$F_z = \frac{5\sqrt{2}\pi}{2} \frac{(\varepsilon_r \varepsilon_0)^2 (kT)^3}{(z_1 e)^4 c_\infty} \frac{a\sqrt{a}}{h^2\sqrt{h}} \left(\frac{G_P}{D_1} + \frac{H_P}{D_2} \right)^2 (U + a\Omega)^2 \tag{2.8.2}$$

Warszynski & van de Ven (2000)'s theory for the same conditions, given by (1.4.5), predicts a force half as large. Their theory, given by (1.2.33), at the leading order [i.e. at $O(\in^4)$] for an uncharged particle but with the charged wall predicts a normal component of the force of magnitude

$$F_z = \frac{\sqrt{2}\pi}{8} \frac{(\varepsilon_r \varepsilon_0)^2 (kT)^3}{(z_1 e)^4 c_\infty} \frac{a\sqrt{a}}{h^2\sqrt{h}} \left(\frac{G_W}{D_1} + \frac{H_W}{D_2} \right)^2 U^2 \tag{2.8.3}$$

which is the same as that predicted by the present theory for the same conditions [c.f., (2.6.69)]. For an uncharged wall but with a charged particle the present theory for the translation of the particle predicts a force of order $\in^4$ of magnitude

$$F_z = \frac{9\sqrt{2}\pi}{8} \frac{(\varepsilon_r \varepsilon_0)^2 (kT)^3}{(z_1 e)^4 c_\infty} \frac{\sqrt{a}}{h^2\sqrt{h}} \left(\frac{G_P}{D_1} + \frac{H_P}{D_2} \right)^2 U^2 \tag{2.8.4}$$

but, Warszynski & van de Ven (2000)'s theory predicts no force of order $\in^4$, only a force of order $\in^6$ (i.e. just the contribution from the perturbation in potential) of magnitude

$$F_z = \frac{7\sqrt{2}\pi}{16} \frac{(\varepsilon_r \varepsilon_0)^3 (kT)^4}{(z_1 e)^6 c_\infty^2} \frac{a\sqrt{a}}{h^3\sqrt{h}} \left(\frac{G_P}{D_1} - \frac{H_P}{D_2} \right)^2 U^2 \tag{2.8.5}$$

which makes no physical sense, since for both cases [i.e. ($\psi_p = 0$, $\psi_w \neq 0$) and ($\psi_p \neq 0$, $\psi_w = 0$)] we expect to have a perturbation in the flow field, which must result in a lift force of order $\in^4$. From these three comparisons it follows that they obtained the force by considering only the tangential movement of the ions in the diffuse double layer on the wall. This is clearly verified by the relationships (2.6.67a, b) which indicate that for identical ζ-potentials half of the contribution to the force comes from the wall and the other half comes from the particle surface and hence by neglecting the latter they obtained only half the force for identical ζ-potentials, the exact value for the case when $\psi_P = 0$, and no force for $\psi_W = 0$.

The drag component of the force, given by (2.6.64), is exactly the same as that obtained by Cox, given by (1.2.32d). For the normal component, Cox's theory, presented in Wu *et al.* (1996), given by (1.2.32a), for the translation of a particle predicts a force of magnitude

$$F_z = \frac{\sqrt{2}\pi}{8} \frac{(\varepsilon_r \varepsilon_0)^2 (kT)^3}{(z_1 e)^4 c_\infty} \frac{a\sqrt{a}}{h^2 \sqrt{h}} \times \left[9\left(\frac{G_P}{D_1} + \frac{H_P}{D_2}\right)^2 + \left(\frac{G_W}{D_1} + \frac{H_W}{D_2}\right)^2 + 10\left(\frac{G_P}{D_1} + \frac{H_P}{D_2}\right)\left(\frac{G_W}{D_1} + \frac{H_W}{D_2}\right)\right] U^2 \qquad (2.8.6)$$

which is the same as that determined by (2.6.69). But, for the rotation of a particle his theory predicts a different value for the force as can be seen (for a special case of the problem) by comparing formals (1.4.4) and (2.8.2). Cox's theory for just rotation of a particle predicts

$$F_z = \frac{\sqrt{2}\pi}{8} \frac{(\varepsilon_r \varepsilon_0)^2 (kT)^3}{(z_1 e)^4 c_\infty} \frac{a\sqrt{a}}{h^2 \sqrt{h}} \times \left[\left(\frac{G_P}{D_1} + \frac{H_P}{D_2}\right)^2 - 3\left(\frac{G_W}{D_1} + \frac{H_W}{D_2}\right)^2 - 2\left(\frac{G_P}{D_1} + \frac{H_P}{D_2}\right)\left(\frac{G_W}{D_1} + \frac{H_W}{D_2}\right)\right] (a\Omega)^2 \qquad (2.8.7)$$

which indicates that for a charged particle but uncharged wall (i.e. $G_w = 0, H_w = 0$) the force is positive, for an uncharged particle and charged wall the force is negative, and also for identical ζ-potentials the force is negative, which does not make sense.

In deriving the present theory, in all calculations from the beginning to the end, the dimensionless linear velocity (1) and angular one $(\tilde{\Omega})$ appeared combined [i.e. either as $(1 - \tilde{\Omega})$, $(1 + \tilde{\Omega})$ or their product], and hence if the derived coefficient of the linear velocity in the force is correct, the coefficient of the angular velocity must be correct, if at the first step (i.e. in the hydrodynamic part) they combined together correctly and in addition if the new combination of them, $\left(1+\widetilde{\Omega}\right)$, which is involved in the calculation after the integral (2.4.47) is correct. It is easily verified by observing that the boundary conditions (2.3.13, 14) are true and they are also satisfied by the flow field, given by (2.3.40, 41), and the integration (2.4.47) is correct. In Cox's original formula, presented in Wu *et al.* (1996), instead of the linear and angular velocity, U and aΩ, the velocity of the nearest point of the cylinder to the wall, V (V = U - aΩ), and its angular velocity, aΩ, appeared. Therefore, this discrepancy may be explained by the possibility that Cox obtained the hydrodynamics of the problem in a fixed coordinate system instead of the moving coordinate system used here, but to remove the time dependency of the electroviscous ion concentrations which appeared at O(Pe^2) [c.f., Eq.s (1.3.60a, 2.4.10)] instead of subtracting the linear velocity of the particle, U, from the x-component of the velocity, he subtracted the velocity of the cylinder at the closest point to the wall, V = U-aΩ, which is obviously not correct. In other words, his calculation up to O(Pe^2) is correct, and hence the derived drag component of the force is valid for both translation and rotation, but for the normal component, in addition to the linear velocity, an excess angular velocity (for removing the time dependency) is involved in the Eq. (2.4.46) to be accounted for the invalidity of the normal component of the force for the rotation of the particle. This is verified by recalculating the problem after adding the term $\widetilde{\Omega}$ in the x-component of velocity appearing in the integral (2.4.47).

The purely hydrodynamic force determined by (2.6.12, 13) is the same as that obtained by Cox and Warszynski & van de Ven (2000).

From the above discussion it can be concluded that Cox's theory for the drag component of the electroviscous force is valid for both translation and rotation of a cylinder parallel to the wall, but its normal component, reported in Wu, *et al.* (1996), is valid only for translation of a cylinder. Warszynski & van de Ven's theory (2000) is valid only for a charged wall, but with an uncharged cylinder under translation parallel to a wall.

Chapter Three

Electroviscous Sphere-Wall Interactions

3.1 - Introduction

Observations by Alexander and Prieve (1987) of the change in the distance to the wall of a 9 μm spherical latex particle moving parallel to a glass wall (with velocity 50 μm/s) in a slit-like flow cell apparatus containing a glycerol-water solution attracted the attention of scientists to explain this interesting phenomenon. The pioneering work was by Prieve & Bike (1987) who attempted to formulate a theory based on the lubrication approximation. They concluded that the discrepancy between experiment and their theory was due to the invalidity of the lubrication theory. In their latest papers which appeared in the literature in1995, they released the lubrication theory, and obtained a complete solution of the problem. Although they could improve their results, the theory underestimated the force by several orders of magnitude. Many other theories appeared in the literature in the late eighties and early nineties, none of which could predict the right order of the force. As mentioned in Chapter one, the common problem encountered in these theories is that it is assumed that the perturbation of potential determines the force by applying the Maxwell stress tensor, however this is not the dominant contribution to the force. Although Cox predicted the right order of magnitude of the force in his *general theory(1997),* the problem of the sphere-wall interactions remained unsolved. The objective of this chapter is to present a solution for the problem of a sphere which is under translation and rotation with a small clearance between particle and wall for low Peclet numbers. As for the case of cylinder-wall interactions, the assumption of a small clearance allows an easier analytical approach to solve the hydrodynamic part of the problem and equally the low Peclet number assumption allows one to analyze the electroviscous part by applying the usual procedure of matched asymptotic expansions. Since hydrodynamics is involved in the electroviscous equations, the electoviscous effects are determined in the expansion of both the clearance parameter and the Peclect number.

Following the problem statement, the inner solution of the purely hydrodynamic problem in an expansion of the small clearance is presented in § 3.3. The perturbation of ion concentrations in an expansion of low Peclet number is given in § 3.4. It contains outer and inner regions, and inner region solutions at orders Pe and Pe^2, respectively. The perturbation of potential is determined in § 3.5. The ectroviscous force is obtained in § 3.6. It includes the tangential derivative of the electroviscous ion concentrations and potential, the determination of the stress tensor for the translation of the particle parallel and normal to the wall and applying them to obtain the drag and lift components of the force. Finally, results and conclusions are given in § 3.7

3.2 - Problem Statement

Consider a charged spherical particle translating parallel to a charged stationary plane wall with velocity U, and rotating around its diameter, parallel to the wall and normal to U, with angular velocity Ω, in a symmetric electrolyte at rest, as shown in Fig. 3.1. The radius of the sphere is a, and the gap width between the sphere and wall is denoted by h. The surface of the particle is given by S_p and that of the wall by S_w, the particle surface potential by ζ_P and that of the wall by ζ_W. The purely hydrodynamic problem is denoted by the flow field $(\vec{u}, p)$, the electroviscous ion concentration (of either of co-and counter-ions) by c_2 and the electroviscous potential by ψ_2.

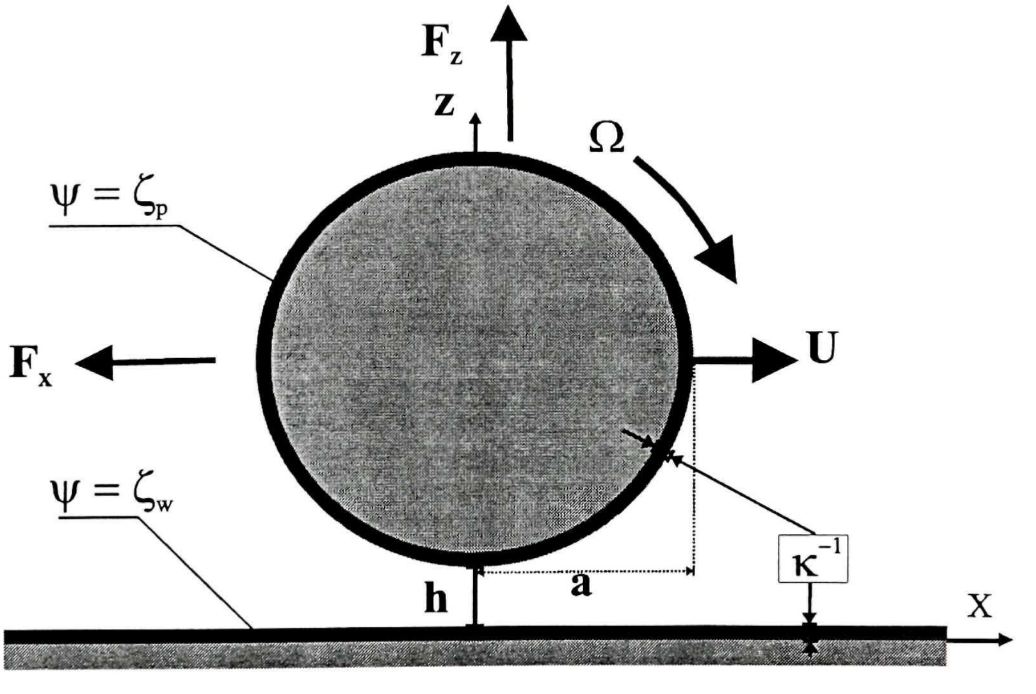


Fig. 3.1- A charged sphere under translation and rotation near a charged plane wall.

The (x, y, z) coordinates with unit base vectors $\left(\vec{i}_x, \vec{i}_y, \vec{i}_z\right)$ constitute a right-handed rectangular Cartesian coordinate system having their origin on the wall, defined by z = 0. The z-axis passes through the sphere center, O, whose coordinates are (x = 0, y = 0, z = a + h). The particle surface and that of the wall may be written in this coordinate system as

$$z - a - h = \pm \sqrt{a^2 - \left(x^2 + y^2\right)} \qquad \text{on } S_p, \qquad z = 0 \qquad \text{on } S_W \tag{3.2.1}$$

The + sign corresponds to the upper part of the sphere and the - one to the lower part. Associated with this coordinate system is a cylindrical coordinate system (ρ, θ, z), described in Appendix A.

In order to make quantities dimensionless, shown with a tilde, the length scale is taken to be identical to the radius of sphere and the characteristic velocity is taken to be the particle translation velocity. Thus, quantities are made dimensionless according to the relation (1.3.2) in which L = a and V = U. From this it follows that

$$\tilde{U} = 1, \tilde{\Omega} = \frac{a\Omega}{U}, \delta = \frac{h}{a}, \mathrm{Pe} = \frac{aU}{D_1}, \lambda = \frac{2c_\infty akT}{\eta U}, \vec{F} = \eta aU\tilde{\vec{F}}, \epsilon = \left[\frac{\varepsilon_r \varepsilon_0 kT}{2\left(az_1e\right)^2 c_\infty}\right]^{1/2} \tag{3.2.2}$$

where δ is the dimensionless gap width between particle and wall.

The surfaces of the particle and wall, given by (3.2.1), may be expressed in the dimensionless coordinate system as

$$\tilde{z} - 1 - \delta = \pm\sqrt{1 - \left(\tilde{x}^2 + \tilde{y}^2\right)} \qquad \text{on } S_p, \qquad \tilde{z} = 0 \qquad \text{on } S_W \tag{3.2.3}$$

and the unit vector outward to them, $\vec{n}_J$ (J = P, W), as [c.f., (A.13)]

$$\vec{n}_P = \tilde{x}\vec{i}_x + \tilde{y}\vec{i}_y + (\tilde{z} - 1 - \delta)\vec{i}_z \qquad \text{on } S_P, \qquad \vec{n}_W = \vec{i}_z \qquad \text{on } S_W \tag{3.2.4}$$

It is assumed that the Reynolds number based on the velocity U, the sphere radius, a, and the fluid viscosity, ν, defined by (2.3.1), is much smaller than unity. Therefore, the governing equation of motion around the particle may be considered the Stokes equations which may be written in dimensionless form as

$$\tilde{\nabla}^2\tilde{\vec{u}} - \tilde{\nabla}\tilde{p} = 0 \tag{3.2.5}$$

$$\tilde{\nabla} \cdot \tilde{\vec{u}} = 0 \tag{3.2.6}$$

By translating the coordinate system $(\tilde{x}, \tilde{y}, \tilde{z})$ with velocity $\vec{i}_x$ the problem reduces to a steady state one in which the particle just rotates, with angular velocity $\tilde{\Omega}$,and the undisturbed fluid and wall translate with velocity $-\vec{i}_x$. Doing so, the corresponding boundary conditions on the sphere may be written as

$$\vec{\tilde{u}} = \tilde{u}_x \vec{i}_x + \tilde{u}_y \vec{i}_y + \tilde{u}_z \vec{i}_z = \vec{\tilde{\Omega}} \times \vec{\tilde{r}} = \begin{vmatrix} \vec{i}_x & \vec{i}_y & \vec{i}_z \\ \tilde{\Omega}_x & \tilde{\Omega}_y & \tilde{\Omega}_z \\ \tilde{x} & \tilde{y} & (\tilde{z}-1-\delta) \end{vmatrix} = \quad \text{on } S_p \tag{3.2.7}$$

$$\left[(\tilde{z}-1-\delta)\tilde{\Omega}_y - \tilde{y}\tilde{\Omega}_z\right]\vec{i}_x - \left[(\tilde{z}-1-\delta)\tilde{\Omega}_x - \tilde{x}\tilde{\Omega}_z\right]\vec{i}_y + \left[\tilde{y}\tilde{\Omega}_x - \tilde{x}\tilde{\Omega}_y\right]\vec{i}_z$$

Letting

$$\vec{\tilde{\Omega}} = \tilde{\Omega}_x \vec{i}_x + \tilde{\Omega}_y \vec{i}_y + \tilde{\Omega}_z \vec{i}_z = 0\vec{i}_x + \tilde{\Omega}\vec{i}_y + 0\vec{i}_z \tag{3.2.8}$$

it may be expressed as

$$\tilde{u}_x = (\tilde{z}-1-\delta)\tilde{\Omega}, \qquad \tilde{u}_y = 0, \qquad \tilde{u}_z = -\tilde{x}\tilde{\Omega} \qquad \text{on } S_P \tag{3.2.9}$$

and those on the wall $(\tilde{z} = 0)$ and at far distances $\left(\text{as } |\vec{\tilde{r}}| \to \infty\right)$ may be expressed as

$$\tilde{u}_x = -1, \qquad \tilde{u}_y = 0, \qquad \tilde{u}_z = 0 \qquad \text{on } S_W \tag{3.2.10}$$

$$\tilde{u}_x = -1, \qquad \tilde{u}_y = 0, \qquad \tilde{u}_z = 0 \qquad \text{as } |\vec{\tilde{r}}| \to \infty \tag{3.2.11}$$

A search for a solution of the problem for the case when the particle is very close to the wall but the double layer thickness is much smaller than the gap width, that is

$$\epsilon = \frac{1}{\kappa a} << \delta = \frac{h}{a} << 1 \tag{3.2.12}$$

along with the condition of low Peclet number, $Pe << 1$, is considered in this chapter.

3.3 - Hydrodynamics

3.3.1 - Flow in Inner Region

As for the problem of cylinder-wall interactions, since the clearance between the sphere and wall is very small, it is justified to apply the lubrication theory to analyze the flow field within the gap (the inner region). Therefore, we may define the inner variables denoted by a hat (^) as

$$\widetilde{x} = \delta^{1/2}\hat{x}, \quad \widetilde{y} = \delta^{1/2}\hat{y}, \left(\widetilde{\rho} = \delta^{1/2}\hat{\rho}\right), \qquad \widetilde{z} = \delta\,\hat{z}$$
$$\widetilde{u}_x = \hat{u}_x, \widetilde{u}_y = \hat{u}_y, \left(\widetilde{u}_\rho = \hat{u}_\rho, \widetilde{u}_\theta = \hat{u}_\theta\right), \qquad \widetilde{u}_z = \delta^{1/2}\,\hat{u}_z, \qquad \widetilde{p} = \delta^{-3/2}\hat{p} \tag{3.3.1}$$

Thus, the creeping flow equations for the outer region written in the Cartesian coordinate system are

$$\frac{\partial^2 \widetilde{u}_x}{\partial \widetilde{x}^2} + \frac{\partial^2 \widetilde{u}_x}{\partial \widetilde{y}^2} + \frac{\partial^2 \widetilde{u}_x}{\partial \widetilde{z}^2} = \frac{\partial \widetilde{p}}{\partial \widetilde{x}}, \tag{3.3.2a}$$

$$\frac{\partial^2 \widetilde{u}_y}{\partial \widetilde{x}^2} + \frac{\partial^2 \widetilde{u}_y}{\partial \widetilde{y}^2} + \frac{\partial^2 \widetilde{u}_y}{\partial \widetilde{z}^2} = \frac{\partial \widetilde{p}}{\partial \widetilde{y}}, \tag{3.3.2b}$$

$$\frac{\partial^2 \widetilde{u}_z}{\partial \widetilde{x}^2} + \frac{\partial^2 \widetilde{u}_z}{\partial \widetilde{y}^2} + \frac{\partial^2 \widetilde{u}_z}{\partial \widetilde{z}^2} = \frac{\partial \widetilde{p}}{\partial \widetilde{z}}, \tag{3.3.2c}$$

$$\frac{\partial \widetilde{u}_x}{\partial \widetilde{x}} + \frac{\partial \widetilde{u}_y}{\partial \widetilde{y}} + \frac{\partial \widetilde{u}_z}{\partial \widetilde{z}} = 0, \tag{3.3.3}$$

And for the inner region they are

$$\frac{\partial^2 \hat{u}_x}{\partial \hat{z}^2} + \delta\left(\frac{\partial^2 \hat{u}_x}{\partial \hat{x}^2} + \frac{\partial^2 \hat{u}_x}{\partial \hat{y}^2}\right) = \frac{\partial \hat{p}}{\partial \hat{x}} \tag{3.3.4}$$

$$\frac{\partial^2 \hat{u}_y}{\partial \hat{z}^2} + \delta\left(\frac{\partial^2 \hat{u}_y}{\partial \hat{x}^2} + \frac{\partial^2 \hat{u}_y}{\partial \hat{y}^2}\right) = \frac{\partial \hat{p}}{\partial \hat{y}} \tag{3.3.5}$$

$$\delta\frac{\partial^2 \hat{u}_z}{\partial \hat{z}^2} + \delta^2\left(\frac{\partial^2 \hat{u}_z}{\partial \hat{x}^2} + \frac{\partial^2 \hat{u}_z}{\partial \hat{y}^2}\right) = \frac{\partial \hat{p}}{\partial \hat{z}} \tag{3.3.6}$$

$$\frac{\partial \hat{u}_x}{\partial \hat{x}} + \frac{\partial \hat{u}_y}{\partial \hat{y}} + \frac{\partial \hat{u}_z}{\partial \hat{z}} = 0 \tag{3.3.7}$$

The corresponding boundary conditions, given by (3.2.9, 10), for the inner region are

$$\hat{u}_x = -\left[1 + \delta(1 - z)\right]\widetilde{\Omega}, \qquad \hat{u}_y = 0, \qquad \hat{u}_z = -\hat{x}\widetilde{\Omega} \qquad \text{on } \hat{z} = \hat{H} \tag{3.3.8}$$

$$\hat{u}_x = -1, \qquad \hat{u}_y = 0, \qquad \hat{u}_z = 0 \qquad \text{on } \hat{z} = 0 \tag{3.3.9}$$

where we have written [cf., Eq. (3.2.1)]

$$\hat{z}\Big|_{S_p} = 1 + \frac{1}{2}\left(\hat{x}^2 + \hat{y}^2\right) + O(\delta)\Big|_{S_p} = \hat{H} + O(\delta) \tag{3.3.10a}$$

in which $\hat{H}$ defined by

$$\hat{H} = 1 + \frac{1}{2}\left(\hat{x}^2 + \hat{y}^2\right) = 1 + \frac{1}{2}\hat{\rho}^2 \tag{3.3.10b}$$

is the surface of the particle for the inner region. The flow field in the outer region (outside of the gap) is bounded (i.e. it is of order unity) as $\delta \to 0$, so that the inner flow field has to match onto the outer flow at order δ^0 as $(\hat{x}, \hat{y}) \to \infty$. This means that the matching condition is required to satisfy [c.f., (3.3.1)]

$$\hat{u}_x = O(1), \quad \hat{u}_y = O(1) \quad \hat{u}_z = O(\hat{\rho}), \quad \hat{p} = O\left[\hat{\rho}^{-3}\right] \quad \text{as}(\hat{\rho}) \to \infty \tag{3.3.11}$$

Expanding the flow field in δ as

$$\begin{aligned} \hat{u}_x &= \hat{u}_{x0} + \delta\, \hat{u}_{x1} + \cdots, & \hat{u}_y &= \hat{u}_{y0} + \delta\, \hat{u}_{y1} + \cdots \\ \hat{u}_z &= \hat{u}_{z0} + \delta\, \hat{u}_{z1} + \cdots, & \hat{p} &= \hat{p}_0 + \delta\, \hat{p}_1 + \cdots \end{aligned} \tag{3.3.12}$$

the equations of motion at the lowest order satisfy

$$\frac{\partial^2 \hat{u}_{x0}}{\partial \hat{z}^2} = \frac{\partial \hat{p}_0}{\partial \hat{x}} \tag{3.3.13}$$

$$\frac{\partial^2 \hat{u}_{y0}}{\partial \hat{z}^2} = \frac{\partial \hat{p}_0}{\partial \hat{y}} \tag{3.3.14}$$

$$\frac{\partial \hat{p}_0}{\partial \hat{z}} = 0 \tag{3.3.15}$$

$$\frac{\partial \hat{u}_{x0}}{\partial \hat{x}} + \frac{\partial \hat{u}_{y0}}{\partial \hat{y}} + \frac{\partial \hat{u}_{z0}}{\partial \hat{z}} = 0 \tag{3.3.16}$$

with boundary conditions

$$\hat{u}_{x0} = -\tilde{\Omega}, \qquad \hat{u}_{y0} = 0, \qquad \hat{u}_{z0} = -\hat{x}\tilde{\Omega} \qquad \text{on } \hat{z} = \hat{H} \tag{3.3.17}$$

$$\hat{u}_{x0} = -1, \qquad \hat{u}_{y0} = 0, \qquad \hat{u}_{z0} = 0 \qquad \text{on } \hat{z} = 0 \tag{3.3.18}$$

and with matching condition

$$\hat{u}_{x0} = O(1), \hat{u}_{y0} = O(1), \hat{u}_{z0} = O(\hat{x}, \hat{y}), \hat{p}_0 = O\left[(\hat{x}, \hat{y})^{-3}\right] \text{as}(\hat{x}, \hat{y}) \to \infty \tag{3.3.19}$$

Eq. (3.3.15) indicates that $\hat{p}_0$ is independent of $\hat{z}$, so that Eq. (3.3.13) may easily be integrated twice with respect to $\hat{z}$ to give

$$\hat{u}_{x0} = \frac{1}{2}\left(\frac{\partial \hat{p}_0}{\partial \hat{x}}\right)\hat{z}^2 + A\hat{z} + B$$

Imposing B.C.s (3.3.17a, 18a) gives the value of A and B:

$$B = -1, \qquad A = -\frac{1}{2}\left(\frac{\partial \hat{p}_0}{\partial \hat{x}}\right)\hat{H} + \left(1-\tilde{\Omega}\right)\hat{H}^{-1}$$

From this $\hat{u}_{xo}$ is obtained as

$$\hat{u}_{x0} = \frac{1}{2}\left(\frac{\partial \hat{p}_0}{\partial \hat{x}}\right)\left(\hat{z}^2 - \hat{H}\,\hat{z}\right) + \left(1-\tilde{\Omega}\right)\hat{H}^{-1}\hat{z} - 1 \qquad (3.3.20)$$

Similarly, $\hat{u}_{yo}$ is obtained from Eq. (3.3.14) as

$$\hat{u}_{y0} = \frac{1}{2}\left(\frac{\partial \hat{p}_0}{\partial \hat{y}}\right)\left(\hat{z}^2 - \hat{H}\,\hat{z}\right) \qquad (3.3.21)$$

Differentiating Eq. (3.3.20) with respect to $\hat{x}$, Eq.(3.3.21) with respect to $\hat{y}$ and introducing them to the continuity equation (3.3.16) yields a differential equation for $\hat{u}_{zo}$:

$$\frac{\partial \hat{u}_{z0}}{\partial \hat{z}} = -\frac{1}{2}\left(\frac{\partial^2 \hat{p}_0}{\partial \hat{x}^2} + \frac{\partial^2 \hat{p}_0}{\partial \hat{y}^2}\right)\left(\hat{z}^2 - \hat{H}\hat{z}\right) + \frac{1}{2}\left(\frac{\partial \hat{p}_0}{\partial \hat{x}}\hat{x} + \frac{\partial \hat{p}_0}{\partial \hat{y}}\hat{y}\right)\hat{z} + \left(1-\tilde{\Omega}\right)\hat{x}\hat{H}^{-2}\hat{z} \qquad (3.3.22)$$

from which and upon imposing B.C. (3.3.18c), $\hat{u}_{zo}$ is obtained as

$$\hat{u}_{z0} = -\frac{1}{2}\left(\frac{\partial^2 \hat{p}_0}{\partial \hat{x}^2} + \frac{\partial^2 \hat{p}_0}{\partial \hat{y}^2}\right)\left(\frac{1}{3}\hat{z}^3 - \frac{1}{2}\hat{H}\hat{z}^2\right) + \frac{1}{4}\left(\frac{\partial \hat{p}_0}{\partial \hat{x}}\hat{x} + \frac{\partial \hat{p}_0}{\partial \hat{y}}\hat{y}\right)\hat{z}^2 + \frac{1}{2}\left(1-\tilde{\Omega}\right)\hat{x}\hat{H}^{-2}\hat{z}^2$$

(3.3.23)

Imposing B.C. (3.3.17c) leads to a differential equation for the pressure $\hat{p}_0$:

$$\frac{1}{6}\left(\frac{\partial^2 \hat{p}_0}{\partial \hat{x}^2} + \frac{\partial^2 \hat{p}_0}{\partial \hat{y}^2}\right)\hat{H}^3 + \frac{1}{2}\left(\frac{\partial \hat{p}_0}{\partial \hat{x}}\hat{x} + \frac{\partial \hat{p}_0}{\partial \hat{y}}\hat{y}\right)\hat{H}^2 + \left(1+\tilde{\Omega}\right)\hat{x} = 0$$

or

$$\frac{\partial}{\partial \hat{x}}\left(\hat{H}^3\frac{\partial \hat{p}_0}{\partial \hat{x}}\right) + \frac{\partial}{\partial \hat{y}}\left(\hat{H}^3\frac{\partial \hat{p}_0}{\partial \hat{y}}\right) + 6\left(1+\tilde{\Omega}\right)\hat{x} = 0 \qquad (3.3.24)$$

which is similar to the Reynold's equation in the lubrication theory. The matching condition (3.3.19d) suggests to seek for a solution of the form

$$\hat{p}_0 = \alpha\;\hat{x}\hat{H}^{-2} + \beta\;\hat{y}\hat{H}^{-2} \qquad (3.3.25)$$

But, since the flow field is symmetric with respect to the $(\hat{x}, \hat{y})$-plane, the pressure cannot be an odd function of $\hat{y}$, so that the second term on the right hand side is rejected. Differentiating (3.3.25) with respect to $\hat{x}$ and $\hat{y}$ results in [c.f., (3.3.10b)]

$$\frac{\partial \hat{p}_0}{\partial \hat{x}} = \alpha\left(\hat{H}^{-2} - 2\hat{x}^2\hat{H}^{-3}\right) \tag{3.3.26}$$

$$\frac{\partial \hat{p}_0}{\partial \hat{y}} = -2\alpha\ \hat{x}\hat{y}\hat{H}^{-3} \tag{3.3.27}$$

Substituting these in Eq. (3.3.24) leads to the following expression:

$$-3\alpha\ \hat{x} - 2\alpha\ \hat{x} + 6\left(1+\tilde{\Omega}\right)\hat{x} = 0$$

from which it follows that

$$\alpha = \frac{6}{5}\left(1+\tilde{\Omega}\right), \qquad \beta = 0$$

Thus, the particular solution of the pressure and its derivatives are determined by

$$\hat{p}_0 = \frac{6}{5}\left(1+\tilde{\Omega}\right)\hat{x}\hat{H}^{-2} \tag{3.3.28}$$

$$\frac{\partial \hat{p}_0}{\partial \hat{x}} = \frac{6}{5}\left(1+\tilde{\Omega}\right)\left(\hat{H}^{-2} - 2\hat{x}^2\hat{H}^{-3}\right), \qquad \frac{\partial \hat{p}_0}{\partial \hat{y}} = -\frac{12}{5}\left(1+\tilde{\Omega}\right)\hat{x}\hat{y}\hat{H}^{-3} \tag{3.3.29}$$

As for the general solution, it is more convenient to transform Eq. (3.3.24) in a polar cylindrical coordinate system by the aid of relationship (A.2) in Appendix A. Doing so, results in

$$\rho^2\frac{\partial^2 \hat{p}_0}{\partial \rho^2} + \frac{\partial^2 \hat{p}_0}{\partial \theta^2} + \left(\frac{3\rho^3}{\hat{H}} + \rho\right)\frac{\partial \hat{p}_0}{\partial \rho} = 0 \tag{3.3.30}$$

Since [c.f., relation (3.10b)]

$$\hat{H} = 1 + \frac{1}{2}\hat{\rho}^2 \rightarrow \frac{1}{2}\hat{\rho}^2 \qquad \text{as } \hat{\rho} \rightarrow \infty \tag{3.3.31a}$$

for large values of $\hat{\rho}$, Eq. (3.30) reduces to

$$\rho^2\frac{\partial^2 \hat{p}_0}{\partial \rho^2} + \frac{\partial^2 \hat{p}_0}{\partial \theta^2} + 7\rho\frac{\partial \hat{p}_0}{\partial \rho} = 0 \qquad \text{as} \qquad \rho \rightarrow \infty \tag{3.3.31b}$$

Eq. (3.3.31b) may be solved by the usual manner of the separation of variables. Thus, letting

$\hat{\rho}_0 = P.\Theta$ (where P is a function of only $\hat{\rho}$ and Θ is a function of just θ), putting its derivatives with respect to $\hat{\rho}$ and θ in Eq. (3.3.31b), and dividing it by P.Θ leads to the following equation:

$$\frac{\hat{\rho}^2}{P}\frac{\partial^2 P}{\partial\hat{\rho}^2} + \frac{7\hat{\rho}}{P}\frac{\partial P}{\partial\hat{\rho}} = -\frac{\partial^2\Theta}{\partial\theta^2} \tag{3.3.32}$$

Since the left hand side is just a function of $\hat{\rho}$ and the right hand side is a function of θ the only choice for them is that they would be equal to a constant, λ say. Therefore, we have to solve

$$\frac{d^2\Theta}{d\theta^2} = -\lambda \tag{3.3.33a}$$

$$\frac{\hat{\rho}^2}{P}\frac{d^2 P}{d\hat{\rho}^2} + \frac{7\hat{\rho}}{P}\frac{dP}{d\hat{\rho}} = \lambda \tag{3.3.33b}$$

But the physics of the problem implies that λ is positive, equal to k^2 say, that is the pressure is periodic in θ. Therefore, the solution of Eq. (3.3.33a) is

$$\Theta = C_1 \sin(k\theta) + C_2 \cos(k\theta) \tag{3.3.34}$$

Since the period of the pressure is equal to 2π (i.e. any point of the domain, upon rotation by an angle 2π, around the z-axis, reaches to the same point of the liquid to experience the same pressure), the only choice for k is to be equal to unity. Therefore, Eq (3.3.33b) may be written as

$$\hat{\rho}^2\frac{d^2 P}{d\hat{\rho}^2} + 7\hat{\rho}\frac{dP}{d\hat{\rho}} - P = 0 \tag{3.3.35}$$

which has a solution in the form of $\hat{\rho}^n$. Thus, substituting its first and second derivatives in the equation results in

$$\hat{\rho}^2 n(n-1)\hat{\rho}^{n-2} + 7n\hat{\rho}\,\hat{\rho}^{n-1} - \hat{\rho}^n = 0$$

Equating the coefficient of $\hat{\rho}^n$ to zero leads to

$$n = -3 \pm \sqrt{10}$$

which does not satisfy the matching condition (3.3.11c) and hence the general solution is rejected. Therefore, from the derivatives of the particular solution of the pressure, the flow field at the lowest order, given by Eq.s (3.3.20-23), is completely determined with the result

$$\hat{u}_{x0} = \frac{3}{5}\left(1+\tilde{\Omega}\right)\left(\hat{H}^{-2} - 2\hat{x}^2\hat{H}^{-3}\right)\left(\hat{z}^2 - \hat{H}\,\hat{z}\right) + \left(1-\tilde{\Omega}\right)\hat{H}^{-1}\hat{z} - 1 \qquad (3.3.36)$$

$$\hat{u}_{y0} = -\frac{6}{5}\left(1+\tilde{\Omega}\right)\hat{x}\hat{y}\hat{H}^{-3}\left(\hat{z}^2 - \hat{H}\,\hat{z}\right) \qquad (3.4.37)$$

$$\hat{u}_{z0} = \frac{x}{5}\left(1+\tilde{\Omega}\right)\left[\left(-4\hat{H}^{-3} + 12\hat{H}^{-4}\right)\hat{z}^3 + \left(\frac{3}{2}\hat{H}^{-2} - 12\hat{H}^{-3}\right)\hat{z}^2\right] + \frac{1}{2}\left(1-\tilde{\Omega}\right)\hat{x}\hat{H}^{-2}\hat{z}^2$$

(3.3.38)

Let us compare this result with those reported in the literature. Goldman, Cox & Brenner (1967) solved this problem asymptotically. Their result agrees with the asymptotic result of the solution presented here for large values of $\hat{x}$.

O'Neill & Stewartson (1967) considered the translation of the particle parallel to a wall. Using a cylindrical coordinate system, they obtained the exact solution of the problem which may be written as

$$\hat{p}_0 = \frac{6}{5}\hat{\rho}\cos\theta\hat{H}^{-2} \qquad (3.3.39)$$

$$\hat{u}_{\rho 0} = \frac{\cos\theta}{5}\left[\left(-9\hat{H}^{-2} + 12\hat{H}^{-3}\right)\hat{z}^2 + \left(14\hat{H}^{-1} - 12\hat{H}^{-2}\right)\hat{z}\right] \qquad (3.3.40)$$

$$\hat{u}_{\theta 0} = -\frac{\sin\theta}{5}\left(3\hat{H}^{-2}\hat{z}^2 + 2\hat{H}^{-1}\hat{z}\right) \qquad (3.3.41)$$

$$\hat{u}_{z0} = \frac{\hat{\rho}\cos\theta}{5}\left[4\left(-\hat{H}^{-3} + 3\hat{H}^{-4}\right)\hat{z}^3 + \left(4\hat{H}^{-2} - 12\hat{H}^{-3}\right)\hat{z}^2\right] \qquad (3.3.42)$$

Cooley & O'Neill (1968) considered the rotation of the particle near a plane wall with angular velocity $\vec{\tilde{\Omega}} = \left(0, \Omega, 0\right)$. Using the same procedure as O'Neill & Stewartson (1967)'s, they obtained a solution:

$$\hat{p}_0 = \frac{6}{5}\hat{\rho}\cos\theta\hat{H}^{-2} \qquad (3.3.43)$$

$$\hat{u}_{\rho 0} = \frac{\cos\theta}{5}\left[\left(-9\hat{H}^{-2} + 12\hat{H}^{-3}\right)\hat{z}^2 + \left(4\hat{H}^{-1} - 12\hat{H}^{-2}\right)\hat{z}\right] \qquad (3.3.44)$$

$$\hat{u}_{\theta 0} = \frac{\sin\theta}{5}\left(-3\hat{H}^{-2}z^2 + 8\hat{H}^{-1}z\right) \tag{3.3.45}$$

$$\hat{u}_{z0} = \frac{\hat{\rho}\cos\theta}{5}\left[\left(-4\hat{H}^{-3} + 12\hat{H}^{-4}\right)\hat{z}^3 - \left(\hat{H}^{-2} + 12\hat{H}^{-3}\right)\hat{z}^2\right] \tag{3.3.46}$$

Applying relationships (3.3.10b, A.1, 11) the flow field determined by (3.3.28, 36-38), may be expressed in a cylindrical coordinate system as

$$\hat{p}_0 = \frac{6}{5}\left(1+\widetilde{\Omega}\right)\hat{\rho}\cos\theta\hat{H}^{-2} \tag{3.3.47}$$

$$\begin{aligned}\hat{u}_{\rho 0} = \frac{\cos\theta}{5}\Big\{&\left[\left(-9\hat{H}^{-2} + 12\hat{H}^{-3}\right)\hat{z}^2 + \left(14\hat{H}^{-1} - 12\hat{H}^{-2}\right)\hat{z} - 5\right] \\ &+\widetilde{\Omega}\left[\left(-9\hat{H}^{-2} + 12\hat{H}^{-3}\right)\hat{z}^2 + \left(4\hat{H}^{-1} - 12\hat{H}^{-2}\right)\hat{z}\right]\Big\}\end{aligned} \tag{3.3.48}$$

$$\hat{u}_{\theta 0} = -\frac{\sin\theta}{5}\left[\left(3\hat{H}^{-2}\hat{z}^2 + 2\hat{H}^{-1}\hat{z} - 5\right) + \widetilde{\Omega}\left(+3\hat{H}^{-2}\hat{z}^2 - 8\hat{H}^{-1}\hat{z}\right)\right] \tag{3.3.49}$$

$$\begin{aligned}\hat{u}_{z0} = \frac{\hat{\rho}\cos\theta}{5}\Big\{&\left[4\left(-\hat{H}^{-3} + 3\hat{H}^{-4}\right)\hat{z}^3 + \left(4\hat{H}^{-2} - 12\hat{H}^{-3}\right)\hat{z}^2\right] \\ &+\widetilde{\Omega}\left[\left(-4\hat{H}^{-3} + 3\hat{H}^{-4}\right)\hat{z}^3 + 2\left(\hat{H}^{-2} + 12\hat{H}^{-3}\right)\hat{z}^2\right]\Big\}\end{aligned} \tag{3.3.50}$$

Thus, for the rotation of the particle with angular velocity $\widetilde{\Omega} = 1$ we recover Cooley & O'Neill (1968)'s results and for its translation with unit velocity $\left(\widetilde{U} = 1\right)$ we recover O'Neill & Stewartson (1967)'s ones, except for the extra terms + sin θ in $\hat{u}_{\theta 0}$ and - sin θ in $\hat{u}_{\rho 0}$. This appears because we consider a stationary sphere with the wall and the fluid at infinity moves with velocity $-\vec{i}_x$. For the calculation of the hydrodynamic force, these two solutions are equivalent since the variations of the velocity are involved in the stress tensor not the velocity, and hence the constant velocity of the fluid at infinity c.f., Eq. (3.3.36)] does not affect the results.

3.4 - Electroviscous Ion Concentrations

3.4.1 - Outer Region

As for the cylinder and wall, the equation and boundary conditions of the electroviscous ion concentration for the outer region, given by (1.3. 60), imply that, for low

Peclet number, $\widetilde{c}_2$ is of order Pe. Thus, if we expand $\widetilde{c}_2$ in this parameter as[1]

$$\widetilde{c}_2 = \text{Pe}\,\widetilde{c}_{21} + \text{Pe}^2\left(\frac{D_1 + D_2}{2D_2}\right)\widetilde{c}_{22} + \cdots \tag{3.4.1}$$

at the lowest order, $\widetilde{c}_{21}$ for the steady state satisfies

$$\widetilde{\nabla}^2\widetilde{c}_{21} = 0 \qquad \text{or} \qquad \frac{\partial^2\widetilde{c}_{21}}{\partial\widetilde{x}^2} + \frac{\partial^2\widetilde{c}_{21}}{\partial\widetilde{y}^2} + \frac{\partial^2\widetilde{c}_{21}}{\partial\widetilde{z}^2} = 0 \tag{3.4.2}$$

with boundary conditions, upon the use of the definition of the unit vector outward to the solid surfaces, given by (3.2.4),

$$\vec{n}\cdot\nabla c_{21} = \widetilde{x}\frac{\partial\widetilde{c}_{21}}{\partial\widetilde{x}} + \widetilde{y}\frac{\partial\widetilde{c}_{21}}{\partial\widetilde{y}} + (\widetilde{z} - 1 - \delta)\frac{\partial\widetilde{c}_{21}}{\partial\widetilde{z}} = F_{cP}\left(\vec{n}\cdot\widetilde{\nabla}\right)\left(\vec{n}\cdot\widetilde{\nabla}\right)\left(\vec{n}\cdot\vec{\widetilde{u}}\right) \text{ on } S_P \tag{3.4.3}$$

$$\frac{\partial\widetilde{c}_{21}}{\partial\widetilde{z}} = F_{cW}\left(\vec{n}\cdot\widetilde{\nabla}\right)\left(\vec{n}\cdot\widetilde{\nabla}\right)\left(\vec{n}\cdot\vec{\widetilde{u}}\right) \qquad \text{on } S_W \tag{3.4.4}$$

$$\widetilde{c}_{21} \to 0 \qquad \text{as } |\vec{\widetilde{r}}| \to \infty \tag{3.4.5}$$

in which $\left(F_{cP}, F_{cW}\right)$ are defined by the relation (1.3.60e). For order Pe^2 we have

$$\nabla^2\widetilde{c}_{22} = \vec{\widetilde{u}}\cdot\nabla\widetilde{c}_{21} = \left[\widetilde{u}_x\frac{\partial}{\partial\widetilde{x}}\widetilde{u}_x\frac{\partial}{\partial\widetilde{x}} + \widetilde{u}_z\frac{\partial}{\partial\widetilde{z}} + \right]\widetilde{c}_{21} \tag{3.4.7}$$

with boundary conditions

$$\vec{n}\cdot\nabla\widetilde{c}_{22} = \widetilde{x}\frac{\partial\widetilde{c}_{22}}{\partial\widetilde{x}} + \widetilde{y}\frac{\partial\widetilde{c}_{22}}{\partial\widetilde{y}} + (\widetilde{z} - 1 - \delta)\frac{\partial\widetilde{c}_{22}}{\partial\widetilde{z}} = 0 \quad \text{on } S_P \tag{3.4.8}$$

$$\vec{n}\cdot\nabla\widetilde{c}_{22} = \frac{\partial\widetilde{c}_{22}}{\partial\widetilde{z}} = 0 \qquad \text{on } S_W \tag{3.4.9}$$

$$\widetilde{c}_{22} \to 0 \qquad \text{as } |\vec{\widetilde{r}}| \to \infty\ 0 \tag{3.4.10}$$

3.4.2 - Inner Region

In view of (3.2.4), the unit vector outward to the sphere for the inner region is

$$\vec{n} = \delta^{1/2}\left(\hat{x}\vec{i}_x + \hat{y}\vec{i}_y\right) + \left[-1 + \delta(\hat{z} - 1)\right]\vec{i}_z \qquad \text{on } \hat{z} = \hat{H} \tag{3.4.11}$$

---

[1]The last indices of electroviscous variables denote the order of those variable in Pe.

Thus, the normal derivative of the normal derivative of the normal component of the purely hydrodynamic velocity appearing in the boundary condition of the electroviscous ion concentration, $\hat{c}_{21}$, given by (3.4.3), for the inner region, is determined by

$$\vec{n}\cdot\vec{\tilde{u}} = \delta^{1/2}\left(\hat{x}\hat{u}_x + \hat{y}\hat{u}_y\right) + \left[-\delta^{1/2} + \delta^{3/2}(\hat{z}-1)\right]\hat{u}_z$$

$$\left(\vec{n}\cdot\tilde{\nabla}\right)\left(\vec{n}\cdot\tilde{\nabla}\right) = \left\{\left(\hat{x}\frac{\partial}{\partial\hat{x}} + \hat{y}\frac{\partial}{\partial\hat{y}}\right) + (\hat{z}-1) - \delta^{-1}\frac{\partial}{\partial\hat{z}}\right\}$$

$$\left[\left(\hat{x}\frac{\partial}{\partial\hat{x}} + \hat{y}\frac{\partial}{\partial\hat{y}}\right) + \left(\hat{z}-1-\delta^{-1}\right)\frac{\partial}{\partial\hat{z}}\right] = \delta^{-2}\frac{\partial^2}{\partial\hat{z}^2} + \delta^{-1}\left[\hat{x}\frac{\partial}{\partial\hat{x}} + \hat{y}\frac{\partial}{\partial\hat{y}} - (\hat{z}-1)\frac{\partial}{\partial\hat{z}} + 1\right]\frac{\partial}{\partial\hat{z}} + \cdots$$

From this and from the expansion of the velocity, given by (3.3.12), it follows that

$$\left(\vec{n}\cdot\tilde{\nabla}\right)\left(\vec{n}\cdot\tilde{\nabla}\right)\left(\vec{n}\cdot\vec{\tilde{u}}\right) = \delta^{-3/2}\frac{\partial^2}{\partial\hat{z}^2}\left(\hat{x}\hat{u}_{x0} + \hat{y}\hat{u}_{y0} - \hat{u}_{z0}\right) \qquad \text{on } \hat{z} = \hat{H}$$

$$+\delta^{-1/2}\left\{\left[\hat{x}\frac{\partial}{\partial\hat{x}} + \hat{y}\frac{\partial}{\partial\hat{y}} - (\hat{z}-1)\frac{\partial}{\partial\hat{z}} + 1\right]\frac{\partial}{\partial\hat{z}}\left(\hat{x}\hat{u}_{x0} + \hat{y}\hat{u}_{y0} - \hat{u}_{z0}\right) + 2\frac{\partial\hat{u}_{z0}}{\partial\hat{z}} + (\hat{z}-1)\frac{\partial^2\hat{u}_{z0}}{\partial\hat{z}^2}\right\} + \cdots \tag{3.4.12}$$

The unit vector normal to the wall is $\vec{i}_z$, so that the normal derivative of the normal derivative of the normal component of the velocity appears in B.C. (3.4.4), at the lowest order in δ, is

$$\left(\vec{n}\cdot\tilde{\nabla}\right)\left(\vec{n}\cdot\tilde{\nabla}\right)\left(\vec{n}\cdot\vec{\tilde{u}}\right) = \delta^{-3/2}\frac{\partial^2\hat{u}_{z0}}{\partial\hat{z}^2} + O\left(\delta^{-1/2}\right) \qquad \text{on } \hat{z} = 0 \tag{3.4.13}$$

Thus, if we define the electroviscous ion concentration for the inner region as

$$\tilde{c}_2 = \delta^{-3/2}\hat{c}_2 \tag{3.4.14}$$

at order Pe it satisfies [c.f., Eq.s (3.4.2-4)],

$$\frac{\partial^2\hat{c}_{21}}{\partial\hat{z}^2} + \delta\left(\frac{\partial^2\hat{c}_{21}}{\partial\hat{x}^2} + \frac{\partial^2\hat{c}_{21}}{\partial\hat{y}^2}\right) = 0 \tag{3.4.15}$$

with boundary conditions

$$-\frac{\partial\hat{c}_{21}}{\partial\hat{z}} + \delta\left[\hat{x}\frac{\partial\hat{c}_{21}}{\partial\hat{x}} + \hat{y}\frac{\partial\hat{c}_{21}}{\partial\hat{y}} + (\hat{z}-1)\frac{\partial\hat{c}_{21}}{\partial\hat{z}}\right]$$

$$= \delta\, F_{cP}\frac{\partial^2}{\partial\hat{z}^2}\left(\hat{x}\hat{u}_{x0} + \hat{y}\hat{u}_{y0} - \hat{u}_{z0}\right) + O\left(\delta^2\right) \qquad \text{on } \hat{z} = \hat{H}$$

$$\frac{\partial \hat{c}_{21}}{\partial \hat{z}} = \delta\, F_{cw} \frac{\partial^2 \hat{u}_{z0}}{\partial \hat{z}^2} + O(\delta^2) \qquad \text{on } \hat{z} = 0$$

The second derivative of $\hat{u}_{z0}$ with respect to $\hat{z}$, appearing in these boundary conditions, may be determined from Eq. (3.3.22) as

$$\frac{\partial^2 \hat{u}_{z0}}{\partial \hat{z}^2} = -\frac{1}{2}\left(\frac{\partial^2 \hat{p}_0}{\partial \hat{x}^2} + \frac{\partial^2 \hat{p}_0}{\partial \hat{y}^2}\right)(2\hat{z} - \hat{H}) + \frac{1}{2}\left(\frac{\partial \hat{p}_0}{\partial \hat{x}}\hat{x} + \frac{\partial \hat{p}_0}{\partial \hat{y}}\hat{y}\right) + (\tilde{\Omega} + 1)\hat{x}\hat{H}^{-2}$$

from which and from Eq.s (3.3.20, 21), the boundary conditions may be evaluated on the solid surfaces with the result

$$-\frac{\partial \hat{c}_{21}}{\partial \hat{z}} + \delta\left[\hat{x}\frac{\partial \hat{c}_{21}}{\partial \hat{x}} + \hat{y}\frac{\partial \hat{c}_{21}}{\partial \hat{y}} + (\hat{H} - 1)\frac{\partial \hat{c}_{21}}{\partial \hat{z}}\right] \qquad \text{on } \hat{z} = \hat{H}$$
$$= \delta F_{cP}\left\{\frac{1}{2}\left[\frac{\partial}{\partial \hat{x}}\left(\hat{H}\frac{\partial \hat{p}_0}{\partial \hat{x}}\right) + \frac{\partial}{\partial \hat{y}}\left(\hat{H}\frac{\partial \hat{p}_0}{\partial \hat{y}}\right)\right] - (1 - \tilde{\Omega})\hat{x}\hat{H}^{-2}\right\} + O(\delta^2) \qquad (3.4.16)$$

$$\frac{\partial \hat{c}_{21}}{\partial \hat{z}} = \delta F_{cW}\left\{\frac{1}{2}\left[\frac{\partial}{\partial \hat{x}}\left(\hat{H}\frac{\partial \hat{p}_0}{\partial \hat{x}}\right) + \frac{\partial}{\partial \hat{y}}\left(\hat{H}\frac{\partial \hat{p}_0}{\partial \hat{y}}\right)\right] + (1 - \tilde{\Omega})\hat{x}\hat{H}^{-2}\right\} + O(\delta^2) \qquad (3.4.17)$$
$$\text{on } \hat{z} = 0$$

Definitions (3.3.1, 4.1, 14) indicate that the matching condition is required to satisfy

$$\hat{c}_{21} = O\left[(\hat{x}, \hat{y})^{-3}\right] \qquad \text{as} (\hat{x}, \hat{y}) \to \infty \qquad (3.4.18)$$

The equation along with boundary conditions at order Pe^2, given by (3.4.7-9), for the inner region is

$$\frac{\partial^2 \hat{c}_{22}}{\partial \hat{z}^2} + \delta\left(\frac{\partial^2 \hat{c}_{22}}{\partial \hat{x}^2} + \frac{\partial^2 \hat{c}_{22}}{\partial \hat{y}^2}\right) = \delta^{3/2}\left(\hat{u}_{x0}\frac{\partial \hat{c}_{21}}{\partial \hat{x}} + \hat{u}_{y0}\frac{\partial \hat{c}_{21}}{\partial \hat{y}} + \hat{u}_{z0}\frac{\partial \hat{c}_{21}}{\partial \hat{z}}\right) \qquad (3.4.19)$$

with

$$-\frac{\partial \hat{c}_{22}}{\partial \hat{z}} + \delta\left[\hat{x}\frac{\partial \hat{c}_{22}}{\partial \hat{x}} + \hat{y}\frac{\partial \hat{c}_{22}}{\partial \hat{y}} + (\hat{z} - 1)\frac{\partial \hat{c}_{22}}{\partial \hat{z}}\right] = 0 \qquad \text{on } \hat{z} = \hat{H} \qquad (3.4.20)$$

$$\frac{\partial \hat{c}_{22}}{\partial \hat{z}} = 0 \qquad \text{on } \hat{z} = 0 \qquad (3.4.21)$$

It has also to satisfy the matching condition

$$\hat{c}_{22} = O\left[(\hat{x},\hat{y})^{-3}\right] \qquad \text{as } (\hat{x},\hat{y}) \to \infty \qquad (3.4.22)$$

3.4.2.1 - Inner Solution of Order Pe

The equation and boundary conditions at the first order in Pe, given by (3.4.15-17), suggest an expansion for $\hat{c}_{21}$ in δ as

$$\hat{c}_{21} = \hat{c}_m + \delta\,\hat{c}_n + \cdots \qquad (3.4.23)$$

Upon substitution of this expansion in (3.4.15-17), $\hat{c}_m$ satisfies

$$\frac{\partial^2 \hat{c}_m}{\partial \hat{z}^2} = 0 \qquad (3.4.24)$$

with boundary conditions

$$\frac{\partial \hat{c}_m}{\partial \hat{z}} = 0 \qquad \text{on } \hat{z} = \hat{H} \qquad (3.4.25)$$

$$\frac{\partial \hat{c}_m}{\partial \hat{z}} = 0 \qquad \text{on } \hat{z} = 0 \qquad (3.4.26)$$

and with the matching condition

$$\hat{c}_m = O\left[(\hat{x},\hat{y})^{-3}\right] \qquad \text{as } (\hat{x},\hat{y}) \to \infty \qquad (3.4.27)$$

Whilst $\hat{c}_n$ satisfies

$$\frac{\partial^2 \hat{c}_n}{\partial \hat{z}^2} + \left(\frac{\partial^2 \hat{c}_m}{\partial \hat{x}^2} + \frac{\partial^2 \hat{c}_m}{\partial \hat{y}^2}\right) = 0 \qquad (3.4.28)$$

with boundary conditions

$$-\frac{\partial \hat{c}_n}{\partial \hat{z}} + \left[\hat{x}\frac{\partial \hat{c}_m}{\partial \hat{x}} + \hat{y}\frac{\partial \hat{c}_m}{\partial \hat{y}} + (\hat{H}-1)\frac{\partial \hat{c}_m}{\partial \hat{z}}\right] = F_{cP}\left\{\frac{1}{2}\left[\frac{\partial}{\partial \hat{x}}\left(\hat{H}\frac{\partial \hat{p}_0}{\partial \hat{x}}\right) + \frac{\partial}{\partial \hat{y}}\left(\hat{H}\frac{\partial \hat{p}_0}{\partial \hat{y}}\right)\right] + (1-\tilde{\Omega})\hat{x}\hat{H}^{-2}\right\} \qquad \text{on } \hat{z} = \hat{H} \qquad (3.4.29)$$

$$\frac{\partial \hat{c}_n}{\partial \hat{z}} = F_{cW}\left\{\frac{1}{2}\left[\frac{\partial}{\partial \hat{x}}\left(\hat{H}\frac{\partial \hat{p}_0}{\partial \hat{x}}\right) + \frac{\partial}{\partial \hat{y}}\left(\hat{H}\frac{\partial \hat{p}_0}{\partial \hat{y}}\right)\right] + (1-\tilde{\Omega})\hat{x}\hat{H}^{-2}\right\} \qquad \text{on } \hat{z} = 0 \qquad (3.4.30)$$

and with matching condition

$$\hat{c}_n = O\left[\left(\hat{x}, \hat{y}\right)^{-2}\right] \qquad \text{as}\left(\hat{x}, \hat{y}\right) \to \infty \tag{3.4.31}$$

Eq. (3.4.24) together with B.C.s (3.4.25, 26) guaranties that

$$\hat{c}_m = \text{Func}\left(\hat{x}, \hat{y}\right) \tag{3.4.32}$$

Thus, Eq. (3.4.28) may easily be integrated with respect to $\hat{z}$ to give

$$\frac{\partial \hat{c}_n}{\partial \hat{z}} = -\left(\frac{\partial^2 \hat{c}_m}{\partial \hat{x}^2} + \frac{\partial^2 \hat{c}_m}{\partial \hat{y}^2}\right)\hat{z} + A\left(\hat{x}, \hat{y}\right) \tag{3.4.33}$$

Imposing B.C. (3.4.30) results in

$$A = \frac{F_{cW}}{2}\left[\frac{\partial}{\partial \hat{x}}\left(\hat{H}\frac{\partial \hat{p}_0}{\partial \hat{x}}\right) + \frac{\partial}{\partial \hat{y}}\left(\hat{H}\frac{\partial \hat{p}_0}{\partial \hat{y}}\right)\right] + \left(1 - \widetilde{\Omega}\right)\hat{x}\hat{H}^{-2}$$

Imposing B.C. (3.4.29) leads to a differential equation for $\hat{c}_m$:

$$\frac{\partial}{\partial \hat{x}}\left(\hat{H}\frac{\partial \hat{c}_m}{\partial \hat{x}}\right) + \frac{\partial}{\partial \hat{y}}\left(\hat{H}\frac{\partial \hat{c}_m}{\partial \hat{y}}\right) = \frac{1}{2}\left(F_{cP} + F_{cW}\right)\left[\frac{\partial}{\partial \hat{x}}\left(\hat{H}\frac{\partial \hat{p}_0}{\partial \hat{x}}\right) + \frac{\partial}{\partial \hat{y}}\left(\hat{H}\frac{\partial \hat{p}_0}{\partial \hat{y}}\right)\right] - \left(F_{cP} - F_{cW}\right)\left(1 - \widetilde{\Omega}\right)\hat{x}\hat{H}^{-2} \tag{3.4.34}$$

From now on, to simplify the calculations, we consider the case in which the particle surface potential, and that of the wall are the same, or equivalently $F_{cP} = F_{cW}$. An approximate solution for the general case is determined in an indirect fashion based on the analogy of inner and exact solutions of the problem, as is done in Chapter four § 4.7. Therefore, the solution of Eq. (3.4.34) for $\hat{c}_m$ is straight forward determined from Eq. (3.3.28) or Eq. (3.3.47) to be as

$$\hat{c}_m = \frac{1}{2}\left(F_{cP} + F_{cW}\right)\hat{P}_0 = \frac{3}{5}\left(F_{cP} + F_{cW}\right)\left(1 + \widetilde{\Omega}\right)\hat{\rho}\hat{H}^{-2}\cos\theta \tag{3.4.35}$$

which satisfies the matching condition (3.4.27). That is,

$$\hat{c}_m\Big|_{\text{as}\,\hat{\rho}\to\infty} \to \frac{12}{5}\left(F_{cP} + F_{cW}\right)\left(1 + \widetilde{\Omega}\right)\hat{\rho}^{-3}\cos\theta \tag{3.4.36}$$

Its complementary solution is rejected, since for large value of $\hat{\rho}$ it tends to $\hat{\rho}^{-1\pm\sqrt{2}}$ which does not satisfies the prescribed matching condition. Thus, $\hat{c}_{21}$ at the lowest order in δ, given by (3.4.23), is determined by

$$\hat{c}_{21} = \frac{3}{5}\left(F_{cP} + F_{cW}\right)\left(1+\tilde{\Omega}\right)\hat{\rho}\hat{H}^{-2}\cos\theta + O(\delta) \qquad (3.4.37)$$

3.4.2.2 - Inner Solution of Order Pe^2

Equation (3.4.19) implies an expansion in δ for $\hat{c}_{22}$ as

$$\hat{c}_{22} = \delta^{1/2}\hat{c}_p + \delta^{3/2}\,\hat{c}_q + \cdots \qquad (3.4.38)$$

Upon substitution of this in Eq.(3.4.19) and B.C.s (3.4.20-21) as well as the matching condition (3.4.22), we see that $\hat{c}_p$ satisfies the same equation and boundary conditions as those for $\hat{c}_m$, given by (3.4.24-26), together with the matching condition

$$\hat{c}_p = O\left[\left(\hat{x},\hat{y}\right)^{-2}\right] \qquad \text{as}\left(\hat{x},\hat{y}\right)\to\infty \qquad (3.4.39)$$

whilst $\hat{c}_q$ has to satisfy

$$\frac{\partial^2\hat{c}_q}{\partial\hat{z}^2} + \left(\frac{\partial^2\hat{c}_p}{\partial\hat{x}^2} + \frac{\partial^2\hat{c}_p}{\partial\hat{y}^2}\right) = \vec{\hat{u}}\cdot\hat{\nabla}\hat{c}_m \qquad (3.4.40)$$

in which $\hat{c}_m$ and $\hat{c}_p$ are functions of $(\hat{x}, \hat{y})$ with boundary conditions

$$\left.\frac{\partial\hat{c}_q}{\partial\hat{z}}\right|_{\hat{z}=0} = 0 \qquad (3.4.41)$$

$$\left.\frac{\partial\hat{c}_q}{\partial\hat{z}}\right|_{\hat{z}=\hat{H}} = -\left(\hat{x}\frac{\partial\hat{c}_m}{\partial\hat{x}} + \hat{y}\frac{\partial\hat{c}_m}{\partial\hat{y}}\right) \qquad (3.4.42)$$

and matching condition

$$\hat{c}_q = O\left[\left(\hat{x},\hat{y}\right)^{-1}\right] \qquad \text{as}\left(\hat{x},\hat{y}\right)\to\infty \qquad (3.4.43)$$

Differentiating Eq. (3.4.40) with respect to $\hat{z}$ and then imposing B.C.s (3.4.41, 42) leads to the following differential equation for $\hat{c}_p$:

$$\frac{\partial}{\partial\hat{x}}\left(\hat{H}\frac{\partial\hat{c}_p}{\partial\hat{x}}\right) + \frac{\partial}{\partial\hat{y}}\left(\hat{H}\frac{\partial\hat{c}_p}{\partial\hat{y}}\right) = \hat{\nabla}\hat{c}_m\cdot\int_0^{\hat{H}}\vec{\hat{u}}\,d\hat{z} \qquad (3.4.44)$$

in which $\hat{c}_m$ is given by (3.4.35) and $\vec{\hat{u}}$ by (3.3.48-50). Upon integration of the velocity, it may be expressed in the cylindrical coordinate system by the use of relationships (A.2, 7) as

$$\frac{\partial^2 \hat{c}_p}{\partial \hat{\rho}^2} + \left(\frac{\hat{\rho}}{\hat{H}} + \frac{1}{\hat{\rho}}\right)\frac{\partial \hat{c}_p}{\partial \hat{\rho}} + \frac{1}{\hat{\rho}^2}\frac{\partial^2 \hat{c}_p}{\partial \theta^2} = \frac{3}{25}\left(F_{cP} + F_{cW}\right)\left(1+\widetilde{\Omega}\right)^2 \times$$
$$\left[\left(\frac{7}{2}\hat{\rho}^2\hat{H}^{-3} - 4\hat{\rho}^4\hat{H}^{-4}\right)\cos(2\theta) - 3\hat{H}^{-2} + \frac{7}{2}\hat{\rho}^2\hat{H}^{-3} - 4\hat{\rho}^4\hat{H}^{-4}\right] \tag{3.4.45}$$

Because of the symmetry, as can be observed from the right hand side of Eq. (3.4.45), we should look for a solution in the form of

$$\hat{c}_p = \frac{3}{25}\left(F_{cP} + F_{cW}\right)\left(1+\widetilde{\Omega}\right)^2\left[\hat{c}_{2P}\cos(2\theta) + \hat{c}_{0P}\right] \tag{3.4.46}$$

Substituting its derivatives in Eq. (3.4.45) results in

$$\left[\frac{\partial^2 \hat{c}_{2P}}{\partial \hat{\rho}^2} + \left(\frac{\hat{\rho}}{\hat{H}} + \frac{1}{\hat{\rho}}\right)\frac{\partial \hat{c}_{2P}}{\partial \hat{\rho}} - \frac{4\hat{c}_{2P}}{\hat{\rho}^2}\right]\cos(2\theta) + \left[\frac{\partial^2 \hat{c}_{2P}}{\partial \hat{\rho}^2} + \left(\frac{\hat{\rho}}{\hat{H}} + \frac{1}{\hat{\rho}}\right)\frac{\partial \hat{c}_{2P}}{\partial \hat{\rho}}\right] =$$
$$\left[\left(\frac{7}{2}\hat{\rho}^2\hat{H}^{-3} - 4\hat{\rho}^4\hat{H}^{-4}\right)\cos(2\theta) - 3\hat{H}^{-2} + \frac{7}{2}\hat{\rho}^2\hat{H}^{-3} - 4\hat{\rho}^4\hat{H}^{-4}\right]$$

Since this equation must hold for any value of θ, it must be independent of θ. Thus, upon equating the coefficients of $(\cos 2\theta)^n$ $(n = 0, 1)$ to zero, it reduces to two ordinary differential equations to be solved

$$\frac{d^2 \hat{c}_{2P}}{d\hat{\rho}^2} + \left(\frac{\hat{\rho}}{\hat{H}} + \frac{1}{\rho}\right)\frac{d\hat{c}_{2P}}{d\hat{\rho}} - \frac{4\hat{c}_{2P}}{\hat{\rho}^2} = \frac{7}{2}\hat{\rho}^2\hat{H}^{-3} - 4\hat{\rho}^2\hat{H}^{-4} \tag{3.4.47}$$

$$\frac{d^2 \hat{c}_{0P}}{d\hat{\rho}^2} + \left(\frac{\hat{\rho}}{\hat{H}} + \frac{1}{\rho}\right)\frac{d\hat{c}_{0P}}{d\hat{\rho}} = -3\hat{H}^{-2} + \frac{7}{2}\hat{\rho}^2\hat{H}^{-3} - 4\hat{\rho}^2\hat{H}^{-4} \tag{3.4.48}$$

In the calculation of the electroviscous forces the solution of Eq. (3.4.47), as seen in § 3.6, is not required. The solution of Eq.(3.4.48) would be as a sum of particular solution denoted by $\hat{c}_{0P}$Par and general one denoted by $\hat{c}_{0P}$Gen. Its particular solution has been found to be

$$\hat{c}_{0P}\text{Par} = \frac{1}{2}\left(\hat{H}^{-1} + \hat{H}^{-2}\right) \tag{3.4.49}$$

which satisfies the matching condition (3.4.39), that is

$$\hat{c}_{0P}\text{Par}\Big|_{\text{as}\,\hat{\rho}\to\infty} \to \hat{\rho}^{-2} + 2\hat{\rho}^{-4} \tag{3.4.50}$$

The general solution is

$$\hat{c}_{0P}\text{Gen} = C_1 \ln\left(\frac{\hat{\rho}}{\sqrt{\hat{H}}}\right) + C_2 \tag{3.4.51}$$

Neither $\ln\left(\hat{\rho}/\sqrt{\hat{H}}\right)$ nor the constant C_2 satisfy the matching condition, since for large values of $\hat{\rho}$ both of them are of order δ^0. Thus, $\hat{c}_{0P}$ is determined to be equal to its particular solution from which $\hat{c}_{22}$, given by (3.4.38), is obtained as

$$\hat{c}_{22} = \delta^{\frac{1}{2}} \frac{3}{25}\left(F_{cP} + F_{cW}\right)\left(1+\widetilde{\Omega}\right)^2\left[\hat{c}_{2P}\cos(2\theta) + \frac{1}{2}\left(\hat{H}^{-1} + \hat{H}^{-2}\right)\right] + O\left(\delta^{\frac{3}{2}}\right) \tag{3.4.52}$$

and $\hat{c}_{21}$ is given by (3.4.37). Thus, the electroviscous ion concentration in the expansion (3.4.1) for the inner region, by the aid of (3.4.14, 46), at the lowest order in δ, is determined by

$$\begin{aligned}\widetilde{c}_2 = \frac{3}{25}\left(F_{cP} + F_{cW}\right)&\Big\{\delta^{-\frac{3}{2}}\text{Pe}\left(1+\widetilde{\Omega}\right)\left[\hat{\rho}\hat{H}^{-2}\cos(\theta) + O(\delta)\right] \\ &+\delta^{-1}\text{Pe}^2\frac{D_2 + D_1}{2D_2}\left(1+\widetilde{\Omega}\right)^2\left\{\left[\hat{c}_{2P}\cos(2\theta) + \frac{1}{2}\left(\hat{H}^{-1} + \hat{H}^{-2}\right)\right] + O(\delta)\right\}\Big\} + \cdots\end{aligned} \tag{3.4.53a}$$

in which $\left(F_{cP}, F_{cP}\right)$ are defined by the relation (1.3.60f) as

$$F_{cJ} = \frac{1}{2D_2}\left[\left(D_2 - D_1\right)\widetilde{\psi}_J - 4\left(D_2 + D_1\right)\ln\left(\cosh\frac{\widetilde{\psi}_J}{4}\right)\right] \qquad J = (P, W) \tag{3.4.53b}$$

3.5 - Electroviscous Potential

The equation and boundary conditions for the electroviscous potential denoted here by $\widetilde{\psi}_2$ are given by relationships (1.3.61). The electroviscous ion concentration appearing in this equation is already determined. The second term in this equation, ϕ, satisfies the same equation and boundary conditions as those for the electroviscous ion concentration of order Pe given by (3.4.2-5) in which (F_{cp}, F_{cw}) are, respectively, replaced by ($F_{\phi p}$, $F_{\phi w}$), defined by (1.3.61f), as

$$F_{\phi J} = \frac{2D_1}{D_1 + D_2} \qquad (J = P, W) \tag{3.5.1}$$

Thus, such as for electroviscous ion concentrations, if we define

$$\tilde{\psi}_2 = \delta^{-\frac{3}{2}} \hat{\psi}_2 \tag{3.5.2}$$

by the aid of relationships (3.4.37, 53) the electroviscous potential for the inner region at the lowest order in δ in the expansion of Pe may be determined to be

$$\begin{aligned} \tilde{\psi}_2 = \frac{3}{5}\left(F_{\psi P} + F_{\psi W}\right)\Bigg\{ & \delta^{-\frac{3}{2}} \mathrm{Pe}\left(1+\tilde{\Omega}\right)\left[\hat{\rho}\hat{H}^{-2}\cos\theta + O(\delta)\right] \\ & + \delta^{-1}\frac{D_2 - D_1}{2D_2}\mathrm{Pe}^2\left(1+\tilde{\Omega}\right)^2\left[\hat{c}_{2P}\cos 2\theta + \frac{1}{2}\left(\hat{H}^{-1} + \hat{H}^{-2}\right) + O(\delta)\right]\Bigg\} + \cdots \end{aligned} \tag{3.5.3a}$$

in which, in view of the definitions (3.4.53b, 5.1), $\left(F_{\psi P}, F_{\psi W}\right)$ are defined by

$$F_{\psi J} = \frac{D_2 - D_1}{D_2 + D_1} F_{cJ} + \frac{2D_1}{D_2 + D_1}\tilde{\psi}_J \qquad J = (P, W) \tag{3.5.3b}$$

3.6 - Electroviscous Force

The electroviscous force, $\vec{\tilde{F}}$, is determined by applying the Lorentz reciprocal theorem, given by(1.3.69). It may be written in vectorial form as

$$\vec{\tilde{F}} = \epsilon^4\, \vec{\tilde{F}}_4^* = \epsilon^4 \left[\int_{S_P} \vec{\tilde{B}}_P \cdot \vec{\vec{\tilde{\sigma}}}_P \cdot d\vec{\tilde{S}}_P + \int_{S_W} \vec{\tilde{B}}_W \cdot \vec{\vec{\tilde{\sigma}}}_W \cdot d\vec{\tilde{S}}_W \right] \tag{3.6.1a}$$

in which $\vec{\tilde{B}}_J$, given by (1.3.59e-h), may be expressed as

$$\vec{\tilde{B}}_J = \lambda\left[\nabla - \vec{n}_J\left(\vec{n}_J \cdot \nabla\right)\right]\left\{-4\ln\left[\cosh\left(\frac{\tilde{\psi}_J}{4}\right)\right]\left(\tilde{c}_2\big|_J\right) + \tilde{\psi}_J\left(\tilde{\psi}_2\big|_J\right)\right\}, J = (P, W) \tag{3.6.1b}$$

which represents tangential derivatives of the electroviscous ion concentrations and the electroviscous potential evaluated on the solid surface J. $\vec{\vec{\tilde{\sigma}}}_J$ is the stress tensor due to the translation of the particle with unit velocity in the direction of the force under determination, evaluated on the solid surface J. Its integrand may be expressed in cylindrical coordinates as

$$\vec{\tilde{B}}_J \cdot \vec{\vec{\tilde{\sigma}}}_J \cdot d\vec{\tilde{S}}_J = \tilde{B}_{J\rho}\left[\tilde{\sigma}_{J\rho\rho} n_{J\rho} + \tilde{\sigma}_{J\rho\theta} n_{J\theta} + \tilde{\sigma}_{J\rho z} n_{Jz}\right] d\tilde{S}_J$$
$$+ \tilde{B}_{J\theta}\left[\tilde{\sigma}_{J\theta\rho} n_{J\rho} + \tilde{\sigma}_{J\theta\theta} n_{J\theta} + \tilde{\sigma}_{J\theta z} n_{Jz}\right] d\tilde{S}_J \tag{3.6.2}$$
$$+ \tilde{B}_{Jz}\left[\tilde{\sigma}_{Jz\rho} n_{J\rho} + \tilde{\sigma}_{Jz\theta} n_{J\theta} + \tilde{\sigma}_{Jzz} n_{Jz}\right] d\tilde{S}_J$$

$\vec{n}_J$ is the unit vector outward to the surface J, given by (3.2.4), in view of which the integrand reduces to

$$\vec{\tilde{B}}_W \cdot \vec{\vec{\tilde{\sigma}}}_W \cdot d\vec{\tilde{S}}_W = \left(\tilde{B}_{W\rho}\tilde{\sigma}_{W\rho z} + \tilde{B}_{W\theta}\tilde{\sigma}_{W\theta z} + \tilde{B}_{Wz}\tilde{\sigma}_{Wzz}\right) d\tilde{S}_W \tag{3.6.3}$$

and

$$\vec{\tilde{B}}_P \cdot \vec{\vec{\tilde{\sigma}}}_P \cdot d\vec{\tilde{S}}_P = \tilde{B}_{P\rho}\left[\tilde{\sigma}_{P\rho\rho}\tilde{\rho} + \tilde{\sigma}_{P\rho z}(\tilde{z} - 1 - \delta)\right] d\tilde{S}_P$$
$$+ \tilde{B}_{P\theta}\left[\tilde{\sigma}_{P\theta\rho}\tilde{\rho} + \tilde{\sigma}_{P\theta z}(\tilde{z} - 1 - \delta)\right] d\tilde{S}_P \tag{3.6.4}$$
$$+ \tilde{B}_{Jz}\left[\tilde{\sigma}_{Pz\rho}\tilde{\rho} + \tilde{\sigma}_{Pzz}(\tilde{z} - 1 - \delta)\right] d\tilde{S}_P$$

3.6.1 - Determination of $\vec{\tilde{B}}_J$

By the aid of relationships (A.14, 17) the normal derivative, appearing in Eq. (3.6.1b), may be written as

$$\vec{n}_W\left(\nabla \cdot \vec{n}_W\right) = \vec{i}_z \frac{\partial}{\partial \tilde{z}} = \delta^{-1}\vec{i}_z \frac{\partial}{\partial \hat{z}}$$

$$\vec{n}_P\left(\nabla \cdot \vec{n}_P\right) = \left[\vec{i}_\rho\tilde{\rho} + \vec{i}_z(\tilde{z} - 1 - \delta)\right]\left[\tilde{\rho}\frac{\partial}{\partial\tilde{\rho}} + (\tilde{z} - 1 - \delta)\frac{\partial}{\partial\tilde{z}}\right]$$

$$= \vec{i}_\rho\delta^{\frac{1}{2}}\hat{\rho}\left[\hat{\rho}\frac{\partial}{\partial\hat{\rho}} + \left(-\delta^{-1} + \hat{z} - 1\right)\frac{\partial}{\partial\hat{z}}\right] + \vec{i}_z(-1 + \delta\hat{z} - \delta)\left[\hat{\rho}\frac{\partial}{\partial\hat{\rho}} + \left(-\delta^{-1} + \hat{z} - 1\right)\frac{\partial}{\partial\hat{z}}\right]$$

from which $\vec{B}_J$ are evaluated on the solid surface J with the result

$$\vec{\tilde{B}}_W = \lambda\delta^{-\frac{1}{2}}\left[\vec{i}_\rho\frac{\partial}{\partial\hat{\rho}} + \vec{i}_\theta\frac{1}{\hat{\rho}}\frac{\partial}{\partial\theta}\right]\left\{-4\ln\left[\cosh\left(\frac{\tilde{\psi}_W}{4}\right)\tilde{c}_2\big|_{\hat{z}=0} + \tilde{\psi}_W\tilde{\psi}_2\big|_{\hat{z}=0}\right]\right\} \tag{3.6.5}$$

$$\tilde{\vec{B}}_P = \lambda\left\{\left[\left[\delta^{-\frac{1}{2}} + O\left(\delta^{\frac{1}{2}}\right)\right]\frac{\partial}{\partial\hat{\rho}} + \left[\delta^{-1} + O(1)\right]\frac{\partial}{\partial\hat{z}}\right]\vec{i}_\rho + \delta^{-\frac{1}{2}}\frac{1}{\hat{\rho}}\frac{\partial}{\partial\theta}i_\theta\right.$$

$$\left.+\left[\left[\hat{\rho} + O(\delta)\right]\frac{\partial}{\partial\hat{\rho}} + \left[2\delta^{-1} + O(1)\right]\frac{\partial}{\partial\hat{z}}\right]\vec{i}_z\right\} \tag{3.6.6}$$

$$\left\{-4\ln\left[\cosh\left(\frac{\tilde{\psi}_P}{4}\right)\right]\tilde{c}_2\Big|_{\hat{z}=\hat{H}} + \tilde{\psi}_P\tilde{\psi}_2\Big|_{\hat{z}=\hat{H}}\right\}$$

in which $\tilde{c}_2$ and $\tilde{\psi}_2$ are given by (3.4.53) and (3.5.3). Since at a first approximation they are independent of $\hat{z}$, their values on the wall surface ($\hat{z} = 0$) and on the particle surface ($\hat{z} = \hat{H}$) are the same, and also their derivatives with respect to $\hat{z}$ vanish. Therefore, $\tilde{\vec{B}}_W$ is obtained as

$$\tilde{B}_{W\rho} = \frac{3}{5}\lambda Pe\delta^{-2}L^1W_{P+W}\left(1+\tilde{\Omega}\right)\left[\left(-3\hat{H}^{-2} + 4\hat{H}^{-3}\right)\cos\theta + O(\delta)\right]$$
$$+\frac{3}{50}\lambda Pe^2\delta^{-\frac{3}{2}}L^2W_{P+W}\left(1+\tilde{\Omega}\right)^2\left[\left(\frac{\partial\hat{c}_{2P}}{\partial\hat{\rho}}\cos(2\theta) - \hat{\rho}\left(\hat{H}^{-2} + 2\hat{H}^{-3}\right)\right) + O(\delta)\right] + \cdots \tag{3.6.7a}$$

$$\tilde{B}_{W\theta} = \frac{3}{5}\lambda Pe\delta^{-2}L^1W_{P+W}\left(1+\tilde{\Omega}\right)\left[-\hat{H}^{-2}\sin\theta + O(\delta)\right]$$
$$+\frac{3}{50}\lambda Pe^2\delta^{-\frac{3}{2}}L^2W_{P+W}\left(1+\tilde{\Omega}\right)^2\left[-\frac{2}{\hat{\rho}}\hat{c}_{2P}\sin(2\theta) + O(\delta)\right] + \cdots \tag{3.6.7b}$$

$$\tilde{B}_{Wz} = 0 \tag{3.6.7c}$$

and $\tilde{\vec{B}}_P$ as

$$\tilde{B}_{P\rho} = \frac{3}{5}\lambda Pe\delta^{-2}L^1P_{P+W}\left(1+\tilde{\Omega}\right)\left[\left(-3\hat{H}^{-2} + 4\hat{H}^{-3}\right)\cos\theta + O(\delta)\right]$$
$$+\frac{3}{50}\lambda Pe^2\delta^{-\frac{3}{2}}L^2P_{P+W}\left(1+\tilde{\Omega}\right)^2\left[\left(\frac{\partial\hat{c}_{2P}}{\partial\hat{\rho}}\cos(2\theta) - \hat{\rho}\left(\hat{H}^{-2} + 2\hat{H}^{-3}\right)\right) + O(\delta)\right] + \cdots \tag{3.6.8a}$$

$$\tilde{B}_{P\theta} = \frac{6}{5}\lambda Pe\delta^{-2}L^1P_{P+W}\left(1+\tilde{\Omega}\right)\left[-\hat{H}^{-2}\sin\theta + O(\delta)\right]$$
$$+\frac{6}{25}\lambda Pe^2\delta^{-\frac{3}{2}}L^2P_{P+W}\left(1+\tilde{\Omega}\right)^2\left[-\frac{2}{\hat{\rho}}\hat{c}_{2P}\sin(2\theta) + O(\delta)\right] + \cdots \tag{3.6.8b}$$

$$\widetilde{B}_{Pz} = \frac{6}{5}\lambda Pe\delta^{-\frac{3}{2}}L^1P_{P+W}\left(1+\widetilde{\Omega}\right)\left[\hat{\rho}\left(-3\hat{H}^{-2}+4\hat{H}^{-3}\right)\cos\theta + O(\delta)\right]$$
$$+\frac{3}{50}\lambda Pe^2\delta^{-1}L^2P_{P+W}\left(1+\widetilde{\Omega}\right)^2\left[\left(\hat{\rho}\frac{\partial\hat{c}_{2P}}{\partial\hat{\rho}}\cos(2\theta)-\hat{\rho}^2\left(\hat{H}^{-2}+2\hat{H}^{-3}\right)\right)+O(\delta)\right]+\cdots \tag{3.6.8c}$$

in which L^1P_{P+W} and L^2P_{P+W} are defined by (2.6.26, 27).

3.6.2 - Stress Tensor

Since the system is symmetric with respect to the (x, z)-plane we do not expect any force to be experienced by the particle in the y-direction. Thus, it remains to determine the stress tensor for flow parallel and normal to the wall to obtain the components of the force in the x and z-directions, respectively.

3.6.2.1 - Translation Parallel to Wall

The flow field for the translation of a particle with unit velocity parallel to the wall is already determined in § 3.3 and the stress tensor is given by relationship (A.22). It may be written in terms of inner variables as

$$\widetilde{\sigma}_{J\rho\rho} = \delta^{-\frac{3}{2}}\hat{p} + \delta^{-\frac{1}{2}}2\frac{\partial\hat{u}_\rho}{\partial\hat{\rho}}\bigg|_{S_J} \qquad \widetilde{\sigma}_{J\theta z} = \delta^{-1}\frac{\partial\hat{u}_\theta}{\partial\hat{z}} + \delta^0\frac{1}{\hat{\rho}}\frac{\partial\hat{u}_z}{\partial\theta}\bigg|_{S_J}$$
$$\widetilde{\sigma}_{J\rho\theta} = \delta^{-\frac{1}{2}}\left[\frac{\partial\hat{u}_\theta}{\partial\hat{\rho}} + \frac{1}{\hat{\rho}}\frac{\partial\hat{u}_\rho}{\partial\theta} - \frac{\hat{u}_\theta}{\hat{\rho}}\right]\bigg|_{S_J} \qquad \widetilde{\sigma}_{Jzz} = -\delta^{-\frac{3}{2}}\hat{p} + \delta^{-\frac{1}{2}}2\frac{\partial\hat{u}_z}{\partial\hat{z}}\bigg|_{S_J} \tag{3.6.9}$$
$$\widetilde{\sigma}_{J\rho z} = +\delta^{-1}\frac{\partial\hat{u}_\rho}{\partial\hat{z}} + \delta^0\frac{\partial\hat{u}_z}{\partial\hat{\rho}}\bigg|_{S_J}$$

Thus, letting $\widetilde{\Omega} = 0$ in the flow field given by (3.3.47-50), the required components of the stress tensor at the lowest order are obtained as

$$\left.\begin{aligned}
\widetilde{\sigma}_{J\rho\rho} &= \widetilde{\sigma}_{Jzz} = -\delta^{-\frac{3}{2}}\frac{6}{5}\hat{\rho}\hat{H}^{-2}\cos\theta + O\left(\delta^{-\frac{1}{2}}\right)\\
\widetilde{\sigma}_{J\rho\theta} &= \delta^{-\frac{1}{2}}\frac{\sin\theta}{5}\left[12\hat{\rho}\hat{H}^{-3}\hat{z}^2 - 4\hat{\rho}\hat{H}^{-2}\hat{z} + O(\delta)\right]\\
\widetilde{\sigma}_{J\rho z} &= \delta^{-1}\frac{\cos\theta}{5}\left[-6\left(3\hat{H}^{-2}-4\hat{H}^{-3}\right)\hat{z} + 2\left(7\hat{H}^{-1}-6\hat{H}^{-2}\right)\right] + O\left(\delta^0\right)\\
\widetilde{\sigma}_{J\theta z} &= \delta^{-1}\frac{\sin\theta}{5}\left[-6\hat{H}^{-2}\hat{z} - 2\hat{H}^{-1}\right] + O\left(\delta^0\right)
\end{aligned}\right\}\text{ on } S_J \tag{3.6.10}$$

3.6.2.2 - Translation Normal to Wall

A suitable expansion for variables of the flow field, produced by translation of the particle with unit velocity normal to and away from the wall is

$$\tilde{x} = \delta^{\frac{1}{2}}\hat{x}, \qquad \tilde{y} = \delta^{\frac{1}{2}}\hat{y}, \qquad \tilde{z} = \delta\hat{z}$$
$$\tilde{u}_x = \delta^{-\frac{1}{2}}\hat{u}_x, \qquad \tilde{u}_y = \delta^{-\frac{1}{2}}\hat{u}_y, \qquad \tilde{u}_z = \hat{u}_x, \qquad \tilde{p} = \delta^{-2}\hat{p} \qquad (3.6.11)$$

Introducing it to Stokes equations, given by (3.3.2, 3), results in

$$\delta^{-\frac{3}{2}}\left(\frac{\partial^2 \hat{u}_x}{\partial \hat{x}^2} + \frac{\partial^2 \hat{u}_x}{\partial \hat{y}^2}\right) + \delta^{-\frac{5}{2}}\frac{\partial^2 \hat{u}_x}{\partial \hat{z}^2} = \delta^{-\frac{5}{2}}\frac{\partial \hat{p}}{\partial \hat{x}} \qquad (3.6.12.a)$$

$$\delta^{-\frac{3}{2}}\left(\frac{\partial^2 \hat{u}_y}{\partial \hat{x}^2} + \frac{\partial^2 \hat{u}_y}{\partial \hat{y}^2}\right) + \delta^{-\frac{5}{2}}\frac{\partial^2 \hat{u}_y}{\partial \hat{z}^2} = \delta^{-\frac{5}{2}}\frac{\partial \hat{p}}{\partial \hat{y}} \qquad (3.6.12b)$$

$$\delta^{-1}\left(\frac{\partial^2 \hat{u}_z}{\partial \hat{x}^2} + \frac{\partial^2 \hat{u}_z}{\partial \hat{y}^2}\right) + \delta^{-2}\frac{\partial^2 \hat{u}_z}{\partial \hat{z}^2} = \delta^{-3}\frac{\partial \hat{p}}{\partial \hat{z}} \qquad (3.6.12c)$$

$$\delta^{-1}\left(\frac{\partial \hat{u}_x}{\partial \hat{x}} + \frac{\partial \hat{u}_y}{\partial \hat{y}} + \frac{\partial \hat{u}_z}{\partial \hat{z}}\right) = 0 \qquad (3.6.12d)$$

together with boundary conditions

$$\hat{u}_x = \hat{u}_y = \hat{u}_z = 0 \qquad \text{on } \hat{z} = 0 \qquad (3.6.12e)$$

$$\hat{u}_x = \hat{u}_y = 0, \qquad \hat{u}_z = 1 \qquad \text{on } \hat{z} = 0 \qquad (3.6.12f)$$

If we expand the flow field as that given by (3.3.12) to the lowest order it satisfies the same equations as those given by (3.3.13-16) with boundary conditions

$$\hat{u}_{x0} = \hat{u}_{y0} = \hat{u}_{z0} = 0 \qquad \text{on } \hat{z} = 0 \qquad (3.6.13a)$$

$$\hat{u}_{x0} = \hat{u}_{y0} = 0, \qquad \hat{u}_{z0} = 1 \qquad \text{on } \hat{z} = 0 \qquad (3.6.13b)$$

Integrating Eq.s (3.3.13, 14) twice with respect to $\hat{z}$ and imposing the corresponding boundary conditions given by (3.6.13) leads to

$$\hat{u}_{x0} = \frac{1}{2}\left(\hat{z}^2 - \hat{H}\hat{z}\right)\frac{\partial \hat{p}_0}{\partial \hat{x}} \qquad (3.6.14a)$$

$$\hat{u}_{y0} = \frac{1}{2}\left(\hat{z}^2 - \hat{H}\hat{z}\right)\frac{\partial \hat{p}_0}{\partial \hat{y}} \tag{3.6.14b}$$

Differentiating the former with respect to $\hat{x}$ and the latter with respect to $\hat{y}$ and then introducing them in the continuity equation, leads to the following differential equation:

$$\frac{\partial \hat{u}_{z0}}{\partial \hat{z}} = -\frac{1}{2}\left[\left(\frac{\partial^2 \hat{p}_0}{\partial \hat{x}^2} + \frac{\partial^2 \hat{p}_0}{\partial \hat{y}^2}\right)\left(\hat{z}^2 - \hat{H}\hat{z}\right) - \left(\hat{x}\frac{\partial \hat{p}_0}{\partial \hat{x}} + \hat{y}\frac{\partial \hat{p}_0}{\partial \hat{y}}\right)\hat{z}\right] \tag{3.6.15a}$$

Its integration is

$$\hat{u}_{z0} = -\frac{1}{2}\left[\left(\frac{\partial^2 \hat{p}_0}{\partial \hat{x}^2} + \frac{\partial^2 \hat{p}_0}{\partial \hat{y}^2}\right)\left(\frac{1}{3}\hat{z}^3 - \frac{1}{2}\hat{H}\hat{z}^2\right) - \frac{1}{2}\left(\hat{x}\frac{\partial \hat{p}_0}{\partial \hat{x}} + \hat{y}\frac{\partial \hat{p}_0}{\partial \hat{y}}\right)\hat{z}^2\right] + C \tag{3.6.15b}$$

Imposing its boundary conditions leads to the following differential equation for the pressure

$$\frac{\partial}{\partial \hat{x}}\left(\hat{H}^3\frac{\partial \hat{p}_0}{\partial \hat{x}}\right) + \frac{\partial}{\partial \hat{y}}\left(\hat{H}^3\frac{\partial \hat{p}_0}{\partial \hat{y}}\right) = 12 \tag{3.6.16a}$$

the particular solution of which is

$$\hat{p}_0 = -3\hat{H}^{-2} \tag{3.6.16b}$$

By the same argument as that presented in § 3.3, its general solution must be rejected. Now, the flow field is completely determined. Upon introducing derivatives of the pressure in Eq.s (3.6.14. 15b), we obtain the results

$$\begin{aligned}
\hat{u}_{x0} &= 3\hat{x}\hat{H}^{-3}\left(\hat{z}^2 - \hat{H}\hat{z}\right) \\
\hat{u}_{y0} &= 3\hat{y}\hat{H}^{-3}\left(\hat{z}^2 - \hat{H}\hat{z}\right) \\
\hat{u}_{z0} &= \left(3\hat{H}^{-4} - 4\hat{H}^{-3}\right)\left(2\hat{z}^3 - 3\hat{H}\hat{z}^2\right) + 3\left(\hat{H}^{-3} - \hat{H}^{-2}\right)\hat{z}^2
\end{aligned} \tag{3.6.17a}$$

It may be written in the cylindrical coordinate system as

$$\begin{aligned}
\hat{\rho}_0 &= -3\hat{H}^{-2} \\
\hat{u}_{\rho 0} &= 3\hat{\rho}\hat{H}^{-3}\left(\hat{z}^2 - \hat{H}\hat{z}\right) \\
\hat{u}_{\theta 0} &= 0 \\
\hat{u}_{z0} &= \left(3\hat{H}^{-4} - 4\hat{H}^{-3}\right)\left(2\hat{z}^3 - 3\hat{H}\hat{z}^2\right) + 3\left(\hat{H}^{-3} - \hat{H}^{-2}\right)\hat{z}^2
\end{aligned} \tag{3.6.17b}$$

From the symmetry property around the z-axis it was expected that the flow field is independent on the azimuth angle θ and hence the velocity in the θ-direction is equal to zero. Thus, letting $\sigma_{\rho\theta} = \sigma_{\theta\theta} = \sigma_{z\theta} = 0$, the other components of the stress tensor may be written in terms of inner variables as

$$\left.\begin{aligned}\tilde{\sigma}_{J\rho\rho} &= -\delta^{-2}\hat{p} + \delta^{-1}2\frac{\partial \hat{u}_\rho}{\partial \hat{\rho}} \\ \tilde{\sigma}_{J\rho z} &= \delta^{-3/2}\frac{\partial \hat{u}_\rho}{\partial \hat{z}} + \delta^{-1/2}\frac{\partial \hat{u}_z}{\partial \hat{\rho}} \\ \tilde{\sigma}_{Jzz} &= -\delta^{-2}\hat{p} + \delta^{-1}2\frac{\partial \hat{u}_z}{\partial \hat{z}}\end{aligned}\right\} \quad \text{on } S_J \tag{3.6.18a}$$

Combining it with the relationship (3.6.17) results in

$$\left.\begin{aligned}\tilde{\sigma}_{J\rho\rho} &= \tilde{\sigma}_{Jzz} = \delta^{-2}3\hat{H}^{-2} + O\left(\delta^{-1}\right) \\ \tilde{\sigma}_{J\rho z} &= \delta^{-\frac{3}{2}}3\hat{\rho}\hat{H}^{-3}\left(2\hat{z} - \hat{H}\right) + O\left(\delta^{-\frac{1}{2}}\right)\end{aligned}\right\} \quad \text{on } S_J \tag{3.6.18b}$$

3.6.3 - Force Parallel to Wall

The required component of stress tensor for flow parallel to the wall, given by (3.6.10), may be evaluated on the wall $(\hat{z} = 0)$ as

$$\begin{aligned}\tilde{\sigma}_{W\rho z} &= \delta^{-1}\frac{1}{5}\left(14\hat{H}^{-1} - 12\hat{H}^{-2}\right)\cos\theta + O(1) \\ \tilde{\sigma}_{W\theta z} &= \delta^{-1}\frac{1}{5}\left(-2\hat{H}^{-1}\right)\sin\theta + O(1) \\ \tilde{\sigma}_{W\rho\rho} &= \tilde{\sigma}_{Wzz} = -\delta^{-3/2}\frac{6}{5}\hat{\rho}\hat{H}^{-2}\cos\theta + O\left(\delta^{-1/2}\right)\end{aligned} \tag{3.6.19}$$

and on the particle surface $\left(\hat{z} = \hat{H}\right)$ as

$$\begin{aligned}\tilde{\sigma}_{P\rho\rho} &= \tilde{\sigma}_{Pzz} = -\delta^{-3/2}\frac{-6}{5}\hat{\rho}\hat{H}^{-2}\cos\theta + O\left(\delta^{-1/2}\right) \\ \tilde{\sigma}_{P\rho\theta} &= \delta^{-1}\frac{-8}{5}\hat{H}^{-1}\sin\theta + O(1) \\ \tilde{\sigma}_{P\rho z} &= \delta^{-1}\frac{1}{5}\left(-4\hat{H}^{-1} + 12\hat{H}^{-2}\right)\cos\theta + O(1) \\ \tilde{\sigma}_{P\rho\theta} &= \delta^{-1/2}\frac{8}{5}\hat{\rho}\hat{H}^{-1}\sin\theta + O\left(\delta^{-1/2}\right)\end{aligned} \tag{3.6.20}$$

Therefore, the integrand evaluated on the wall surface is determined, upon introducing (3.6.19) and (3.6.7) to (3.6.3), by

$$\vec{\tilde{B}}_W \cdot \vec{\vec{\tilde{\sigma}}}_W \cdot d\vec{\tilde{S}}_W = \lambda\left\{\frac{3}{25}L^1 W_{P+W} Pe\delta^{-2}\left(1+\tilde{\Omega}\right)\left[\left(-21\hat{H}^{-3}+46\hat{H}^{-4}-24\hat{H}^{-5}\right)\times\right.\right.$$
$$\left.(1+\cos 2\theta)+\hat{H}^{-3}(1-\cos 2\theta)+O(\delta)\right]$$
$$+\frac{3}{125}L^2 W_{P+W} Pe^2\delta^{-\frac{3}{2}}\left(1+\tilde{\Omega}\right)^2\left\{\left[2\frac{\partial \hat{c}_{2P}}{\partial \hat{\rho}}\cos 2\theta-\hat{\rho}\left(\hat{H}^{-2}+2\hat{H}^{-3}\right)\right]\times\right.$$
$$\left.\left.\left(7\hat{H}^{-1}+6\hat{H}^{-2}\right)\cos\theta+\frac{2}{\hat{\rho}}\hat{c}_{2P}\hat{H}^{-1}\sin(2\theta)\sin\theta+O(\delta)\right\}\right\}\hat{\rho}\,d\theta\,d\hat{\rho}+\cdots$$

(3.6.21a)

and on the particle surface by combing (3.6.20), (3.6.8) and (3.6.4) with the result

$$\vec{\tilde{B}}_P \cdot \vec{\vec{\tilde{\sigma}}}_P \cdot d\vec{\tilde{S}}_P = \lambda\left\{\frac{3}{25}L^1 P_{P+W} Pe\delta^{-2}\left(1+\tilde{\Omega}\right)\left[\left(-10\hat{H}^{-3}+26\hat{H}^{-4}-24\hat{H}^{-5}\right)\right.\right.$$
$$\left.+\left(-4\hat{H}^{-3}+26\hat{H}^{-4}-24\hat{H}^{-5}\right)\cos 2\theta+O(\delta)\right]$$
$$+\frac{3}{125}L^2 P_{P+W} Pe^2\delta^{-2}\left(1+\tilde{\Omega}\right)^2\left\{\left[\frac{8}{\hat{\rho}}\hat{H}^{-1}\hat{c}_{2P}\sin(2\theta)\sin\theta\right.\right. \qquad (3.6.21b)$$
$$\left.\left.+\left(2\hat{H}^{-1}-6\hat{H}^{-2}\right)\cos\theta+O(\delta)\right]\right\}\hat{\rho}\,d\theta\,d\hat{\rho}+$$

The force is obtained upon integration of its integrand determined by (2.6.21) on the solid surfaces bounding the inner region, i.e. for $\hat{\rho}=(0-\infty)$ and $\theta=(0-2\pi)$. Because of the symmetry, integration of all terms containing azimuth angle θ vanishes. Therefore, in view of the integral [c.f., definition (3.3.10)]

$$\int_0^{2\pi}\int_0^{+\infty}\hat{H}^{-n}\hat{\rho}\,d\hat{\rho}\,d\theta=\int_0^{2\pi}\int_0^{+\infty}\left(1+\tfrac{1}{2}\hat{\rho}^2\right)^{-n}\hat{\rho}\,d\hat{\rho}\,d\theta=2\pi\left|\frac{1}{1-n}\left(1+\tfrac{1}{2}\hat{\rho}^2\right)^{1-n}\right|_0^{+\infty}=\frac{2\pi}{n-1},$$

(3.6.22a)

the x-component of the force is obtained as

$$\tilde{F}_x=\frac{2\pi}{25}\epsilon^4\lambda\left(7L^1 P_{P+W}+2L^1 W_{P+W}\right)Pe\delta^{-2}(1+\Omega) \qquad (3.6.22b)$$

or in dimensional form as [c.f., definitions (3.2.2, 2.6.34)]

$$F_x = -\frac{8\pi}{25}\frac{(\varepsilon_r\varepsilon_0)^2(kT)^3}{c_\infty(z_1e)^4}\frac{a}{h^2}\times$$
$$\left[\frac{(7G_P+2G_W)(G_P+G_W)}{D_1}+\frac{(7H_P+2H_W)(H_P+H_W)}{D_2}\right](U+a\Omega) \tag{3.6.23a}$$

in which (G_P, H_P) and (H_P, H_W) are given by (2.6.70). In developing this formula it was assumed that the ζ-potentials of the particle and wall surfaces are identical. Thus, the formula (2.6.23a) may be written as

$$F_x = -\frac{144\pi}{25}\frac{(\varepsilon_r\varepsilon_0)^2(kT)^3}{c_\infty(z_1e)^4}\frac{a}{h^2}\left[\frac{G^2}{D_1}+\frac{H^2}{D_2}\right](U+a\Omega) \tag{3.6.23b}$$

in which $G = G_P = G_W$ and $H = H_P = H_W$.

3.6.4 - Force Normal to Wall

For the determination of the force normal to the wall only terms of order Pe^2 involved, since terms containing the odd function of $\hat{\rho}$ (terms of order Pe) do not contribute to the force. Thus, upon introducing the stress tensor (3.6.18) and relations (3.6.7, 8) to the integrand (3.6.3-4), its required component is obtained as

$$\vec{\tilde{B}}_W\cdot\tilde{\bar{\bar{\sigma}}}_W\cdot d\tilde{S}_W = \frac{9}{25}\lambda L^2 W_{P+W}Pe^2\delta^{-2}\left(1+\tilde{\Omega}\right)^2\times$$
$$\left[\hat{\rho}\hat{H}^{-2}\frac{\partial\hat{c}_{2P}}{\partial\hat{\rho}}\cos 2\theta + \hat{H}^{-3}+\hat{H}^{-4}-2\hat{H}^{-5}+O(\delta)\right]\hat{\rho}\,d\theta\,d\hat{\rho} \tag{3.6.24a}$$

$$\vec{\tilde{B}}_P\cdot\tilde{\bar{\bar{\sigma}}}_P\cdot d\tilde{S}_P = \frac{9}{25}\lambda L^2 P_{P+W}Pe^2\delta^{-2}\left(1+\tilde{\Omega}\right)^2\times$$
$$\left[\hat{\rho}\hat{H}^{-2}\frac{\partial\hat{c}_{2P}}{\partial\hat{\rho}}\cos 2\theta + \hat{H}^{-3}+\hat{H}^{-4}-2\hat{H}^{-5}+O(\delta)\right]\hat{\rho}\,d\theta\,d\hat{\rho} \tag{3.6.24b}$$

Therefore, in view of [c.f., integral (2.6.22a)]

$$\int_0^{2\pi}\int_0^{\infty}\left(\hat{H}^{-3}+\hat{H}^{-4}-2\hat{H}^{-5}\right)\hat{\rho}\,d\hat{\rho}\,d\theta = 2\pi\left|-\frac{1}{2}\hat{H}^{-2}-\frac{1}{3}\hat{H}^{-3}+\frac{1}{2}\hat{H}^{-4}\right|_0^{\infty} = \frac{2\pi}{3}, \tag{3.6.25a}$$

the normal component of the force is determined by

$$\widetilde{F}_z = \frac{6\pi}{25} \epsilon^4 \lambda\left(L^2 W_{P+W} + L^2 P_{P+W}\right) Pe^2 \delta^{-2}\left(1+\widetilde{\Omega}\right)^2 \tag{3.6.25b}$$

or in dimensional form by

$$F_z = \frac{12\pi}{25} \frac{\left(\varepsilon_r \varepsilon_0\right)^2 (kT)^3}{c_\infty \left(z_1 e\right)^4} \frac{a^2}{h^2} \left[\frac{G_P + G_W}{D_1} + \frac{H_P + H_W}{D_2}\right]^2 (U + a\Omega)^2 \tag{3.6.26a}$$

or

$$F_z = \frac{48\pi}{25} \frac{\left(\varepsilon_r \varepsilon_0\right)^2 (kT)^3}{c_\infty \left(z_1 e\right)^4} \frac{a^2}{h^2} \left[\frac{G}{D_1} + \frac{H}{D_2}\right]^2 (U + a\Omega)^2 \tag{3.6.26b}$$

in which G and H, given by (2.6.70), for identical-potentials, $\zeta_P = \zeta_W = \zeta$, may be expressed as

$$G = \ln \frac{1 + e^{-\frac{z_1 e\zeta}{2kT}}}{2}, \qquad H = \ln \frac{1 + e^{\frac{z_1 e\zeta}{2kT}}}{2} \tag{3.6.27}$$

In the formula (3.6.23, 26, 27), $\left(\varepsilon_r \varepsilon_0\right)$ is the permitivity of the medium, (kT) the thermal energy, $\left(z_1 e\right)$ charge of a counterion, c_∞ the number ion bulk concentrations, D_1 and D_2 the diffusivity of counterions and coions, respectively; a is the sphere radius, h the clearance between the sphere and wall, and U is the translation velocity of the sphere and Ω its rotation in the clockwise direction.

3.7 - Results and Conclusions

As for a cylinder-wall, a sphere-wall interaction results in an electroviscous force, experienced by the particle, of order ϵ^4. Its tangential component is explicitly determined by formula (3.6.23), and its normal component by (3.6.26), for identical ζ-potentials. Although, the force is derived under the assumptions of Pe<<1 and δ<<1, it is valid for a larger range of Pe, since the electroviscous ion concentrations and equally the electroviscous potential in fact are obtained under the following expansion [c.f., (3.4.1, 14, 23, 38)]:

$$\widetilde{c}_2 = Pe\delta^{-3/2} + Pe^2\delta^{-1} + O\left(Pe^3\delta^{-1/2}\right) \tag{3.7.1}$$

and this expansion is valid when the truncated term is much smaller than the retained term, that is $Pe^3\delta^{-1/2} << Pe^2\delta^{-1}$, or $Pe << \delta^{-1/2}$ which is larger than $Pe<<1$, and thus, since $\delta << 1$, the expansion applies even for value of Pe larger than one. For example for $\delta=10^{-4}$ the expansion (3.7.1) is valid up to Pe=100. The tangential component of the force is of order Pe, or depends linearly on the velocity and the normal component of $O(Pe^2)$, the same as for a cylinder-wall. Both tangential and normal components of the force are smaller than those of the cylinder-wall interactions by $O(\delta^{1/2})$. Thus, the tangential component is of $O(\epsilon^4 Pe\delta^{-2})$ and the normal component of $O(\epsilon^4 Pe^2\delta^{-2})$. The tangential component of the force depends linearly on the ratio of diffusivity of ions and the normal component on the second power of this ratio, whereas for both normal and tangential components the second powers of the parameters G and H [functions of ζ- potentials defined by (3.6.27)] are involved, the same as for the cylinder-wall interactions. The normal component of the force in dimensionless form $\left(\widetilde{F}_z\right)$ may be written as

$$\widetilde{F}_z = \frac{96\pi}{25} \epsilon^4 \lambda Pe^2\delta^{-2} f_z \tag{3.7.2}$$

where f_z is defined by

$$f_z = \left[G + \frac{D_1}{D_2} H\right]^2 \left(1+\widetilde{\Omega}\right)^2 \tag{3.7.3}$$

The function f_z is plotted versus the ratio of diffusivity of ions in Fig. 3.2 for three different ζ-potentials, $\zeta_p=\zeta_w=-100$ mV, $\zeta_p=\zeta_w=-200$ mV, and $\zeta_p=\zeta_w=-300$ mV. Each curve has a minimum corresponding to $f_z=0$, the same as for identical ζ-potentials of a cylinder and wall. The minimums in these curves occur at D_1/D_2=2.4791, 4.7882, 7.4655, for ζ=-100, -200, -300, respectively. For two special hydrodynamic cases, namely for $U = -a\Omega$ and $U = a\Omega$, the particle experiences no force for the former, and two times the tangential component and four times the normal component of the force (because of the proportionality to the square of the velocity) produced by either the rotation or the translation of the particle for the latter, the same as for identical ζ-potentials of the cylinder and wall. The ratio of the contribution to the tangential component of the force from the sphere surface to that of the wall surface is 3.5 [c.f., (3.6.22)], whilst this ratio for the identical ζ-potentials of the cylinder and wall is 3 [c.f., (2.6.63)]. That ratio for the normal component of the force is the same as that for the cylinder-wall, i.e. it is equal to1 [c.f., (3.6.25b, 2.6.68)]. For small ζ-potentials and for equal mobilities of ions, as a first approximation, the tangential component of the force, is linearly proportional to viscosity of medium, ion radius, a_i, and ζ^2, whereas the normal component is proportional to η^2, a_i^2 and ζ^4, the same as for the cylinder-wall interactions.

It is interesting to compare the drag force for a sphere-wall, given by (3.6.39), with that of sedimentation of a sphere in unbounded flow, given by (1.2.28). It is observed that their ratio always satisfy

$$\frac{F_{\text{Sphere-wall}}}{F_{\text{Sphere}}} = \frac{6}{25}\delta^{-2} \tag{3.7.4}$$

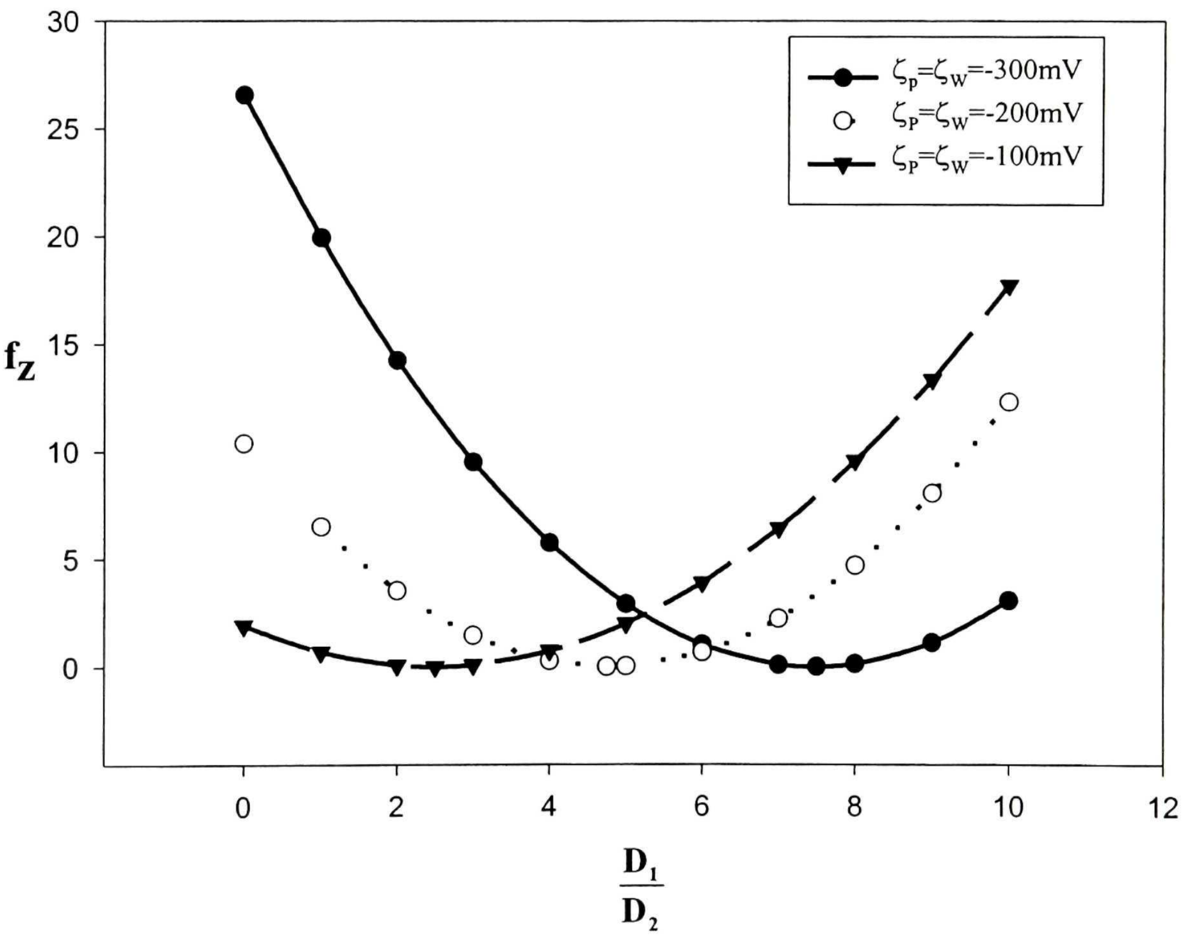


Fig. 3.2 - f_z vs ratio of diffusivity of ions for either translation or rotation of sphere.

It should be noted that the force for the isolated sphere is an exact value, but for the sphere-wall interactions only the contribution from the inner region is taken into account.

The Derjaguin (1934) relationship between the coefficient of force experienced by a cylinder and that of a sphere given by [van de Ven (1989)]

$$F_{Sphere} = F_{Cylinder}\left[h^{-\left(n+\frac{1}{2}\right)}\right]\frac{(2n-2)!!}{(2n-1)!!}2\sqrt{2ah}, \tag{3.7.5}$$

is extensively used for calculations of interactions between colloidal particles. Here $\left[h^{-(n+\frac{1}{2})}\right]$ is the h-dependence of the cylinder force and $k!! = k(k-2)(k-4)\cdots$. To see how it works for the electroviscous force in which $\left[h^{-(n+\frac{1}{2})}\right] = h^{-\frac{5}{2}}$ [c.f., formulas (2.6.63, 67)] or n = 2, it may be written as

$$\frac{F_{Sphere-Wall}}{F_{Cylinder-Wall}} = \frac{4}{3}\sqrt{2ah} \tag{3.7.6}$$

For the drag component of the force, given by (2.6.64) and (3.6.23), this ratio is

$$\frac{F_{xSphere-Wall}}{F_{xCylinder-Wall}} = \frac{18}{25}\sqrt{2ah} \tag{3.7.7}$$

and for the normal component, given by (2.6.69) and (3.6.26)

$$\frac{F_{zSphere-Wall}}{F_{zCylinder-Wall}} = \frac{48}{125}\sqrt{2ah} \tag{3.7.8}$$

It is observed that although in both cases it predicts the right order in $\sqrt{ah}$, it overestimates the force by a factor of 50/27 for the tangential component and by a factor of 125/36 for the normal component of the force.

Chapter Four

Electroviscous Sphere-Wall Interactions: Exact and Numerical Solutions

4.1- Introduction

The problem of a sphere under translation and rotation parallel to a wall is reconsidered. The problem was solved for the inner region, in Chapter three, for the cases of small particle-wall distances and low Peclet numbers. First, the restriction on particle-wall distances is removed. An analytical-numerical solution is obtained valid for the whole domain of interest for low Pe. Second, the restriction on Peclet number is removed. An analytical-numerical solution for both arbitrary particle-wall distances and arbitrary Peclet numbers is presented. The purely hydrodynamic problem, as well as the stress tensor involved in the force integral equation are determined analytically, based on the Jeffery's solution (1912) of the Laplace equation in a bipolar coordinate system. The analytical solution is obtained as a summation of an infinite series.

Although the bipolar coordinate system has the utility of describing the system by a single coordinate (that is both wall and sphere surface are described by only a single coordinate), the cylindrical polar coordinates are useful and are employed as intermediate steps in solving the equations of motion and subsequently the electroviscous ion concentration, the electroviscous potential, and the electroviscous flow field. Some properties of these two coordinate systems are discussed in Appendix A.

For low Pe, the electroviscous ion concentrations and potential at order Pe are obtained both analytically and numerically, from which the analytical and numerical solutions of the tangential component of the force are determined. At order Pe^2 they are determined numerically, resulting in a numerical solution for the normal component of the force. For arbitrary Pe the electroviscous ion concentrations and potential are also calculated numerically, from which the tangential and normal components of the force are determined numerically.

The numerical approach is based on the finite difference approximation. The idea is that the dependent variables at each point of the domain can be determined from the values of its neighborhood by the use of a Taylor series expansion. Thus, the domain of interest is divided into discrete points. For each node we may write a finite difference equation, relating that node to the neighborhood nodes. These equations are simultaneously solved in a way that boundary conditions for the nodes on the solid surfaces and for that at infinity are satisfied, from which the value of those variables for each node are uniquely determined. They are programed in MATLAB; an electronic copy can be provided upon request.

The hydrodynamics is presented in § 4.2. It includes the exact solution of the Stokes equation, the translation of a sphere, the rotation of a sphere, and superimposing them to obtain the solution of the hydrodynamic part of the problem at hand. The electroviscous ion concentrations for low Pe is presented in § 4.3. It contains the electroviscous equation, the analytical solution at order Pe and numerical solutions at orders Pe and Pe^2. The electroviscous potential is determined in § 4.4. The electroviscous force for low Pe is presented in § 4.5. It consists of the determination of the stress tensor for translation of the particle parallel and normal to the wall to determine the tangential and normal components of the force upon applying the Lorentz reciprocal theorem. The numerical solution for arbitrary Pe is given in § 4.6. It contains the electroviscous ion concentration, electroviscous potential and electroviscous force. Finally, results and conclusions are presented in § 4.7.

4.2 - Hydrodynamics

4.2.1 - Solution of Stokes Equations

Equations of motion are assumed to be the Stokes equations given by (3.2.5, 6). Thus, taking the divergence of Eq. (3.2.5) results in:

$$\nabla \cdot \nabla^2 \vec{\tilde{u}} - \nabla \cdot \nabla \tilde{p} = 0, \qquad \text{or} \qquad \nabla^2 \nabla \cdot \vec{\tilde{u}} = \nabla^2 \tilde{p} \tag{4.2.1}$$

Since by the continuity Eq. (3.2.6), $\nabla \cdot \vec{\tilde{u}} = 0$ it follows that:

$$\nabla^2 \tilde{p} = 0 \tag{4.2.2}$$

which indicates that for creeping flows the pressure is harmonic. Using relationships (A.17-20), the pressure, the momentum, and the continuity equations, given by Eq.s (4.2.2, 3.2.5, 6), may be expressed in the cylindrical coordinate system as

$$\frac{1}{\tilde{\rho}}\left(\tilde{\rho}\frac{\partial \tilde{p}}{\partial \tilde{\rho}}\right) + \frac{1}{\tilde{\rho}^2}\frac{\partial^2 \tilde{p}}{\partial \theta^2} + \frac{\partial^2 \tilde{p}}{\partial \tilde{z}^2} = 0 \tag{4.2.3}$$

$$\frac{\partial \tilde{p}}{\partial \tilde{\rho}} = \frac{1}{\tilde{\rho}}\frac{\partial}{\partial \tilde{\rho}}\left(\tilde{\rho}\frac{\partial \tilde{u}_\rho}{\partial \tilde{\rho}}\right) + \frac{1}{\tilde{\rho}^2}\left(\frac{\partial^2 \tilde{u}_\rho}{\partial \theta^2} - \tilde{u}_\rho\right) + \frac{\partial^2 \tilde{u}_\rho}{\partial \tilde{z}^2} - \frac{2}{\tilde{\rho}^2}\frac{\partial \tilde{u}_\theta}{\partial \theta}, \tag{4.2.4}$$

$$\frac{1}{\tilde{\rho}}\frac{\partial \tilde{p}}{\partial \theta} = \frac{1}{\tilde{\rho}}\frac{\partial}{\partial \tilde{\rho}}\left(\tilde{\rho}\frac{\partial \tilde{u}_\theta}{\partial \tilde{\rho}}\right) + \frac{1}{\tilde{\rho}^2}\left(\frac{\partial^2 \tilde{u}_\theta}{\partial \theta^2} - \tilde{u}_\theta\right) + \frac{\partial^2 \tilde{u}_\theta}{\partial \tilde{z}^2} + \frac{2}{\tilde{\rho}^2}\frac{\partial \tilde{u}_\rho}{\partial \theta}, \tag{4.2.5}$$

$$\frac{\partial \tilde{p}}{\partial \tilde{z}} = \frac{1}{\tilde{\rho}}\frac{\partial}{\partial \tilde{\rho}}\left(\tilde{\rho}\frac{\partial \tilde{u}_z}{\partial \tilde{\rho}}\right) + \frac{1}{\tilde{\rho}^2}\frac{\partial^2 \tilde{u}_z}{\partial \theta^2} + \frac{\partial^2 \tilde{u}_z}{\partial \tilde{z}^2}, \tag{4.2.6}$$

$$\frac{1}{\tilde{\rho}}\frac{\partial}{\partial \tilde{\rho}}\left(\tilde{\rho}\,\tilde{u}_\rho\right) + \frac{1}{\tilde{\rho}}\frac{\partial \tilde{u}_\theta}{\partial \theta} + \frac{\partial \tilde{u}_z}{\partial \tilde{z}} = 0 \tag{4.2.7}$$

Now, if we write the flow field in terms of the auxiliary functions Q_1, U_2, U_0, and W_1:

$$\tilde{p} = \frac{Q_1}{c}\cos\theta, \tag{4.2.8}$$

$$\tilde{u}_\rho = \frac{1}{2}\left[\frac{\tilde{\rho}}{c}Q_1 + \left(U_2 + U_0 - 2\right)\right]\cos\theta, \tag{4.2.9}$$

$$\tilde{u}_\theta = \frac{1}{2}\left(U_2 - U_0 + 2\right)\sin\theta, \tag{4.2.10}$$

$$\tilde{u}_z = \frac{1}{2}\left(\frac{\tilde{z}}{c}Q_1 + 2W_1\right)\cos\theta \tag{4.2.11}$$

in which the geometry constant c is defined by the relationship (A.41), we end up with an individual equation for each of the auxiliary functions to be solved (i.e., separation of auxiliary functions). Since the coordinate θ has been used, the auxiliary functions, Q_1, U_2, U_0, and W_1 are functions of only $\tilde{\rho}$ and $\tilde{z}$. Introducing the expressions (4.2.8-11) to the differential equations (4.2.3-7) results in:

$$\frac{\cos\theta}{c}\left(\frac{\partial^2 Q_1}{\partial \tilde{\rho}^2} + \frac{1}{\tilde{\rho}}\frac{\partial Q_1}{\partial \tilde{\rho}} - \frac{Q_1}{\tilde{\rho}^2} + \frac{\partial^2 Q_1}{\partial \tilde{z}^2}\right) = 0, \tag{4.2.12}$$

$$\begin{aligned}\frac{1}{2c}\left(\frac{\partial^2 Q_1}{\partial \tilde{\rho}^2} + \frac{1}{\tilde{\rho}}\frac{\partial Q_1}{\partial \tilde{\rho}} - \frac{Q_1}{\tilde{\rho}^2} + \frac{\partial^2 Q_1}{\partial \tilde{z}^2}\right) + \frac{1}{\tilde{\rho}}\left(\frac{\partial^2 U_0}{\partial \tilde{\rho}^2} + \frac{1}{\tilde{\rho}}\frac{\partial U_0}{\partial \tilde{\rho}} + \frac{\partial^2 U_0}{\partial \tilde{z}^2}\right)\\ + \frac{1}{\tilde{\rho}}\left(\frac{\partial^2 U_2}{\partial \tilde{\rho}^2} + \frac{1}{\tilde{\rho}}\frac{\partial U_2}{\partial \tilde{\rho}} - \frac{4U_2}{\tilde{\rho}^2} + \frac{\partial^2 U_2}{\partial \tilde{z}^2}\right) = 0\end{aligned} \tag{4.2.13}$$

$$\frac{\partial^2 U_0}{\partial \tilde{\rho}^2} + \frac{1}{\tilde{\rho}}\frac{\partial U_0}{\partial \tilde{\rho}} + \frac{\partial^2 U_0}{\partial \tilde{z}^2} - \left(\frac{\partial^2 U_2}{\partial \tilde{\rho}^2} + \frac{1}{\tilde{\rho}}\frac{\partial U_2}{\partial \tilde{\rho}} - \frac{4U_2}{\tilde{\rho}^2} + \frac{\partial^2 U_2}{\partial \tilde{z}^2}\right) = 0 \tag{4.2.14}$$

$$\frac{\tilde{z}}{2c}\left(\frac{\partial^2 Q_1}{\partial\tilde{\rho}^2}+\frac{1}{\tilde{\rho}}\frac{\partial Q_1}{\partial\tilde{\rho}}-\frac{Q_1}{\tilde{\rho}^2}+\frac{\partial^2 Q_1}{\partial\tilde{z}^2}\right)+\frac{\partial^2 W_1}{\partial\tilde{\rho}^2}+\frac{1}{\tilde{\rho}}\frac{\partial W_1}{\partial\tilde{\rho}}-\frac{W_1}{\tilde{\rho}^2}+\frac{\partial^2 W_1}{\partial\tilde{z}^2}=0 \quad (4.2.15)$$

$$\left(3Q_1+\tilde{\rho}\frac{\partial Q_1}{\partial\tilde{\rho}}+\tilde{z}\frac{\partial Q_1}{\partial\tilde{z}}\right)+c\left(\frac{\partial U_2}{\partial\tilde{\rho}}+\frac{2U_2}{\tilde{\rho}}+\frac{\partial U_0}{\partial\tilde{\rho}}+2\frac{\partial W_1}{\partial\tilde{z}}\right)=0 \quad (4.2.16)$$

Thus, Q_1 satisfies [c.f., Eq. (4.2.12)]

$$\frac{\partial^2 Q_1}{\partial\tilde{\rho}^2}+\frac{1}{\tilde{\rho}}\frac{\partial Q_1}{\partial\tilde{\rho}}-\frac{Q_1}{\tilde{\rho}^2}+\frac{\partial^2 Q_1}{\partial\tilde{z}^2}=0, \quad (4.2.17)$$

Introducing Eq. (4.2.12) into Eq.(4.2.13), then adding and subtracting the result to the Eq. (4.2.14) gives the differential equations for U_0 and U_2 to be determined as

$$\frac{\partial^2 U_0}{\partial\tilde{\rho}^2}+\frac{1}{\tilde{\rho}}\frac{\partial U_0}{\partial\tilde{\rho}}+\frac{\partial^2 U_0}{\partial\tilde{z}^2}=0, \quad (4.2.18)$$

$$\frac{\partial^2 U_2}{\partial\tilde{\rho}^2}+\frac{1}{\tilde{\rho}}\frac{\partial U_2}{\partial\tilde{\rho}}-\frac{4U_2}{\tilde{\rho}^2}+\frac{\partial^2 U_2}{\partial\tilde{z}^2}=0, \quad (4.2.19)$$

The differential equation for W_1 is obtained, upon introducing Eq. (4.2.12) into Eq. (4.2.15), as

$$\frac{\partial^2 W_1}{\partial\tilde{\rho}^2}+\frac{1}{\tilde{\rho}}\frac{\partial W_1}{\partial\tilde{\rho}}-\frac{W_1}{\tilde{\rho}^2}+\frac{\partial^2 W_1}{\partial\tilde{z}^2}=0, \quad (4.2.20)$$

The partial differential Eq.s (4.2.17-20) may be written in a general form as

$$L_m^2\Phi=\frac{\partial^2 \Phi}{\partial\tilde{\rho}^2}+\frac{1}{\tilde{\rho}}\frac{\partial \Phi}{\partial\tilde{\rho}}-\frac{m^2\Phi}{\tilde{\rho}^2}+\frac{\partial^2 \Phi}{\partial\tilde{z}^2}=0, \quad (4.2.21)$$

where $\Phi = Q_1, U_2, U_0$, or W_1, and where m is equal to the corresponding indices, that is m=1 for Q_1 and W_1, m = 2 for U_2, and m = 0 for U_0.

The bipolar coordinate system with the transformation function

$$\tilde{\rho}=\frac{c\sin\eta}{\cosh\xi-\cos\eta}, \qquad \tilde{z}=\frac{c\sinh\xi}{\cosh\xi-\cos\eta} \quad (4.2.22a)$$

as shown in Fig. 4.1, best describes the geometry of the problem. The constant c is a geometry constant defined by (A.41) as

$$c = \sinh\alpha, \tag{4.2.22b}$$

in which α is a function of the dimensionless gap width, δ, defined by (A.42) as

$$\alpha = \ln\left[1+\delta+\sqrt{(1+\delta)^2-1}\right] \tag{4.2.22c}$$

In this coordinate system the sphere is defined by $\xi = \alpha$, the plane by $\xi = 0$, the origin by ($\xi = 0$, $\eta = \pi$) and infinity by ($\xi = 0$, $\eta = 0$), c.f., Fig. 4.1. Thus, since both solid surfaces are described by a single coordinate, in order to impose the corresponding boundary conditions, it is more convenient to transform Eq. (4.2.21) into the bipolar coordinate system, by the use of relationships (A.54-59). Doing so, its transformation is obtained as

$$\frac{\partial^2\Phi}{\partial\xi^2}+\frac{\partial^2\Phi}{\partial\eta^2}-\frac{1}{\cosh\xi-\cos\eta}\left(\sinh\xi\frac{\partial\Phi}{\partial\xi}+\frac{1-\cos\eta\cosh\xi}{\sin\eta}\frac{\partial\Phi}{\partial\eta}\right)-\frac{m^2\Phi}{\sin^2\eta}=0 \tag{4.2.23}$$

This equation in essence has been solved analytically by Jeffery (1912). The details of the calculation are presented here for completeness. Letting

$$\Phi = \tilde{\rho}^{-\frac{1}{2}}\Psi = \left(\frac{\cosh\xi-\cos\eta}{c\sin\eta}\right)^{\frac{1}{2}}\Psi \tag{4.2.24}$$

we have the following relation between the derivatives of Φ and Ψ:

$$\frac{\partial\Phi}{\partial\xi}=\frac{1}{\sqrt{c\sin\eta}}\left[\frac{1}{2}\sinh\xi(\cosh\xi-\cos\eta)^{-\frac{1}{2}}\Psi+(\cosh\xi-\cos\eta)^{\frac{1}{2}}\frac{\partial\Psi}{\partial\xi}\right] \tag{4.2.25}$$

$$\begin{aligned}\frac{\partial^2\Phi}{\partial\xi^2}=\frac{1}{\sqrt{c\sin\eta}}\Bigg\{&\frac{1}{2}\left[\cosh\xi(\cosh\xi-\cos\eta)^{-\frac{1}{2}}-\frac{1}{2}\sinh^2\xi(\cosh\xi-\cos\eta)^{-\frac{3}{2}}\right]\Psi\\&+\sinh\xi(\cosh\xi-\cos\eta)^{-\frac{1}{2}}\frac{\partial\psi}{\partial\xi}+(\cosh\xi-\cos\eta)^{-\frac{1}{2}}\frac{\partial^2\psi}{\partial\xi^2}\Bigg\}\end{aligned} \tag{4.2.26}$$

$$\frac{\partial\Phi}{\partial\eta}=\frac{1}{\sqrt{c}}\left[\frac{1}{2}\frac{1-\cos\eta\cosh\xi}{\sin^{\frac{3}{2}}\eta(\cosh\xi-\cos\eta)^{\frac{1}{2}}}\Psi+\frac{(\cosh\xi-\cos\eta)^{\frac{1}{2}}}{\sin^{\frac{1}{2}}\eta}\frac{\partial\Psi}{\partial\eta}\right] \tag{4.2.27}$$

$$\frac{\partial^2\Phi}{\partial\eta^2}=\frac{1}{\sqrt{c}}\left\{\frac{1}{2}\left[\frac{\cosh\xi}{\sin^{\frac{1}{2}}\eta\left(\cosh\xi-\cos\eta\right)^{\frac{1}{2}}}-\frac{3}{2}\frac{\cos\eta\left(1-\cos\eta\cosh\xi\right)}{\sin^{\frac{5}{2}}\eta\left(\cosh\xi-\cos\eta\right)^{\frac{1}{2}}}-\right.\right.$$

$$\left.\left.\frac{1}{2}\frac{\left(1-\cos\eta\cosh\xi\right)}{\sin^{\frac{1}{2}}\eta\left(\cosh\xi-\cos\eta\right)^{\frac{1}{2}}}\right]\Psi+\frac{\left(1-\cos\eta\cosh\xi\right)}{\sin^{\frac{1}{2}}\eta\left(\cosh\xi-\cos\eta\right)^{\frac{1}{2}}}\frac{\partial\Psi}{\partial\eta}+\frac{\left(\cosh\xi-\cos\eta\right)^{\frac{1}{2}}}{\sin^{\frac{1}{2}}\eta}\frac{\partial^2\Psi}{\partial\eta^2}\right\}$$

(4.2.28)

Introducing relationships (4.2.24-28) to Eq.(4.2.23) results in:

$$\sqrt{\frac{\cosh\xi-\cos\eta}{c\sin\eta}}\left\{\frac{\partial^2\Psi}{\partial\xi^2}+\frac{\partial^2\Psi}{\partial\eta^2}-\frac{\Psi}{2}\left[\frac{2m^2}{\sin^2\eta}-\frac{2\cosh\xi}{\cosh\xi-\cos\eta}+\frac{3\sinh^2\xi}{2\left(\cosh\xi-\cos\eta\right)^2}\right.\right.$$

$$\left.\left.+\frac{3\cos\eta\left(1-\cos\eta\cosh\xi\right)}{2\sin^2\eta\left(\cosh\xi-\cos\eta\right)}+\frac{1-\cos\eta\cosh\xi}{2\left(\cosh\xi-\cos\eta\right)^2}+\frac{\left(1-\cos\eta\cosh\xi\right)^2}{\sin^2\eta\left(\cosh\xi-\cos\eta\right)^2}\right]\right\}=0$$

or

$$\frac{\partial^2\Psi}{\partial\xi^2}+\frac{\partial^2\Psi}{\partial\eta^2}+\left(\frac{1}{4}-m^2\right)\Psi=0 \tag{4.2.29}$$

Now, this equation can be solved by the usual manner of the separation of variables. Thus, introducing

$$\Psi=\Xi\cdot N \tag{4.2.30}$$

where $\Xi=f(\xi)$ and $N=g(\eta)$, to Eq.(4.2.29) and then dividing it by Ψ leads to the following relationship:

$$-\frac{1}{\Xi}\frac{d^2\Xi}{d\xi^2}=\frac{1}{N}\frac{d^2N}{d\eta^2}+\frac{1}{\sin^2\eta}\left(\frac{1}{4}-m^2\right) \tag{4.2.31}$$

Since the left hand side is only a function of ξ and the right hand side is only a function of η, and this equality must hold for any values of ξ and η, the only choice for them is to be equal to a constant, $-(n+1/2)^2$ say. Since the problem is related to a sphere, we should seek a spherical harmonic solution, and hence only this choice of a set of constants, namely $(n+1/2)^2$, where n are any integers, ends up in a spherical harmonic equation. But, since the choice $-(n+1)$ instead of n leads to the same constant, that is $-(-n-1+1/2)^2=-(n+1/2)^2$, we consider only one set of integers, namely zero and positive ones. Therefore, we end up with two ordinary differential equations to be solved. The solution of the first equation,

$$\frac{d^2\Xi}{d\xi^2} - \left(n+\frac{1}{2}\right)^2 \Xi = 0, \tag{4.2.32}$$

is

$$\Xi = a_n \cosh\left(n+\frac{1}{2}\right)\xi + b_n \sinh\left(n+\frac{1}{2}\right)\xi \tag{4.2.33}$$

where a_n and b_n each are a set of constants associated with the integer n. The second equation,

$$\frac{d^2N}{d\eta^2} + \left[\left(n+\frac{1}{2}\right)^2 - \frac{1}{\sin^2\eta}\left(m^2 - \frac{1}{4}\right)\right] N = 0, \tag{4.2.34}$$

may be solved by changing the variable as

$$N = X \sin^{\frac{1}{2}} \eta \tag{4.2.35}$$

from which $dN/d\eta$ and $d^2N/d\eta^2$ are determined as:

$$\frac{dN}{d\eta} = \frac{1}{2} X \cos\eta \sin^{-\frac{1}{2}} \eta + \sin^{\frac{1}{2}} \eta \frac{dX}{d\eta} \tag{4.2.36}$$

$$\frac{d^2N}{d\eta^2} = \sqrt{\sin\eta}\left[\frac{d^2X}{d\eta^2} + \frac{\cos\eta}{\sin\eta}\frac{dX}{d\eta} - \frac{1}{2}\left(\frac{1}{2} + \frac{1}{2\sin^2\eta}\right) X\right] \tag{4.2.37}$$

Introducing relationships (4.2.35-37) to Eq. (4.2.34) results in:

$$\frac{d^2X}{d\eta^2} + \frac{\cos\eta}{\sin\eta}\frac{dX}{d\eta} + \left(n^2 + n - \frac{m^2}{\sin^2\eta}\right) X = 0 \tag{4.2.38}$$

Finally, letting

$$\mu = \cos\eta, \tag{4.2.39}$$

then

$$\frac{d}{d\eta} = \frac{d\mu}{d\eta}\frac{d}{d\mu} = -\sin\eta\frac{d}{d\mu} \tag{4.2.40}$$

$$\frac{d^2}{d\eta^2} = \frac{d}{d\eta}\left(-\sin\eta\frac{d}{d\mu}\right) = -\cos\eta\frac{d}{d\mu} + \sin^2\eta\frac{d^2}{d\mu^2} \tag{4.2.41}$$

Introducing the relationships (4.2.39-41) to Eq. (4.2.38) leads to the following equation:

$$\left(1-\mu^2\right)\frac{d^2X}{d\mu^2} - 2\mu\frac{dX}{d\mu} + n(n+1)\,X = \frac{m^2}{1-\mu^2}X \tag{4.2.42}$$

This equation is well known as the associated Legendre equation of order n and degree m. Its solution is

$$X = C_n P_n^m(\mu) + D_n Q_n^m(\mu) \tag{4.2.43}$$

in which C_n and D_n are sets of constants, and $P_n{}^m$ and $Q_n{}^m$ are known as Legendre functions of the first and second kind, respectively, of order n and degree m. They are defined by

$$P_n^m(\mu) = \left(1-\mu^2\right)^{\frac{m}{2}}\frac{d^m}{d\mu^m}P_n(\mu) \tag{4.2.44}$$

$$Q_n^m(\mu) = \left(1-\mu^2\right)^{\frac{m}{2}}\frac{d^m}{d\mu^m}Q_n(\mu) \tag{4.2.45}$$

in which P_n are called Legendre polynomials of order n, Q_n Legendre functions of the second kind, and d^m/du^m are m^{th} derivatives with respect to μ. P_n are finite and continuous at all points of the domain. But, Q_n has singularities at points $\eta = 0$ and $\eta = \pi$, which represents some special physical conditions such as a source or a charge, and hence it cannot be included in the solution. Therefore, the solution of Eq. (4.2.42) is

$$X = C_n P_n^m(\mu) = C_n\left(1-\mu^2\right)^{\frac{m}{2}}\frac{d^m}{d\mu^m}P_n(\mu) \tag{4.2.46}$$

The general solution of the Eq. (4.2.31) is obtained by superimposing all individual solutions, corresponding to n = (0 - ∞), given by (4.2.30, 33, 35, 46), as

$$\Psi = \left(1-\mu^2\right)^{\frac{m}{2}}\sin^{-\frac{1}{2}}\eta\sum_{n=0}^{\infty}\left\{a_n\cosh\left[\left(n+\frac{1}{2}\right)\xi\right] + b_n\sinh\left[\left(n+\frac{1}{2}\right)\xi\right]\right\}\frac{d^m}{d\mu^m}P_n(\mu) \tag{4.2.47}$$

Now, in view of (4.2.24, 39), the general solution of Eq. (4.2. 23) or equivalently Eq. (4.2.21) for Φ representing auxiliary functions W_1, Q_1 U_0, and U_2, corresponding to m = (1, 1, 0, 2), respectively, is determined by

$$W_1 = \left(\cosh\xi-\mu\right)^{\frac{1}{2}}\sin\eta\sum_{n=1}^{\infty}\left[A_n'\cosh\left(n+\frac{1}{2}\right)\xi + A_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n'(\mu) \tag{4.2.48}$$

$$Q_1 = (\cosh\xi - \mu)^{\frac{1}{2}} \sin\eta \sum_{n=1}^{\infty}\left[B_n \cosh\left(n+\frac{1}{2}\right)\xi + C_n \sinh\left(n+\frac{1}{2}\right)\xi\right]P_n'(\mu) \quad (4.2.49)$$

$$U_0 = (\cosh\xi - \mu)^{\frac{1}{2}} \sum_{n=0}^{\infty}\left[D_n \cosh\left(n+\frac{1}{2}\right)\xi + E_n \sinh\left(n+\frac{1}{2}\right)\xi\right]P_n(\mu) \quad (4.2.50)$$

$$U_2 = (\cosh\xi - \mu)^{\frac{1}{2}} \sin^2\eta \sum_{n=2}^{\infty}\left[F_n \cosh\left(n+\frac{1}{2}\right)\xi + G_n \sinh\left(n+\frac{1}{2}\right)\xi\right]P_n''(\mu) \quad (4.2.51)$$

in which

$$P_n' = \frac{dP_n}{d\mu}, \qquad P_n'' = \frac{d^2P_n}{d\mu^2} \quad (4.2.52)$$

and A'_n, A_n, B_n, C_n, D_n, E_n, F_n, and G_n each are a set of constants to be determined by applying the relevant boundary conditions and continuity equation. In deriving (4.2.48-51), the summation over n for W_1 and Q_1 is taken from n = (1- ∞), and for U_2 from n = (2 - ∞), instead of n = (0 - ∞), since

$$P_0' = 0, \qquad P_0'' = P_1'' = 0 \quad (4.2.53)$$

The continuity equation (4.2.16), by the aid of relationship (A.54, 55), may also be expressed in the bipolar coordinate system as

$$3Q_1 - \left[\mu\sinh\xi\frac{\partial}{\partial\xi} + \sin\eta\cosh\xi\frac{\partial}{\partial\eta}\right]Q_1 - \left[\sin\eta\sinh\xi\frac{\partial}{\partial\xi} + (1-\mu\cosh\xi)\frac{\partial}{\partial\eta} + 2\frac{\cosh\xi - \mu}{\sin\mu}\right]U_2$$
$$-\left[\sin\eta\sinh\xi\frac{\partial}{\partial\xi} + (1-\mu\cosh\xi)\frac{\partial}{\partial\eta}\right]U_0 + 2\left[(1-\mu\cosh\xi)\frac{\partial}{\partial\xi} - \sin\eta\sinh\xi\frac{\partial}{\partial\eta}\right]W_1 = 0 \quad (4.2.54)$$

The solution of the Stokes equations in terms of the corresponding auxiliary functions defined by (4.2.8-11) has been used by O'Neill (1964) to solve the problem of the translation of a sphere parallel to a plane and by Dean and O'Neill (1963) for the rotation of a sphere around its diameter parallel to the wall in a quiescent liquids. In the subsequent sections these solutions are presented (in details for the former) and with a minor modification for the problem of a stationary sphere located in a liquid with undisturbed velocity $\widetilde{U} = -1$ parallel to the moving wall with the same velocity vector to remove the time dependency of the problem. This is already imposed in the definition of the auxiliary functions. Then, since the equation of motions are linear, these two solution are superimposed to obtain the flow field for the problem at hand.

4.2.2-Translation Parallel to Wall

The no-slip boundary condition for a stationary sphere relative to a translating coordinate system with unit velocity in a liquid in which the wall and undisturbed fluid translate with unit velocity but with the opposite direction may be written as

$$\tilde{u}_\rho = 0, \qquad \tilde{u}_\theta = 0, \qquad \tilde{u}_z = 0 \qquad \text{on} \quad S_p \tag{4.2.55}$$

$$\tilde{u}_\rho = -\cos\theta, \qquad \tilde{u}_\theta = \sin\theta, \qquad \tilde{u}_z = 0 \qquad \text{on}\ S_w \tag{4.2.56}$$

In view of (4.2.8-11), these boundary conditions may be written in terms of the corresponding auxiliary functions (here, for translation denoted by AT_n, BT_n, CT_n, DT_n, ET_n, FT_n, and GT_n) on the sphere ($\xi = \alpha$) as:

$$\frac{\tilde{\rho}}{c} QT_1 + UT_2 + UT_0 - 2 = 0 \tag{4.2.57}$$

$$UT_2 - UT_0 + 2 = 0 \tag{4.2.58}$$

$$\frac{\tilde{z}}{c} QT_1 + 2WT_1 = 0 \tag{4.2.59}$$

and on the plane ($\xi = 0$)

$$\frac{\tilde{\rho}}{c} QT_1 + UT_2 + UT_0 = 0 \tag{4.2.60}$$

$$UT_2 - UT_0 = 0 \tag{4.2.61}$$

$$\frac{\tilde{z}}{c} QT_1 + 2WT_1 = 0 \tag{4.2.62}$$

Noting that QT_1 similar to the other auxiliary functions is finite, B.C. (4.2.62) indicates that on the wall $(\tilde{z} = 0)$ the value of WT_1 is equal to zero, that is

$$WT_1 = 0 \qquad \text{on}\ \xi = 0 \tag{4.2.63}$$

from which it follows that WT_1, given by (4.2.48), cannot include the terms $\cosh(n + \frac{1}{2})\xi$, and hence $AT'_n = 0$. Therefore, WT_1 reduces to

$$WT_1 = (\cosh\xi - \mu)^{\frac{1}{2}} \sin\eta \sum_{n=1}^{\infty} \left[AT_n \sinh\left(n + \frac{1}{2}\right)\xi \right] P'_n(\mu) \tag{4.2.64}$$

Now, it remains to determine the sets of coefficients AT_n, BT_n, CT_n, DT_n, ET_n, FT_n, and GT_n, appearing in solutions (4.2.49-51, 64). These seven sets of constants are completely determined by imposing six boundary conditions, given by (4.2.57-62), and also applying the continuity equation (4.2.54). Since WT_1 has a more simple form than the other auxiliary functions, it is more convenient to write the boundary conditions (4.2.57-62) in terms of WT_1. Thus, in view of the transformation function (4.2.22), B.C. (4.2.59) is expressed as

$$QT_1 = -\frac{2c}{\tilde{z}} WT_1 = -\frac{2(\cosh\xi - \mu)^{\frac{1}{2}}}{\sinh\xi}\sin\eta \sum_1^{\infty} AT_n(\cosh\xi - \mu)\sinh\left(n + \frac{1}{2}\right)\xi P_n'(\mu)\Big|_{\xi=\alpha} \tag{4.2.65}$$

From B.C.s (4.2.57, 58) it follows that

$$UT_2 = \frac{\tilde{\rho}}{\tilde{z}} WT_1 = \frac{\sin^2\eta}{\sinh\xi}(\cosh\xi - \mu)^{\frac{1}{2}} \sum_1^{\infty} AT_n \sinh\left(n + \frac{1}{2}\right)\xi P_n'(\mu)\Big|_{\xi=\alpha} \tag{4.2.66}$$

Introducing B.C. (4.2.66) to B.C. (4.2.58) gives the boundary condition for UT_0:

$$UT_0 = \frac{\tilde{\rho}}{\tilde{z}} WT_1 + 2 = \frac{\sin^2\eta}{\sinh\xi}(\cosh\xi - \mu)^{\frac{1}{2}} \sum_1^{\infty} AT_n \sinh\left(n + \frac{1}{2}\right)\xi P_n'(\mu)\Big|_{\xi=\alpha} + 2 \tag{4.2.67}$$

Similarly, the boundary condition on the plane are determined by

$$QT_1 = -\lim_{\tilde{z}=0} \frac{2c}{\tilde{z}} WT_1 = -\lim_{\xi=0} \frac{2(\cosh\xi - \mu)^{\frac{1}{2}}}{\sinh\xi}\sin\eta \sum_1^{\infty} AT_n(\cosh\xi - \mu)\sinh\left(n + \frac{1}{2}\right)\xi P_n'(\mu) \tag{4.2.68}$$

$$UT_2 = \lim_{\tilde{z}=0} \frac{\tilde{\rho}}{\tilde{z}} WT_1 = \lim_{\xi=0} \frac{\sin^2\eta}{\sinh\xi}(\cosh\xi - \mu)^{\frac{1}{2}} \sum_1^{\infty} AT_n \sinh\left(n + \frac{1}{2}\right)\xi P_n'(\mu) \tag{4.2.69}$$

$$UT_0 = \lim_{\tilde{z}=0} \frac{\tilde{\rho}}{\tilde{z}} WT_1 = \lim_{\xi=0} \frac{\sin^2\eta}{\sinh\xi}(\cosh\xi - \mu)^{\frac{1}{2}} \sum_1^{\infty} AT_n \sinh\left(n + \frac{1}{2}\right)\xi P_n'(\mu) \tag{4.2.70}$$

Since on the plane $\tilde{z} = 0\,(\xi = 0)$, we take the limit $\xi \to 0$ in order to remove the singularity caused by the dominator.

In view of the recurrence relationship [Macrobert (1967)]

$$(2n+1)\mu P_n'(\mu) = (n+1)P_{n-1}'(\mu) + nP_{n+1}'(\mu) \qquad n \ge 1 \tag{4.2.71}$$

the summation term in B.C.s (4.2.65, 68) (for QT_1) may be written as

$$\sum_1^n AT_n(\cosh\xi - \mu)\sinh\left(n+\frac{1}{2}\right)\xi P_n'(\mu) = \sum_1^n AT_n \cosh\xi \sinh\left(n+\frac{1}{2}\right)\xi P_n'(\mu)$$
$$-\sum_1^n AT_n \sinh\left(n+\frac{1}{2}\right)\xi\left[\frac{n+1}{2n+1}P_{n-1}'(\mu)+\frac{n}{2n+1}P_{n+1}'(\mu)\right] \tag{4.2.72}$$

But, by changing n to n + 1 and n - 1 we have the following relations:

$$\sum_1^\infty AT_n \sinh\left(n+\frac{1}{2}\right)\xi\frac{n+1}{2n+1}P_{n-1}' = \sum_1^\infty AT_{n+1}\sinh\left(n+\frac{3}{2}\right)\xi\frac{n+2}{2n+3}P_n' \tag{4.2.73}$$

$$\sum_1^\infty AT_n \sinh\left(n+\frac{1}{2}\right)\xi\frac{n}{2n+1}P_{n+1}' = \sum_1^\infty AT_{n-1}\sinh\left(n-\frac{1}{2}\right)\xi\frac{n-1}{2n-1}P_n' \tag{4.2.74}$$

In deriving the identities (4.2.73, 74), the limits of summation instead of (0 - ∞) for the right-hand side of (4.2.73) and (2- ∞) for the right-hand side of (4.2.74) are taken to be (1 - ∞) by the use of (4.2.53) and noting that for n =1 the right-hand side of (4.2.74) vanishes. Introducing (4.2.73, 74), written in terms of $\sinh(n+½)\xi$ and $\cosh(n+½)\xi$ by the use of the identities

$$\sinh\left(n+\frac{3}{2}\right)\xi = \sinh\left(n+\frac{1}{2}+1\right)\xi = \sinh\left(n+\frac{1}{2}\right)\xi\cosh\xi + \cosh\left(n+\frac{1}{2}\right)\xi\sinh\xi \tag{4.2.75}$$

$$\sinh\left(n-\frac{1}{2}\right)\xi = \sinh\left(n+\frac{1}{2}-1\right)\xi = \sinh\left(n+\frac{1}{2}\right)\xi\cosh\xi - \cosh\left(n+\frac{1}{2}\right)\xi\sinh\xi \tag{4.2.76}$$

to the relation (4.2.72) leads to

$$\sum_1^n AT_n(\cosh\xi-\mu)\sinh\left(n+\frac{1}{2}\right)\xi P_n'(\mu)$$
$$=\sum_1^\infty\left\{\cosh\xi\sinh\left(n+\frac{1}{2}\right)\xi\left[AT_n-\frac{n+2}{2n+3}AT_{n+1}-\frac{n-1}{2n-1}AT_{n-1}\right]\right.$$
$$\left.+\cosh\left(n+\frac{1}{2}\right)\xi\sinh\xi\left[\frac{n-1}{2n-1}AT_{n-1}-\frac{n+2}{2n+3}AT_{n+1}\right]\right\}P_n' \tag{4.2.77}$$

Now, imposing B.C. (4.2.68) for $\xi = 0$, in the solution (4.2.49), by the use of (4.2.77), results in

$$BT_n = -\operatorname*{Lim}_{\xi=0} \frac{2\sinh\left(n+\frac{1}{2}\right)\xi}{\sinh\xi}\left[AT_n - \frac{n+2}{2n+3}AT_{n+1} - \frac{n-1}{2n-1}AT_{n-1}\right] \qquad (4.2.78)$$

$$-2\left[\frac{n-1}{2n-1}AT_{n-1} - \frac{n+2}{2n+3}AT_{n+1}\right] \qquad n \geq 1$$

or

$$BT_n = (n-1)AT_{n-1} - (2n+1)AT_n + (n+2)AT_{n+1} \qquad n \geq 1 \qquad (4.2.79)$$

Thus, one set of constants of QT_1, namely BT_n, is determined in terms of AT_n by the relationship (4.2.79), upon imposing the no-slip boundary condition on the wall. The other set, namely CT_n, is obtained by imposing the boundary condition on the sphere, given by (4.2.65). Therefore, introducing QT_1, given by (4.2.49), and relationships (4.2.77, 79) to B.C. (4.2.65), for $\xi = \alpha$ results in

$$CT_n \sinh\left(n+\frac{1}{2}\right)\alpha = -\cosh\left(n+\frac{1}{2}\right)\alpha\left[(n-1)AT_{n-1} - (2n+1)AT_n + (n+2)AT_{n+1}\right]$$

$$-2\coth\alpha \sinh\left(n+\frac{1}{2}\right)\alpha\left[\frac{-n+1}{2n-1}AT_{n-1} + AT_n - \frac{n+2}{2n+3}AT_{n+1}\right]$$

$$-2\cosh\left(n+\frac{1}{2}\right)\alpha\left[\frac{n-1}{2n-1}AT_{n-1} - \frac{n+2}{2n+3}AT_{n+1}\right] \qquad n \geq 1$$

(4.2.80)

giving CT_n to be determined by

$$CT_n = -2k_n\left[\frac{n-1}{2n-1}AT_{n-1} - AT_n + \frac{n+2}{2n+3}AT_{n-1}\right] \qquad n \geq 1 \qquad (4.2.81)$$

where we have written

$$k_n = \left(n+\frac{1}{2}\right)\coth\left(n+\frac{1}{2}\right)\alpha - \coth\alpha \qquad (4.2.82)$$

in which the geometry constant α is given by the relation (4.2.22c).

Similarly, from B.C.s (4.2.67, 70) DT_n and ET_n are obtained as

$$DT_n = -\frac{1}{2}(n-1)nAT_{n-1} + \frac{1}{2}(n+1)(n+2)AT_{n+1} \qquad n \geq 0 \qquad (4.2.83)$$

$$ET_n = \frac{2\sqrt{2}e^{-\left(n+\frac{1}{2}\right)\alpha}}{\sinh\left(n+\frac{1}{2}\right)\alpha} + k_n\left[\frac{n(n-1)}{2n-1}AT_{n-1} - \frac{(n+1)(n+2)}{2n+3}AT_{n+1}\right] \quad n \geq 0 \quad (4.2.84)$$

and B.C.s (4.2.66, 69) give FT_n and GT_n to be determined by

$$FT_n = \frac{1}{2}\left(AT_{n-1} - AT_{n+1}\right) \qquad n \geq 2 \qquad (4.2.85)$$

$$GT_n = -k_n\left[\frac{1}{2n-1}AT_{n-1} - \frac{1}{2n+3}AT_{n+1}\right] \qquad n \geq 2 \qquad (4.2.86)$$

In deriving (DT_n, ET_n) and (FT_n, GT_n) the recurence relationships [Macrobert (1967)]

$$(2n+1)\left(1-\mu^2\right)P_n'(\mu) = n(n+1)\left[P_{n-1}(\mu) - P_{n+1}(\mu)\right] \qquad n \geq 1 \qquad (4.2.87)$$

and

$$(2n+1)P_n' = -P_{n-1}'' + P_{n+1}'' \qquad n \geq 1 \qquad (4.2.88)$$

are used, respectively.

In this way, the sets of constants BT_n, CT_n, DT_n, ET_n, FT_n and GT_n are determined in terms of AT_n.

It remains to determine the set of AT_n by the aid of continuity equation, given by (4.2.54). It is observed that each of the following terms, involved in the continuity equation (4.2.54) or equivalently (4.2.16), namely

$$Q_1, \quad \left(\tilde{\rho}\frac{\partial}{\partial\tilde{\rho}} + \tilde{z}\frac{\partial}{\partial\tilde{z}}\right)Q_1, \quad \left(\frac{\partial}{\partial\tilde{\rho}} + \frac{2}{\tilde{\rho}}\right)U_2, \quad \frac{\partial U_0}{\partial\tilde{\rho}}, \quad \frac{\partial W_1}{\partial\tilde{z}}, \qquad (4.2.89)$$

is a particular solution of Eq. (4.2.91) for m = 1, and hence the linear combination of them is a solution of

$$L_1^2\Phi = \frac{\partial^2\Phi}{\partial\tilde{\rho}^2} + \frac{1}{\tilde{\rho}}\frac{\partial\Phi}{\partial\tilde{\rho}} - \frac{\Phi}{\tilde{\rho}^2} + \frac{\partial^2\Phi}{\partial\tilde{z}^2} = 0, \tag{4.2.90}$$

that is the terms in continuity equation may be written as

$$\Phi_1 = (\cosh\xi - \mu)^{\frac{1}{2}} \sin\eta \sum_{n=1}^{\infty}\left[MT_n \cosh\left(n+\frac{1}{2}\right)\xi + NT_n \sinh\left(n+\frac{1}{2}\right)\xi\right]P_n'(\mu) \tag{4.2.91}$$

in which Φ_1 is equal to the sum of all terms appearing in the continuity equation. Thus, if the sets of constant M_n and N_n is equated to zero, the continuity equation

$$\Phi_1 = 0 \tag{4.2.92}$$

is satisfied. Therefore, it remains to write each of the terms appearing in the continuity equation (4.2.54) in the form of relation (4.2.91) to determine the sets of constant M_n and N_n. Q1, given by (4.2.49), is already in this form. The other terms are determined as follows: The first term may be evaluated as

$$\begin{aligned}
&- \mu \sinh\xi \frac{\partial Q_1}{\partial\xi} - \sin\eta \cosh\xi \frac{\partial Q_1}{\partial\eta} = -\frac{1}{2}\mu \sinh\xi \times \\
&\Big\{\sin\eta \sinh\xi(\cosh\xi - \mu)^{-\frac{1}{2}} \sum_{1}^{\infty}\left[BT_n \cosh\left(n+\frac{1}{2}\right)\xi + CT_n \sinh\left(n+\frac{1}{2}\right)\xi\right]P_n' \\
&\sin\eta(\cosh\xi - \mu)^{\frac{1}{2}} \sum_{1}^{\infty}(2n+1)\left[BT_n \sinh\left(n+\frac{1}{2}\right)\xi + CT_n \cosh\left(n+\frac{1}{2}\right)\xi\right]P_n'\Big\} \\
&- \sin\eta \cosh\xi \Bigg\{\left[\frac{1}{2}\sin^2\eta(\cosh\xi - \mu)^{-\frac{1}{2}} - \mu(\cosh\xi - \mu)^{\frac{1}{2}}\right] \times \\
&\sum_{1}^{\infty}\left[BT_n \sinh\left(n+\frac{1}{2}\right)\xi + CT_n \cosh\left(n+\frac{1}{2}\right)\xi\right]P_n' \\
&+ \sin^2\eta(\cosh\xi - \mu)^{+\frac{1}{2}} \sum_{1}^{\infty}\left[BT_n \sinh\left(n+\frac{1}{2}\right)\xi + CT_n \cosh\left(n+\frac{1}{2}\right)\xi\right]P_n''\Bigg\}
\end{aligned} \tag{4.2.93}$$

In view of the relation [Macrobert (1967)]

$$\frac{d}{d\mu}\left[(1-\mu^2)\frac{dP_n}{d\mu}\right] = -n(n+1)P_n = -(n+1)\left(\mu P_n' - P_{n-1}'\right) \qquad n \geq 1 \tag{4.2.94}$$

the relation (4.2.93) may be written in terms of P_n' as

$$-\mu \sinh\xi \frac{\partial Q_1}{\partial \xi} - \sin\eta \cosh\xi \frac{\partial Q_1}{\partial \eta} = \sin\eta(\cosh\xi - \mu)^{\frac{1}{2}} \times$$
$$\sum_1^{\infty} \left\{ \left[\left(\frac{1-n}{2}\right) BT_{n-1} - BT_n + \left(\frac{n+2}{2}\right) BT_{n+1} \right] \cosh\left(n+\frac{1}{2}\right)\xi \right. \tag{4.2.95}$$
$$\left. + \left[\left(\frac{1-n}{2}\right) CT_{n-1} - CT_n + \left(\frac{n+2}{2}\right) CT_{n+1} \right] \sinh\left(n+\frac{1}{2}\right)\xi \right\} P_n'$$

The third term in the continuity equation may also be expressed as

$$-\left[\sin\eta \sinh\xi \frac{\partial}{\partial \xi} + (1-\mu\cosh\xi)\frac{\partial}{\partial \eta} + \frac{2(\cosh\xi-\mu)}{\sin\eta} \right] U_2 = -\sin\eta\sinh\xi \times$$
$$\left\{ \frac{1}{2}\sin^2\eta \sinh\xi(\cosh\xi-\mu)^{-\frac{1}{2}} \sum \left[FT_n \cosh\left(n+\frac{1}{2}\right)\xi + GT_n \sinh\left(n+\frac{1}{2}\right)\xi \right] P_n'' \right.$$
$$\left. + \frac{1}{2}\sin^2\eta \sinh\xi(\cosh\xi-\mu)^{-\frac{1}{2}} \sum \left(n+\frac{1}{2}\right) \left[FT_n \sinh\left(n+\frac{1}{2}\right)\xi + GT_n \cosh\left(n+\frac{1}{2}\right)\xi \right] P_n'' \right\}$$
$$-(1-\mu\cosh\xi) \left\{ \left[\frac{1}{2}\sin^3\eta(\cosh\xi-\mu)^{-\frac{1}{2}} + 2\sin\eta\,\mu(\cosh\xi-\mu)^{\frac{1}{2}} \right] \times \right.$$
$$\sum \left[FT_n \cosh\left(n+\frac{1}{2}\right)\xi + GT_n \sinh\left(n+\frac{1}{2}\right)\xi \right] P_n''$$
$$-\sin^3\eta(\cosh\xi-\mu)^{\frac{1}{2}} \left\{ \sum \left[FT_n \cosh\left(n+\frac{1}{2}\right)\xi + GT_n \sinh\left(n+\frac{1}{2}\right)\xi \right] P_n''' \right\}$$
$$+2\sin\eta(\cosh\xi-\mu)^{\frac{1}{2}} \sum (\cosh\xi-\mu) \left[FT_n \cosh\left(n+\frac{1}{2}\right)\xi + GT_n \sinh\left(n+\frac{1}{2}\right)\xi \right] P_n''$$

(4.2.96)

By the use of relation (4.2.94) and its derivative, the relation (4.2.96) is determined by

$$-\left[\sin\eta \sinh\xi \frac{\partial}{\partial \xi} + (1-\mu\cosh\xi)\frac{\partial}{\partial \eta} + \frac{2(\cosh\xi-\mu)}{\sin\eta} \right] U_2 = \sin\eta(\cosh\xi-\mu)^{\frac{1}{2}} \times$$
$$\sum_1^{\infty} \left\{ \left[\frac{(n-1)(n-2)}{2} FT_{n-1} - (n-1)(n+2)FT_n + \frac{(n+2)(n+3)}{2} FT_{n+1} \right] \cosh\left(n+\frac{1}{2}\right)\xi \right.$$
$$\left. + \left[\frac{(n-1)(n-2)}{2} GT_{n-1} - (n-1)(n+2)GT_n + \frac{(n+2)(n+3)}{2} GT_{n+1} \right] \sinh\left(n+\frac{1}{2}\right)\xi \right\} P_n'$$

(4.2.97)

Similarly,

$$-\left[\sin\eta\sinh\xi\frac{\partial}{\partial\xi}+\left(1-\mu\cosh\xi\right)\frac{\partial}{\partial\eta}\right]U_0=$$

$$\sin\eta\left(\cosh\xi-\mu\right)^{\frac{1}{2}}\sum_1^{\infty}\left\{\left[-\frac{1}{2}DT_{n-1}+DT_n-\frac{1}{2}DT_{n+1}\right]\cosh\left(n+\frac{1}{2}\right)\xi\right. \tag{4.2.98}$$

$$\left.+\left[-\frac{1}{2}ET_{n-1}+ET_n-\frac{1}{2}ET_{n+1}\right]\sinh\left(n+\frac{1}{2}\right)\xi\right\}P_n'$$

$$\left[\left(1-\mu\cosh\xi\right)\frac{\partial}{\partial\xi}-\sin\eta\sinh\xi\frac{\partial}{\partial\eta}\right]W_1=\sin\eta\left(\cosh\xi-\mu\right)^{\frac{1}{2}}\times$$

$$\sum_1^{\infty}\left[-\frac{(n-1)}{2}AT_{n-1}+\left(n+\frac{1}{2}\right)AT_n-\left(\frac{n+2}{2}\right)AT_{n+1}\right]\cosh\left(n+\frac{1}{2}\right)\xi P_n' \tag{4.2.99}$$

Now, in view of (4.2.49, 95, 97-99), the continuity equation (4.2.54) may be written as

$$\sin\eta\left(\cosh\xi-\mu\right)^{\frac{1}{2}}\sum_1^{\infty}\left\{\left[-\left(\frac{n-1}{2}\right)BT_{n-1}+\frac{5}{2}BT_n+\left(\frac{n+2}{2}\right)BT_{n+1}-\frac{1}{2}DT_{n-1}\right.\right.$$

$$+DT_n-\frac{1}{2}DT_{n+1}+\frac{(n-1)(n-2)}{2}FT_{n-1}-(n-1)(n+2)FT_n$$

$$\left.+\frac{(n+2)(n+3)}{2}FT_{n+1}-(n-1)AT_{n-1}+2\left(n+\frac{1}{2}\right)AT_n-(n+2)AT_{n+1}\right]\cosh\left(n+\frac{1}{2}\right)\xi$$

$$+\left[-\left(\frac{n-1}{2}\right)CT_{n-1}+\frac{5}{2}CT_n+\left(\frac{n+2}{2}\right)CT_{n+1}-\frac{1}{2}ET_{n-1}+ET_n-\frac{1}{2}ET_{n+1}\right.$$

$$\left.\left.\frac{(n-1)(n-2)}{2}GT_{n-1}-(n-1)(n+2)GT_n+\frac{(n+2)(n+3)}{2}GT_{n+1}\right]\sinh\left(n+\frac{1}{2}\right)\xi\right\}P_n'=0$$

(4.2.100)

Therefore, it is satisfied for all ξ and η, if the coefficients of $\cosh\left(n+\frac{1}{2}\right)\xi$ and $\sinh\left(n+\frac{1}{2}\right)\xi$ in (4.2.100) are equated to zero, that is

$$\begin{aligned}&-(n-1)BT_{n-1}+5BT_n+(n+2)BT_{n+1}-DT_{n-1}+2DT_n-DT_{n+1}\\&+(n-1)(n-2)FT_{n-1}-2(n-1)(n+2)FT_n+(n+2)(n+3)FT_{n+1}\\&-2(n-1)AT_{n-1}+2(2n+1)AT_n-2(n+2)AT_{n+1}=0\end{aligned} \tag{4.2.101}$$

$$
\begin{aligned}
&-(n-1)CT_{n-1}+5CT_n+(n+2)CT_{n+1}-ET_{n-1}+2ET_n-ET_{n+1}\\
&+(n-1)(n-2)GT_{n-1}-2(n-1)(n+2)GT_n+(n+2)(n+3)GT_{n+1}=0
\end{aligned}
\tag{4.2.102}
$$

If we expressed the relation (4.2.101) and (4.2.102) in terms of A_ns, by the aid of (4.2.79, 81-86), the former is observed to be automatically satisfied, and the latter gives a relation for A_ns:

$$
\begin{aligned}
&\left[(2n-1)k_{n-1}-(2n-3)k_n\right]\left[\frac{n-1}{2n-1}AT_{n-1}-\frac{n}{2n+1}AT_n\right]\\
&-\left[(2n+5)k_n-(2n+3)k_{n+1}\right]\left[\frac{n+1}{2n+1}AT_n-\frac{n+2}{2n+3}AT_{n+1}\right]\\
&=\sqrt{2}\left[2\coth\left(n+\frac{1}{2}\right)\alpha-\coth\left(n-\frac{1}{2}\right)\alpha-\coth\left(n+\frac{3}{2}\right)\alpha\right] \qquad n\geq 1
\end{aligned}
\tag{4.2.103}
$$

in which k_n are given by (4.2.82). This generates n equations for (n+1) unknowns, A_1, A_2,...A_n, A_{n+1}. But, since the flow field is finite, the auxiliary functions, given by (4.2.48-51), have to converge at all points of the domain, and hence, in view of (4.2.79, 81-86), it is required that

$$
A_n \rightarrow 0 \qquad \text{as } n \rightarrow \infty \tag{4.2.104}
$$

Therefore, the set of $A_n^{'}$s up to some level (depending on the desired accuracy), n = N, is completely determined by letting $A_{N+1} = 0$, upon construction of the matrix of the coefficients. By knowing the set of $A_n^{'}$s, the other sets of coefficients are completely determined by relations (4.2.79, 81-86). Their summations over n are programmed in "CoefTran".

The domain of interest is divided into (K+1)×(L+1) nodes constructed by a net of bipolar coordinates in which K is the number of intervals on the ξ- coordinates and L the number of intervals on the η-coordinates. They are illustrated in Fig. 4.1. This figure corresponds to K = 3, L=30, and $\delta = 0.05$. The difference between each coordinates h_ξ and h_η is chosen to be a constant. They are determined by

$$
h_\xi = \frac{\alpha}{K}, \qquad h_\eta = \frac{\pi}{L} \tag{4.2.105}
$$

in which α is given by (A.42). Each node is addressed by its number, j, [j = 1 - (K+1)×(L+1)]. The number of nodes starts at the origin ($\xi = 0$, $\eta = \pi$), increases with increasing the ξ- coordinate and with decreasing the η-coordinate, as shown in Fig 4.1, that is j = 1denotes the nodes located at the origin ($\xi = 0$, $\eta = \pi$); j = K+1 is the node located at nearest point of the sphere to the plane (intersection of the z-axis and the below sphere, $\xi = \alpha$, $\eta = \pi$), j = K+2 the node at the point ($\xi = 0$, $\eta = \pi - h_\eta$), j = 2(K+1) the node at the point ($\xi = \alpha$, $\eta = \pi - h_\eta$); J = (K+1)L +1 the node located at infinity ($\xi = 0$, $\eta = 0$), and j= (K+1)(L+1) the node at intersection of the above z-axis and sphere ($\xi = \alpha$, $\eta = 0$).

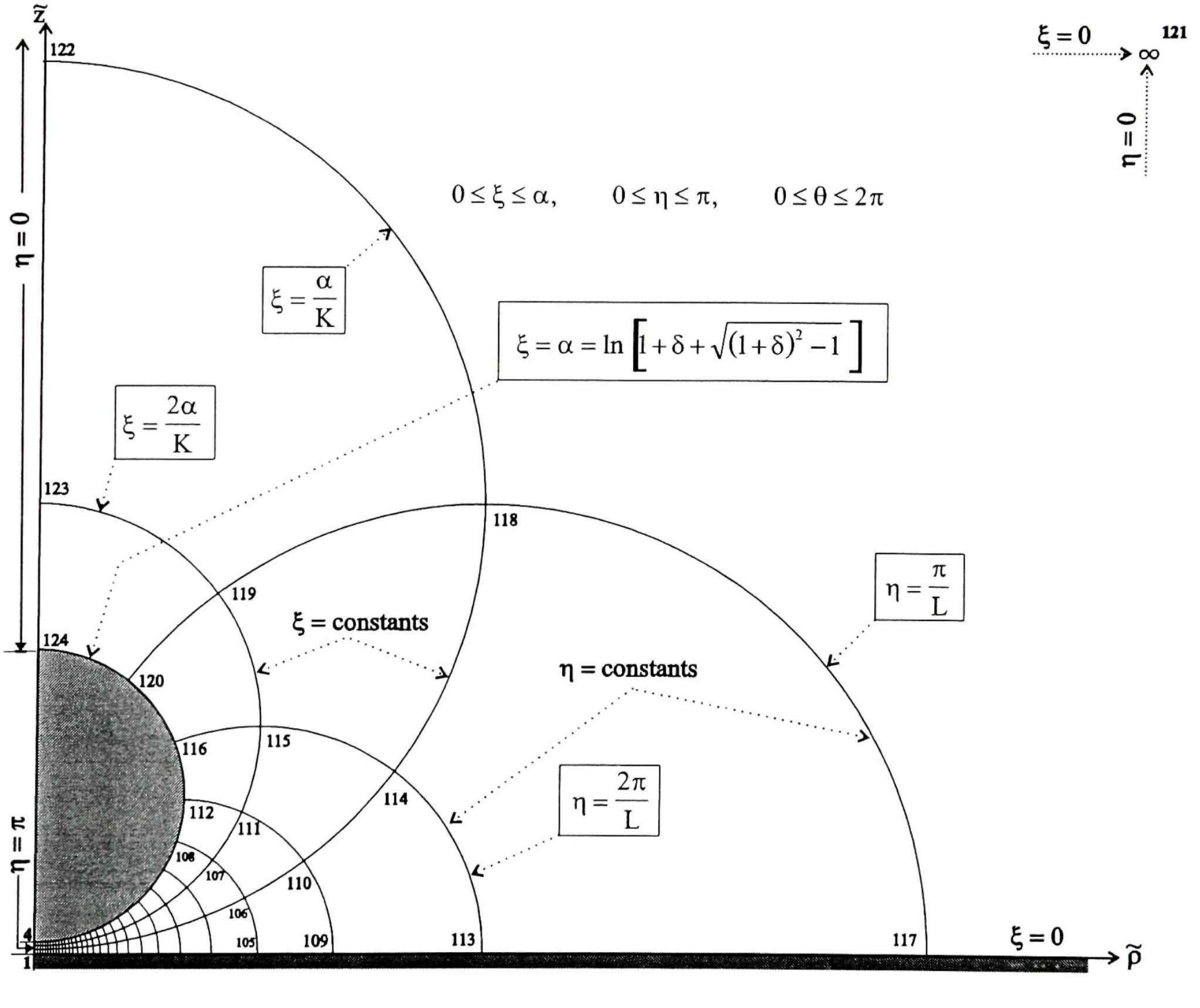


Fig. 4.1 - Distribution of nodes (1 - 124) in bipolar coordinate system (ξ, η, θ) on the plane $\theta = 0$.

The Legendre polynomials, $P_i(\mu)$, ($\mu = \cos\eta$), and their derivatives with respect to μ are generated by the following relations: [Macrobert (1967)]

$$\begin{array}{llll} P_0 = 1, & P_1 = \mu, & P_i = \dfrac{2i-1}{i}\mu P_{i-1} - \dfrac{i-1}{i}P_{i-2} & \text{for } i \geq 2 \\ P_0^{'} = 0, & P_1^{'} = 1, & P_i^{'} = \mu P_{i-1}^{'} + P_{i-1} & \text{for } i \geq 2 \\ P_0^{''} = 0, & P_1^{''} = 0, & P_i^{''} = \mu P_{i-1}^{''} + P_{i-1}^{'} & \text{for } i \geq 2 \\ P_0^{'''} = 0, & P_1^{'''} = 0, & P_i^{''} = \mu P_{i-1}^{'''} + (i+2)P_{i-1}^{''} & \text{for } i \geq 2 \end{array} \tag{4.2.106}$$

They are programmed in “PmuEq42106P” for each node j, with the notation

$$P(i, j) = P_i(\mu_j);\ P1(i, j) = P_i^{'}(\mu_j);\ P2(i, j) = P_i^{''}(\mu_j);\ P3(i, j) = P_i^{'''}(\mu_j) \tag{4.2.107}$$

The summation over n of the auxiliary functions WT_1, QT_1, UT_0 and UT_2 , given by (4.2.64, 49-51), and their derivatives with respect to ξ which are needed in the subsequent section are determined in the programs “W1Eq4264, “Q1Eq4249", “U0Eq4250” and “U2Eq4251”. The cylindrical components of the velocity in (4.2.9-11) may be written as

$$\tilde{u}_\rho T = V_\rho T\cos\theta, \qquad \tilde{u}_\theta T = V_\theta T\sin\theta, \qquad \tilde{u}_z T = V_z T\cos\theta \tag{4.2.108}$$

in which $\left(V_\rho T,\ V_\theta T,\ V_z T\right)$ are defined by

$$V_\rho T = \frac{1}{2}\left[\frac{\tilde{\rho}}{c}Q_1 T + \left(U_2 T + U_0 T - 2\right)\right], \tag{4.2.109}$$

$$V_\theta T = \frac{1}{2}\left(U_2 T - U_0 T + 2\right), \tag{4.2.110}$$

$$V_z T = \frac{1}{2}\frac{\tilde{z}}{c}Q_1 T + W_1 T \tag{4.2.111}$$

The bipolar components of the velocity may be written as

$$\tilde{u}_\xi T = V_\xi T\cos\theta, \qquad \tilde{u}_\theta T = V_\theta T\sin\theta, \qquad \tilde{u}_\eta T = V_\eta T\cos\theta \tag{4.2.112}$$

in which $\left(V_\xi T,\ V_\theta T,\ V_\eta T\right)$ are determined by relations (4.2.109-111) and (A51, 52):

$$V_\xi T = \frac{-\sinh\xi\sin\eta}{\cosh\xi - \cos\eta}V_\rho T + \frac{1-\cosh\xi\cos\eta}{\cosh\xi - \cos\eta}V_z T \tag{4.2.113}$$

$$V_\eta T = \frac{\text{conh}\,\xi \cos\eta - 1}{\cosh\xi - \cos\eta} V_\rho T + \frac{-\sinh\xi \sin\eta}{\cosh\xi - \cos\eta} V_z T \tag{4.2.114}$$

The cylindrical and bipolar components of the velocity are determined by the program "VTBConTran", upon the use of relations (4.2.108-114). Since the bipolar coordinate system has a singularity at infinity ($\xi = 0, \eta = 0$) [c.f., (4.2.22)], to avoid this singularity in the dominator, this node is excluded in the calculation, the value of which is pre-described by imposing the boundary condition at infinity.

To see how this solution works, an example of the distribution of the flow field in the plane $\theta = 0$, for a mesh size (K=3, L =30) is tabulated in Tables B1-5 for $\delta = 0.05$ (which is correspond to Fig. 4.1), in Table B6 for $\delta = 2$, and in Table B7 for $\delta = 10^{-6}$. These Tables are located in Appendix B. For $\delta = 0.05$, hundred and twenty terms (N=120) are considered in the summation over n (n = 0 -120) in Eq.s (4.49-51, 64), for calculation of the auxiliary functions. Tables B1-5 shows that boundary conditions are satisfied up to fourteen digits of accuracy for all points of the domain. For $\delta = 2$, only twenty two terms are considered (N=22) in the summation for which the boundary conditions are satisfied with the same accuracy at all points except for the two points located at the intersection of the sphere and z-axis (c.f., Table B6 nodes 5 and 124) which is within thirteen digits of accuracy. If one more term were added to the summation (i.e. for N = 23), the approximation of these two points would be improved beyond fourteen digits of accuracy. For $\delta = 10^{-6}$, N is taken to be 5600 terms, the maximum capacity for MATLAB software. It is observed from Table B7 that despite this large number of terms the accuracy is less than two digits (c.f., node number 4). To improve the accuracy of the flow field for this case the addition of many more terms is required.

Therefore, though there is no restriction for the particle wall distances, the smaller the gap width, the slower the convergence, that is as $\delta \to 0$, (the rate of convergent)$\to 0$, and for $\delta = 0$, since the problem is faced with a singularity at the origin, it never converges.

4.2.3-Rotation of Particle

Since the flow at infinity is already imposed on the definition of the auxiliary functions for the translation of the particle, given by (4.2.8-11), for the rotation of the particle the suitable auxiliary function with a minor modification of the original solution are

$$\tilde{p}_R = \tilde{\Omega}\,\frac{QR_1}{c}\cos\theta, \tag{4.2.115}$$

$$\tilde{u}_{\rho R} = \frac{\tilde{\Omega}}{2}\left[\frac{\tilde{\rho}}{c}QR_1 + \left(UR_2 + UR_0\right)\right]\cos\theta, \tag{4.2.116}$$

$$\tilde{u}_{\theta R} = \frac{\tilde{\Omega}}{2}\left(UR_2 - UR_0\right)\sin\theta, \tag{4.2.117}$$

$$\tilde{u}_{zR} = \frac{\tilde{\Omega}}{2}\left(\frac{\tilde{z}}{c}QR_1 + 2WR_1\right)\cos\theta \tag{4.2.118}$$

Here, the indices R denote the rotation. Thus, they satisfy the same equations as those for the translation of the particle, since the reduction of the constant velocity at infinity does not affect the derivative of the velocity appearing in the equations of motion, and hence their solutions are the same as those obtained by (4.2. 49-51, 64). Its boundary conditions on the sphere are [c.f., B.C.s (3.2.8-10)]

$$\tilde{u}_{\rho R} = \tilde{\Omega}(\tilde{z} - d)\cos\theta,\ \tilde{u}_{\theta R} = -\tilde{\Omega}(\tilde{z} - d)\sin\theta,\ \tilde{u}_{zR} = -\tilde{\Omega}\,\tilde{\rho}\cos\theta,\quad \text{on}\, S_P \tag{4.2.119}$$

in which $d = 1 + \delta$, and those on the wall $(\tilde{z} = 0)$

$$\tilde{u}_{\rho R} = 0, \qquad \tilde{u}_{\theta R} = 0, \qquad \tilde{u}_{zR} = 0 \qquad \text{on}\ S_W \tag{4.2.120}$$

and at far distances from the origin

$$\tilde{u}_{\rho R} = 0, \qquad \tilde{u}_{\theta R} = 0, \qquad \tilde{u}_{zR} = 0 \qquad \text{as}\ |\vec{\tilde{r}}| \to \infty \tag{4.2.121}$$

The boundary conditions on the sphere may be expressed in terms of the auxiliary functions as

$$\frac{\tilde{\rho}}{c}QR_1 + \left(UR_2 + UR_0\right) = 2(\tilde{z} - 1 - \delta), \qquad \text{on}\ \xi = \alpha \tag{4.2.122}$$

$$UR_2 - UR_0 = -2(\tilde{z} - 1 - \delta), \qquad \text{on}\ \xi = \alpha \tag{4.2.123}$$

$$\frac{\tilde{z}}{c}QR_1 + 2WR_1 = -2\tilde{\rho} \qquad \text{on}\ \xi = \alpha \tag{4.2.124}$$

and on the wall and at infinity as

$$\frac{\tilde{\rho}}{c}QR_1 + \left(UR_2 + UR_0\right) = 0, \qquad \text{on } \xi = 0 \tag{4.2.125}$$

$$UR_2 - UR_0 = 0, \qquad \text{on } \xi = 0 \tag{4.2.126}$$

$$\frac{\tilde{z}}{c}QR_1 + 2WR_1 = 0 \qquad \text{on } \xi = 0 \tag{4.2.127}$$

Dean and O'Neill (1963), by imposing these boundary conditions in the solution of auxiliary functions, given by (4.2.49-51, 64), and by applying the continuity equation, given by (4.2.54), obtained the coefficients of the auxiliary functions, with the same procedure as that outlined for the translation of the particle as

$$\begin{aligned}
&\left[(2n-1)k_{n-1} - (2n-3)k_n\right]\left[\frac{n-1}{2n-1}AR_{n-1} - \frac{n}{2n+1}AR_n\right] \\
&-\left[(2n+5)k_n - (2n+3)k_{n+1}\right]\left[\frac{n+1}{2n+1}AR_n - \frac{n+2}{2n+3}AR_{n+1}\right] = \\
&\frac{\sqrt{2}e^{-\left(n+\frac{1}{2}\right)\alpha}}{(2n+1)}\left[2(2n+1)^2\left(\frac{e^{\alpha}}{2n-1} + \frac{e^{-\alpha}}{2n+3}\right)\operatorname{cosech}\left(n+\frac{1}{2}\right)\alpha\right. \\
&\left.-(2n-1)\operatorname{cosech}\left(n-\frac{1}{2}\right)\alpha - (2n+3)\operatorname{cosech}\left(n+\frac{3}{2}\right)\alpha\right] \qquad n \geq 1
\end{aligned} \tag{4.2.128}$$

$$BR_n = (n-1)AR_{n-1} - (2n+1)AR_n + (n+2)AR_{n+1} \qquad n \geq 1 \tag{4.2.129}$$

$$\begin{aligned}
CR_n &= 4\lambda_n \operatorname{cosech}\left(n+\frac{1}{2}\right)\alpha \\
&-2k_n\left[\frac{n-1}{2n-1}AR_{n-1} - AR_n + \frac{n+2}{2n+3}AT_{n-1}\right] \qquad n \geq 1
\end{aligned} \tag{4.2.130}$$

$$DR_n = -\frac{1}{2}(n-1)nAR_{n-1} + \frac{1}{2}(n+1)(n+2)AR_{n+1} \qquad n \geq 0 \tag{4.2.131}$$

$$FR_n = \frac{1}{2}\left(AR_{n-1} - AR_{n+1}\right) \qquad n \geq 2 \tag{4.2.132}$$

$$ER_n = \left[\sqrt{2}(2n+1)e^{-\left(n+\frac{1}{2}\right)\alpha} \text{sihh}\alpha - \lambda_n\right] \text{cosech}\left(n+\frac{1}{2}\right)\alpha$$

$$+k_n\left[\frac{n(n-1)}{2n-1}AR_{n-1} - \frac{(n+1)(n+2)}{2n+3}AR_{n+1}\right] \quad n \geq 0 \tag{4.2.133}$$

$$GR_n = -4\lambda_n \text{cosech}\left(n+\frac{1}{2}\right)\alpha - k_n\left[\frac{1}{2n-1}AR_{n-1} - \frac{1}{2n+3}AR_{n+1}\right] \qquad n \geq 2$$

(4.2.134)

in which α and k_n are given by the relations (4.2.22c, 82) and λ_n is defined by

$$\lambda_n = -\frac{\sqrt{2}}{2}\left[\frac{e^{-\left(n-\frac{1}{2}\right)\alpha}}{2n-1} - \frac{e^{-\left(n+\frac{3}{2}\right)\alpha}}{2n+3}\right] \tag{4.2.135}$$

They are programed in "CoefRot" from which the velocity field, given by (4.2.109-11), is determined in the program"VR".

The cylindrical components of the velocity in (4.2.116-118) may be written as

$$\tilde{u}_\rho R = V_\rho R\cos\theta, \qquad \tilde{u}_\theta R = V_\theta R\sin\theta, \qquad \tilde{u}_z R = V_z R\cos\theta \tag{4.2.136}$$

in which $\left(V_\rho R,\ V_\theta R,\ V_z R\right)$ are defined by

$$V_\rho R = \frac{1}{2}\left[\frac{\tilde{\rho}}{c}Q_1 R + \left(U_2 R + U_0 R\right)\right], \tag{4.2.137}$$

$$V_\theta R = \frac{1}{2}\left(U_2 R - U_0 R\right), \tag{4.2.138}$$

$$V_z R = \frac{1}{2}\frac{\tilde{z}}{c}Q_1 R + W_1 R \tag{4.2.139}$$

The bipolar components of the velocity may be expressed as

$$\tilde{u}_\xi R = V_\xi R\cos\theta, \qquad \tilde{u}_\theta R = V_\theta R\sin\theta, \qquad \tilde{u}_\eta R = V_\eta R\cos\theta \tag{4.2.140}$$

in which $\left(V_\xi R,\ V_\theta R,\ V_\eta R\right)$ are determined by relations (4.2.136-139) and (A51, 52) as

$$V_\xi R = \frac{-\sinh\xi\sin\eta}{\cosh\xi - \cos\eta}V_\rho R + \frac{1-\text{conh}\,\xi\cos\eta}{\cosh\xi-\cos\eta}V_z R \tag{4.2.141}$$

$$V_\eta R = \frac{\text{conh}\,\xi \cos\eta - 1}{\cosh\xi - \cos\eta} V_\rho R + \frac{-\sinh\xi \sin\eta}{\cosh\xi - \cos\eta} V_z R \tag{4.2.142}$$

An example of its calculation for $\widetilde{\Omega} = 1$ and $\delta = 0.05$ is tabulated in Table B8, 9 for $\widetilde{u}_{\rho R}$ and $\widetilde{u}_{zR}$ on the plane $\theta = 0$, and in Table B10 for $\widetilde{u}_{\theta R}$ on the plane $\theta = \pi/2$, given in Appendix B. In the calculation N =120. We see how boundary conditions, especially on the intersections of the sphere and z-axis (nodes 4 and 124), and on the leading point of the sphere (c.f., Fig. 4.1, node 112) are satisfied up to 14 digits of accuracy.

4.2.4 - Translation and Rotation of Particle

The flow field produced by translation and rotation of a sphere with linear velocity $\vec{u} = (U, 0, 0)$ and angular velocity $\vec{\Omega} = (0, \Omega, 0)$, with the ratio of which given by r (= aΩ/U), is obtained upon the linear combination (superimposition) of the solution for translation and rotation of the particle determined in § 4.2.2 and § 4.2.3. The bipolar components of the velocity may be expressed as

$$\widetilde{u}_\xi = V_\xi \cos\theta, \qquad \widetilde{u}_\theta = V_\theta \sin\theta, \qquad \widetilde{u}_\eta = V_\eta \cos\theta \tag{4.2.143}$$

where we have written

$$V_\xi = qV_\xi T + rV_\xi R,\ V_\theta = qV_\theta T + rV_\theta R,\ V_\eta = qV_\eta T + rV_\eta R,\ r = \frac{a\Omega}{U},\ q = (1 \text{ or } 0) \tag{4.2.144}$$

from which the steady state components of the velocity are determined by

$$\begin{aligned} V_\xi = -\frac{1}{2}\sin\eta(\cosh\xi - \mu)^{-\frac{1}{2}}\Bigg\{ & -2(1-\mu\cosh\xi)\sum_1^\infty A_n \sinh\left(n+\frac{1}{2}\right)\xi P_n' \\ & +\mu\sinh\xi\sum_1^\infty\left[B_n\cosh\left(n+\frac{1}{2}\right)\xi + C_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n' \\ & +(1-\mu^2)\sinh\xi\sum_2^\infty\left[F_n\cosh\left(n+\frac{1}{2}\right)\xi + G_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n'' \\ & +\sinh\xi\sum_0^\infty\left[D_n\cosh\left(n+\frac{1}{2}\right)\xi + E_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n\Bigg\} + \frac{\sinh\xi\sin\eta}{\cosh\xi - \cos\eta} \end{aligned} \tag{4.2.145}$$

$$V_\eta = -\frac{1}{2}(\cosh\xi - \mu)^{-\frac{1}{2}}\left\{2\sin^2\eta\sinh\xi\sum_1^\infty A_n \sinh\left(n+\frac{1}{2}\right)\xi P_n^{'}\right.$$
$$+(1-\mu\cosh\xi)\sinh\xi\sum_0^\infty\left[D_n\cosh\left(n+\frac{1}{2}\right)\xi + E_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n$$
$$+\sin^2\eta(1-\mu\cosh\xi)\sum_2^\infty\left[F_n\cosh\left(n+\frac{1}{2}\right)\xi + G_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n^{''}$$
$$\left.+\sin^2\eta\cosh\xi\sum_1^\infty\left[B_n\cosh\left(n+\frac{1}{2}\right)\xi + C_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n^{'}\right\} + \frac{\text{conh}\,\xi\cos\eta - 1}{\cosh\xi - \cos\eta} \tag{4.2.146}$$

$$V_\theta = \frac{1}{2}(\cosh\xi - \mu)^{\frac{1}{2}}\left\{\sum_0^\infty\left[D_n\cosh\left(n+\frac{1}{2}\right)\xi + E_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n(\mu)\right.$$
$$\left.+\sin^2\eta\sum_2^\infty\left[F_n\cosh\left(n+\frac{1}{2}\right)\xi + G_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n^{''}(\mu)\right\} - 1 \tag{4.2.147}$$

where we have written

$$K_n = qKT_n + rKR_n \qquad K = (A, B, C, D, E, F, G), \qquad \mu = \cos\eta \tag{4.2.148}$$

When just rotation of the particle is considered $q = 0$ and $r = 1$, otherwise $q = 1$ and $r = a\Omega/U$. For the former, the characteristic velocity would be $a\Omega$ instead of U.

4.3 - Electroviscous Ion Concentrations for Low Pe

4.3.1- Electroviscous Equations

The equations and boundary conditions for electroviscous ion concentrations in the expansion (3.4.1), for Pe << 1, at order Pe are given by (3.4.2-5), and at order Pe^2 by (3.4.7-10). They may be expressed in the bipolar coordinate system (ξ, η, θ), for $\tilde{c}_{21}$ as [c.f., (A.45)]

$$\left[(\cosh\xi - \cos\eta)\left(\frac{\partial^2}{\partial\xi^2} + \frac{\partial^2}{\partial\eta^2} + \frac{1}{\sin^2\eta}\frac{\partial^2}{\partial\theta^2}\right)\right.$$
$$\left.-\sinh\xi\frac{\partial}{\partial\xi} + \frac{\cosh\xi\cos\eta - 1}{\sin\eta}\frac{\partial}{\partial\eta}\right]\tilde{c}_{21} = 0 \tag{4.3.1}$$

with boundary conditions [c.f., (A.44)]

$$\frac{\partial \tilde{c}_{21}}{\partial \xi} = F_{cJ}(\cosh\xi - \cos\eta)\frac{\partial}{\partial \xi}\left[(\cosh\xi - \cos\eta)\frac{\partial}{\partial \xi}\right]\tilde{u}_{\xi} \qquad \text{on } S_J \quad J = (P, W) \tag{4.3.2}$$

$$\tilde{c}_{21} \to 0 \qquad \text{as}(\xi, \eta) \to 0 \tag{4.3.3}$$

and for $\tilde{c}_{22}$ as

$$\frac{1}{c^2}\left[(\cosh\xi - \cos\eta)^2\left(\frac{\partial^2 \tilde{c}_{22}}{\partial \xi^2} + \frac{\partial^2 \tilde{c}_{22}}{\partial \eta^2} + \frac{1}{\sin^2\eta}\frac{\partial^2 \tilde{c}_{22}}{\partial \theta^2}\right) + (\cosh\xi - \cos\eta)\left(-\sinh\xi\frac{\partial \tilde{c}_{22}}{\partial \xi} + \frac{\cosh\xi\cos\eta - 1}{\sin\eta}\frac{\partial \tilde{c}_{22}}{\partial \eta}\right)\right] = \vec{\tilde{u}} \cdot \nabla \tilde{c}_{21} \tag{4.3.4}$$

with

$$\frac{\partial \tilde{c}_{22}}{\partial \xi} = 0 \qquad \text{on } S_J \tag{4.3.5}$$

$$\tilde{c}_{22} \to 0 \qquad \text{as}(\xi, \eta) \to 0 \tag{4.3.6}$$

The geometry constant c in Eq. (4.3.4) is defined by (A.41). Because of symmetry properties, as observed in Chapter 3, if we define

$$\tilde{c}_{21} = F_{cP} C_{21} \cos\theta, \tag{4.3.7}$$

$$\tilde{c}_{22} = F_{cP}(C_{20} + C_{22}\cos 2\theta) \tag{4.3.8}$$

at order Pe, C_{21} satisfies

$$\left[(\cosh\xi - \cos\eta)\left(\frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2} - \frac{1}{\sin^2\eta}\right) - \sinh\xi\frac{\partial}{\partial \xi} + \frac{\cosh\xi\cos\eta - 1}{\sin\eta}\frac{\partial}{\partial \eta}\right]C_{21} = 0$$

with boundary conditions [c.f., (4.2.134)] (4.3.9)

$$\frac{\partial C_{21}}{\partial \xi} = (\cosh\xi - \cos\eta)\frac{\partial}{\partial \xi}\left[(\cosh\xi - \cos\eta)\frac{\partial}{\partial \xi}\right]V_{\xi} \qquad \text{on } \xi = \alpha \tag{4.3.10}$$

$$\frac{\partial C_{21}}{\partial \xi} = R(\cosh\xi - \cos\eta)\frac{\partial}{\partial \xi}\left[(\cosh\xi - \cos\eta)\frac{\partial}{\partial \xi}\right]V_{\xi} \qquad \text{on } \xi = 0 \tag{4.3.11}$$

$$C_{21} \to 0 \qquad \text{as}(\xi, \eta) \to 0 \tag{4.3.12}$$

in which R is defined by

$$R = \frac{F_{cW}}{F_{cP}} \tag{4.3.13}$$

and at order Pe^2 ($C_{20} + C_{22}\cos2\theta$) [c.f., A.44)]

$$\left[\left(\cosh\xi - \cos\eta\right)\left(\frac{\partial^2}{\partial\xi^2} + \frac{\partial^2}{\partial\eta^2} - \frac{1}{\sin^2\eta}\frac{\partial^2}{\partial\theta^2}\right) - \sinh\xi\frac{\partial}{\partial\xi} + \frac{\cosh\xi\cos\eta - 1}{\sin\eta}\frac{\partial}{\partial\eta}\right]\left(C_{20} + C_{22}\cos2\theta\right) = c\left[\frac{1+\cos2\theta}{2}\left(V_\xi\frac{\partial C_{21}}{\partial\xi} + V_\eta\frac{\partial C_{21}}{\partial\eta}\right) - \frac{1-\cos2\theta}{2}V_\theta\frac{C_{21}}{\sin\eta}\right] \tag{4.3.14}$$

with

$$\frac{\partial}{\partial\xi}\left(C_{20} + C_{22}\cos2\theta\right)\Big|_{S_J} = 0, C_{20} + C_{22}\cos2\theta \to 0 \quad \text{as}\left(\xi,\eta\right)\to 0 \tag{4.3.15}$$

Since these equations must hold for any value of θ, at order unity we have

$$\left[\left(\cosh\xi - \cos\eta\right)\left(\frac{\partial^2}{\partial\xi^2} + \frac{\partial^2}{\partial\eta^2}\right) - \sinh\xi\frac{\partial}{\partial\xi} + \frac{\cosh\xi\cos\eta - 1}{\sin\eta}\frac{\partial}{\partial\eta}\right]C_{20} = \frac{c}{2}\left[V_\xi\frac{\partial C_{21}}{\partial\xi} + V_\eta\frac{\partial C_{21}}{\partial\eta} - V_\theta\frac{C_{21}}{\sin\eta}\right] \tag{4.3.16}$$

with

$$\frac{\partial C_{20}}{\partial\xi}\Big|_{\xi=1} = 0, \quad \frac{\partial C_{20}}{\partial\xi}\Big|_{\xi=0} = 0, \quad C_{20}\to 0 \quad \text{as}\left(\xi,\eta\right)\to 0 \tag{4.3.17}$$

and at order $\cos(2\theta)$

$$\left[\left(\cosh\xi - \cos\eta\right)\left(\frac{\partial^2}{\partial\xi^2} + \frac{\partial^2}{\partial\eta^2} - \frac{4}{\sin^2\eta}\right) - \sinh\xi\frac{\partial}{\partial\xi} + \frac{\cosh\xi\cos\eta - 1}{\sin\eta}\frac{\partial}{\partial\eta}\right]C_{22} = \frac{c}{2}\left[V_\xi\frac{\partial C_{21}}{\partial\xi} + V_\eta\frac{\partial C_{21}}{\partial\eta} + V_\theta\frac{C_{21}}{\sin\eta}\right] \tag{4.3.18}$$

with

$$\frac{\partial C_{22}}{\partial\xi}\Big|_{\xi=1} = 0, \quad \frac{\partial C_{22}}{\partial\xi}\Big|_{\xi=0} = 0, \quad C_{22}\to 0 \quad \text{as}\left(\xi,\eta\right)\to 0 \tag{4.3.19}$$

4.3.2 - Analytical Solution at Order Pe

The electroviscous ion concentration at order Pe, C_{21}, satisfies the same equation as that given by (4.2.23) for which m = 1, so that its solution is

$$C_{21} = (\cosh\xi - \mu)^{\frac{1}{2}} \sin\eta \sum_{n=1}^{\infty}\left[I_n \cosh\left(n+\frac{1}{2}\right)\xi + J_n \sinh\left(n+\frac{1}{2}\right)\xi\right]P_n'(\mu) \quad (4.3.20)$$

The sets of constants, J_n and I_n are determined upon imposing the boundary conditions on the solid surfaces. The derivative of the solution (4.3.20), with respect to ξ is

$$\frac{\partial C_{21}}{\partial\xi} = \sin\eta\left\{\frac{1}{2}\sinh\xi(\cosh\xi - \mu)^{-\frac{1}{2}}\sum_{1}^{\infty}\left[I_n \cosh\left(n+\frac{1}{2}\right)\xi + J_n \sinh\left(n+\frac{1}{2}\right)\xi\right]P_n'\right.$$
$$\left.+(\cosh\xi - \mu)^{\frac{1}{2}}\sum_{n=1}^{\infty}\left(n+\frac{1}{2}\right)\left[I_n \sinh\left(n+\frac{1}{2}\right)\xi + J_n \cosh\left(n+\frac{1}{2}\right)\xi\right]P_n'\right\}$$

the value of which evaluated on the boundary $\xi = 0$ is (4.3.21)

$$\left.\frac{\partial C_{21}}{\partial\xi}\right|_{\xi=0} = \sin\eta(1-\mu)^{\frac{1}{2}}\sum_{n=1}^{\infty}\left(n+\frac{1}{2}\right)J_n P_n' \quad (4.3.22)$$

from which and upon the use of B.C. (4.3.11), the set of J_n is determined. V_ξ appearing in B.C. (4.3.11) is given by (4.2.145). It may be expressed as

$$V_\xi = -\frac{\sin\eta}{2}\left[(\cosh\xi - \mu)^{-\frac{1}{2}}M - 2\sinh\xi(\cosh\xi - \mu)^{-1}\right] \quad (4.3.23)$$

in which the parameter M is defined by (C.1) in Appendix C. From this B.C. (4.3.11) may be written as

$$\frac{\partial C_{21}}{\partial\xi} = -\frac{F_{cW}\sin\eta}{2c}\frac{\partial}{\partial\xi}\left\{(\cosh\xi - \mu)\frac{\partial}{\partial\xi}V_\xi\right\} =$$
$$-\frac{R\sin\eta}{2c}\frac{\partial}{\partial\xi}\left\{\left[(\cosh\xi - \mu)\frac{\partial}{\partial\xi}\right](\cosh\xi - \mu)^{-\frac{1}{2}}M - 2\sinh\xi(\cosh\xi - \mu)^{-1}\right\} =$$
$$-\frac{R\sin\eta}{2c}\left\{N + (\cosh\xi - \mu)^{-\frac{3}{2}}\left[\frac{1}{4}\sinh^2\xi M\right]\right.$$
$$\left.+(\cosh\xi - \mu)^{-\frac{1}{2}}\left[-\frac{1}{2}\cosh\xi M\right] + (\cosh\xi - \mu)^{\frac{1}{2}}[S + 2T + O]\right\}$$

(4.2.24)

The functions M, N, S, T, and O are defined by (C.1), (C.2), (C.3) and (C.4) or, in revised forms, by (C.9),(C.10), (C.11) and (C.12) in Appendix C. Now letting $\xi = 0$, B.C. (4.3.24) is evaluated on the wall as

$$\left.\frac{\partial C_{21}}{\partial \xi}\right|_{\xi=0} = -\frac{F_{cW}}{2c}\sin\eta(1-\mu)^{\frac{1}{2}}\sum_{1}^{\infty}\left[(n+2)C_{n+1}+(n-1)C_{n-1}-E_{n+1}+E_{n-1}\right. \\ \left.+(n+2)(n+3)G_{n+1}-(n-2)(n-1)G_{n-1}\right]P_n' \tag{4.3.25}$$

In view of (4.3.22) and (4.3.25) the set of J_n is determined:

$$J_n = -\frac{F_{cW}}{c}\frac{1}{2n+1}\left[(n+2)C_{n+1}+(n-1)C_{n-1}-E_{n+1}+E_{n-1}\right. \\ \left.+(n+2)(n+3)G_{n+1}-(n-2)(n-1)G_{n-1}\right] \qquad n \geq 1 \tag{4.3.26}$$

The other set of constants in the solution (4.3.20), namely I_n, is determined upon imposing the boundary condition on the sphere surface, given by (4.3.10), which requires much more calculation in order to equate it with that deduced from the solution (4.2.20), given by (4.2.21), evaluated on $\xi = \alpha$. This is determined in Appendix C as

$$\frac{(n-2)(n-1)}{2n-1}\sinh\left(n-\frac{3}{2}\right)\alpha I_{n-2} \\ -(n-1)\left[\frac{\sinh\alpha}{2n-1}\cosh\left(n-\frac{1}{2}\right)\alpha+\cosh\alpha\sinh\left(n-\frac{1}{2}\right)\alpha\right]I_{n-1} \\ +\left\{\frac{1}{2}\sinh 2\alpha\cosh\left(n+\frac{1}{2}\right)\alpha \right. \\ \left.+\left[(2n+1)\cosh^2\alpha+\frac{(n+1)(n-1)}{2n-1}+\frac{n(n+2)}{2n+3}\right]\sinh\left(n+\frac{1}{2}\right)\alpha\right\}I_n \\ -(n+2)\left[\frac{\sinh\alpha}{2n+3}\cosh\left(n+\frac{3}{2}\right)\alpha+\cosh\alpha\sinh\left(n+\frac{3}{2}\right)\alpha\right]I_{n+1} \\ +\frac{(n+3)(n+2)}{2n+3}\sinh\left(n+\frac{5}{2}\right)\alpha I_{n+2} = -\chi_n \\ -\frac{F_{cP}}{c}\left[\beta_n+\gamma_n+\tau 1_n+\tau 2_n+\tau 3_n+\omega 1_n+\omega 2_n+\omega 3_n+\omega 4_n+\omega 5_n+\omega 6_n\right]_{\xi=\alpha} \tag{4.3.27}$$

where χ_n, β_n γ_n, $\tau 1_n$, $\tau 2_n$, $\tau 3_n$, $\omega 1_n$, $\omega 2_n$, $\omega 3_n$, $\omega 4_n$, $\omega 5_n$, $\omega 6_n$, are given by (C.33, 22-31).

Eq.s (4.3.26, 27) are solved by the program "CoefAnalyticRot" for the rotation of the particle and in "CoefAnalyticTran" for its translation up to transacting point n = N-1, upon the construction of the matrices of coefficients and the vectors of the right-hand sides. From the known coefficients, I_n and J_n, the electroviscous ion concentrations at order Pe, C21T for translation and C21R for rotation of the particle, are obtained by (4.3.20), programmed in "C21Psi21AnalyticTran" and "C21Psi21AnalyticRot". They are superimposed in Program "ForceParallelAnalytic".

4.3.3 - Numerical Solution at Order Pe

The finite difference approximation is applied to solve Eq. (4.3.9) along with B.C.s (4.3.10-13). The idea is that the electroviscous ion concentration at each point of the domain can be determined from the values of its neighborhood by the use of Taylor series expansions. Thus, if we divide the domain of interest in discrete points as shown in Fig. 4.1, for each node we may write

$$A_0 C_{21} = A_1 C_{21}(1) + A_2 C_{21}(2) + A_3 C_{21}(3) + A_4 C_{21}(4) \tag{4.3.28}$$

in which A_i ($i = 0, 1, 2, 3, 4$) are known as weighted functions and $C_{21}(i)$ ($i = 1, 2, 3, 4$) are the value of C_{21} at four immediate neighborhood nodes, located on the coordinate curves passing at the point under consideration, C_{21}. Here, node (1) is taken to be located in the increasing direction of η, node (2) is its reflection with respect to ξ coordinate, node (3) is in the increasing direction of ξ and node (4) is its reflection with respect to η coordinate, as shown in Fig. 4.2a. Thus, Eq. (4.3.28) may be written, upon the use of Taylor series expansions, as

$$\begin{aligned} &A_1\left[C_{21} + h_\eta \frac{\partial C_{21}}{\partial \eta} + \frac{h_\eta^2}{2}\frac{\partial^2 C_{21}}{\partial \eta^2} + \frac{h_\eta^3}{3!}\frac{\partial^3 C_{21}}{\partial \eta^3} + \cdots\right] \\ &+ A_2\left[C_{21} - h_\eta \frac{\partial C_{21}}{\partial \eta} + \frac{h_\eta^2}{2}\frac{\partial^2 C_{21}}{\partial \eta^2} + O\left(h_\eta^3\right)\right] \\ &+ A_3\left[C_{21} + h_\xi \frac{\partial C_{21}}{\partial \xi} + \frac{h_\xi^2}{2}\frac{\partial^2 C_{21}}{\partial \xi^2} + O\left(h_\xi^3\right)\right] \\ &+ A_4\left[C_{21} - h_\xi \frac{\partial C_{21}}{\partial \xi} + \frac{h_\xi^2}{2}\frac{\partial^2 C_{21}}{\partial \xi^2} + O\left(h_\xi^3\right)\right] - A_0 C_{21} = 0 \end{aligned} \tag{4.3.29}$$

in which h_ξ and h_η are intervals chosen for ξ and η coordinates, respectively.

The electroviscous ion concentration, C_{21}, should simultaneously satisfy the exact equation, given by (4.3.9), and the approximate one given by (4.3.29). Therefore, the weighted functions A_i are determined, upon equating these two equations, then collecting terms with the same derivatives. Because the exact equation does not poses terms of higher order than $\partial^2 C_1/\partial\xi^2$ and $\partial^2 C_1/\partial\eta^2$ we truncate terms of $O(h^3_\xi)$ and those of $O(h^3_\eta)$ in the approximate equation, given by (4.3.29). Thus, the error in this calculation is of order $(h^3_\xi + h^3_\eta)$ and hence the smaller the intervals the more accurate the result. Doing so the weighted functions are obtained as

$$
\begin{aligned}
A_0 &= 2(\cosh\xi - \cos\eta)\left[\frac{\sin^2\eta}{h_\xi^2} + \frac{\sin^2\eta}{h_\eta^2} + \frac{1}{2}\right] \\
A_1 &= \frac{\sin^2\eta(\cosh\xi - \cos\eta)}{h_\eta^2} + \frac{\sin\eta(\cosh\xi\cos\eta - 1)}{2h_\eta}, \\
A_2 &= \frac{\sin^2\eta(\cosh\xi - \cos\eta)}{h_\eta^2} - \frac{\sin\eta(\cosh\xi\cos\eta - 1)}{2h_\eta} \\
A_3 &= \sin^2\eta\left[\frac{(\cosh\xi - \cos\eta)}{h_\xi^2} - \frac{\sinh\xi}{2h_\xi}\right] \\
A_4 &= \sin^2\eta\left[\frac{(\cosh\xi - \cos\eta)}{h_\xi^2} + \frac{\sinh\xi}{2h_\xi}\right]
\end{aligned}
\qquad (4.3.30)
$$

They should be evaluated at the node under consideration. Now, we can apply Eq. (4.3.28) to all individual interior nodes of the domain which have four neighborhood nodes around them. On the boundary of domain on the solid surfaces we have only three neighborhood nodes and at its edge only two. To manipulate the finite difference approximation for such points, we may consider an imaginary node behind the boundary denoted by $C_1(4')$ for the wall and $C_1(3')$ for the sphere surface, as shown in Fig . 4.2b, c. By the aid of the governing Newman boundary conditions (4.3.10, 11), it would be possible to determine the value of such imaginary nodes in terms of inner nodes (i.e., imposing the boundary conditions). Therefore, if we write [c.f., Fig 4.2]

$$\left.\frac{\partial C_{21}}{\partial \xi}\right|_{\xi=0} = \frac{C_{21}(3) - C_{21}(4')}{2h_\xi} \quad \text{on } S_W, \quad \left.\frac{\partial C_{21}}{\partial \xi}\right|_{\zeta=\alpha} = \frac{C_{21}(3') - C_{21}(4)}{2h_\xi} \quad \text{on } S_P \tag{4.3.31}$$

$C_{21}(3')$ and $C_{21}(4')$ are determined in terms of the interior nodes $C_{21}(3)$ and $C_{21}(4)$ as well as the corresponding boundary conditions, that is

$$C_{21}(4') = C_{21}(3) - 2h_x \text{BCWall}, \tag{4.3.32}$$

$$C_{21}(3') = C_{21}(4) + 2h_x \text{BCSphere}, \tag{4.3.33}$$

in which, in view of B.C.s (4.3.10, 11), we have written

$$\text{BCWall} = R(\cosh\xi - \cos\eta)\frac{\partial}{\partial \xi}\left[(\cosh\xi - \cos\eta)\frac{\partial}{\partial \xi}\right]V_\xi \quad \text{on } \xi = 0 \tag{4.3.34}$$

$$\text{BCSphere} = (\cosh\xi - \cos\eta)\frac{\partial}{\partial \xi}\left[(\cosh\xi - \cos\eta)\frac{\partial}{\partial \xi}\right]V_\xi \quad \text{on } \xi = \alpha \tag{4.3.35}$$

Thus, the finite difference equation (4.3.28) may be written as

$$-A_0C_{21} + A_1C_{21}(1) + A_2C_{21}(2) + (A_3 + A_4)C_{21}(3) = 2A_4h_\xi \text{BCWall} \tag{4.3.36}$$

for nodes on S_W and

$$-A_0C_{21} + A_1C_{21}(1) + A_2C_{21}(2) + (A_3 + A_4)C_{21}(4) = -2A_3h_\xi \text{BCSphere} \tag{4.3.37}$$

for those on S_P.

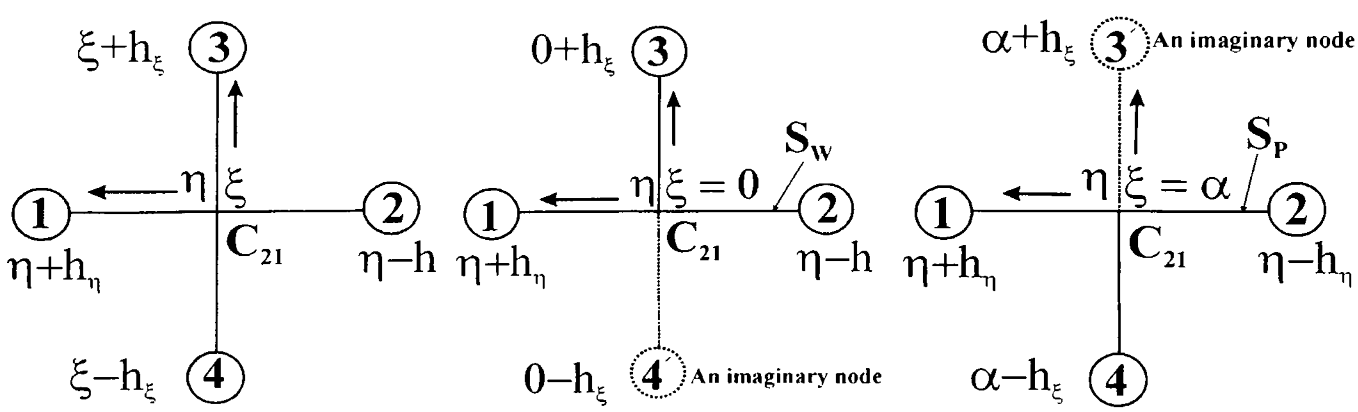


Fig. 4.2 - A node on ξ and η coordinates surrounded by the four immediate neighborhood nodes.

In addition to the solid surfaces for which ζ = constant, we have two other boundaries of the domain for which η is constant, one on the z-axis above the sphere for which $\eta = 0$, and the other is that part of the z-axis below the sphere for which $\eta = \pi$ (c.f., Fig. 4.1). To manipulate the finite difference approximation for such points, we may assume that the curves of the electroviscous ion concentration on the z-axis are piecewise continuous so that the imaginary nodes on the left side of the z-axis are located in such a way that the slope of the left-hand sides and the right-hand sides on the z-axis are the same. Thus, if the nodes behind the boundary $\eta = \pi$ are denoted by $C_{21}(1')$ and those behind the boundary $\eta = 0$ are denoted by $C_{21}(2')$ we may write

$$\left.\frac{\partial C_{21}}{\partial \eta}\right|_{\eta=\pi^-} = \frac{C_{21} - C_{21}(2)}{h_\eta} = \left.\frac{\partial C_{21}}{\partial \eta}\right|_{\eta=\pi^+} = \frac{C_{21}(1') - C_{21}}{h_\eta} \tag{4.3.38}$$

$$\left.\frac{\partial C_{21}}{\partial \eta}\right|_{\eta=0^-} = \frac{C_{21} - C_{21}(2')}{h_\eta} = \left.\frac{\partial C_{21}}{\partial \eta}\right|_{\eta=0^+} = \frac{C_{21}(1) - C_{21}}{h_\eta} \tag{4.3.39}$$

or

$$C_{21}(1') = 2C_{21} - C_{21}(2), \qquad C_{21}(2') = 2C_{21} - C_{21}(1) \tag{4.3.40}$$

from which the finite difference equation (4.2.28) for the interior nodes on these boundaries is determined:

$$(2A_1 - A_0)C_{21} + (A_2 - A_1)C_{21}(2) + A_3C_{21}(3) + A_4C_{21}(4) = 0 \ \text{ on } \eta = \pi \tag{4.3.41}$$

$$(2A_2 - A_0)C_{21} + (A_1 - A_2)C_{21}(1) + A_3C_{21}(3) + A_4C_{21}(4) = 0 \ \text{ on } \eta = 0 \tag{4.3.42}$$

It remains to write down the finite difference equations for the nodes located on the four edges of the boundary which have only two nodes around them, namely the intersection of the z-axis with the wall ($\xi = 0$, $\eta = \pi$), the intersections of the z-axis and the sphere ($\xi = \alpha$, $\eta = \pi$, and $\xi = \alpha$, $\eta = 0$), and the intersection of the ρ and z-axis at infinity ($\xi = 0$, $\eta = 0$), ([c.f., Fig. 4.1). For the node located at infinity we have its value given by B.C. (4.3.12), so it may directly imposed in the matrix of coefficients. For the others, their equations are easily obtained by combining (4.3.32, 33) and (4.3.40):

at $(\eta = \pi, \xi = 0)$

$$(2A_1 - A_0)C_{21} + (A_2 - A_1)C_{21}(2) + (A_3 + A_4)C_{21}(4) = 2h_\xi A_4 BCWall \quad (4.3.43)$$

at $(\eta = \pi, \xi = \alpha)$

$$(2A_1 - A_0)C_{21} + (A_2 - A_1)C_{21}(2) + (A_3 + A_4)C_{21}(3) = -2h_\xi A_3 BCSphere \quad (4.3.44)$$

and at $(\eta = 0, \xi = \alpha)$

$$(2A_2 - A_0)C_{21} + (A_1 - A_2)C_{21}(2) + (A_3 + A_4)C_{21}(3) = -2h_\xi A_3 BCSphere \quad (4.3.45)$$

Now, each discrete node has an individual equation, so that its value is uniquely determined upon the solution of these (K+1)×(L+1) algebraic linear equations simultaneously. This is done by constructing the matrix of coefficients of C_{21}'s and the vector of the right-hand sides in "C21Numeric".

The BCWall and BCSphere, defined by Eqs.(4.3.34, 35), are determined upon the use of solution of the purely hydrodynamic problem. Thus, if we write

$$BCWall = F_{cW} BCW, \qquad BCSphere = F_{cP} BCS \quad (4.3.46)$$

BCW and BCS are determined by evaluating the following relation, obtained from (4.2.145), on the solid surfaces, i.e. by letting $\xi = 0$ and $\xi = \alpha$, for BCW and BCS, respectively:

$$\frac{\partial C_{21}}{\partial \xi} = \frac{1}{c}\left\{\frac{1}{2}\frac{\sin^2\eta \sinh\xi}{(\cosh\xi - \mu)^2}\left[\mu Q_1 + \sin\eta\left(U_0 + U_2 - 2\right)\right]\right.$$
$$- \frac{\frac{1}{2}\sinh^2\xi + 1 - \mu\cosh\xi}{(\cosh\xi - \mu)}\left[\mu\frac{\partial Q_1}{\partial \xi} + \sin\eta\left(\frac{\partial U_0}{\partial \xi} + \frac{\partial U_2}{\partial \xi}\right)\right]$$
$$- \frac{1}{2}\sinh\xi\left[\mu\frac{\partial^2 Q_1}{\partial \xi^2} + \sin\eta\left(\frac{\partial^2 U_0}{\partial \xi^2} + \frac{\partial^2 U_2}{\partial \xi^2}\right)\right]$$
$$\left. - \frac{\sin^2\eta(1 - \mu\cosh\xi)}{(\cosh\xi - \mu)^2}W_1 - \frac{2\sin^2\eta + \mu\cosh\xi - 1}{(\cosh\xi - \mu)}\frac{\partial W_1}{\partial \xi} - (\mu\cosh\xi - 1)\frac{\partial^2 W_1}{\partial \xi^2}\right\}$$
(4.3.47)

BCW and BCS is determined in "VTBConTran" for the translation of the particle and in "VRBConRot" for the rotation of the particle. They are superimposed in "ForceParallelLowPe".

An example of the analytical and numerical solutions of C21 for comparison is illustrated in Table B11, located in Appendix B. In this example Pe is taken to be equal to 0.01 and δ to 0.1, the number of intervals on the ξ-coordinates is taken to be three (K = 3) and those on the η-coordinates is taken to be thirty (L = 30), corresponding to Fig. 4.1. The other parameters are $\psi_p = -50\,\text{mV}$, $\psi_W = -100\,\text{mV}$, $a\Omega / U = 0.5$, $D_1 / D_2 = 2$ and the medium is a univalent electrolyte at room temperature[1]. It shows that within 98% of accuracy the numerical solution agrees with the analytical one, that is the difference between the two solutions is less than 2%.

4.3.4 - Numerical Solution at O (Pe^2)

The equations for electroviscous ion concentrations at order Pe^2 are given by (4.3.16) and (4.3.18) for C_{20} and C_{22}, respectively. The right-hand sides of these equations are completely determined analytically by the use of the analytical solution of C_{21} and the flow field. The suitable finite difference equation for either of them, C_{2i} (i = 0, 2), is

$$-A_0C_{2i} + A_1C_{2i}(1) + A_2C_{2i}(2) + A_3C_{2i}(3) + A_4C_{2i}(4) = RHS_i \qquad (4.3.48)$$

in which RHS_i stand for the right-hand sides, determined by

$$RHSC_{20} = \frac{c}{2}\left[V_\xi \frac{\partial C_{21}}{\partial \xi} + V_\eta \frac{\partial C_{21}}{\partial \eta} - V_\theta \frac{C_{21}}{\sin\eta}\right] \qquad (4.3.49)$$

for C_{20} and

$$RHSC_{22} = \frac{c}{2}\left[V_\xi \frac{\partial C_{21}}{\partial \xi} + V_\eta \frac{\partial C_{21}}{\partial \eta} + V_\theta \frac{C_{21}}{\sin\eta}\right] \qquad (4.3.50)$$

1

Throughout this chapter all examples are for a univalent electrolyte at room temperature, unless otherwise stated for C_{22}. If we expand the finite difference Eq. (4.3.48) by a Taylor series and then equating it to the analytical Eq.s (4.3.16, 18), we see that C_{20} and C_{22} for each node satisfy the same equation as that obtained for C_{21} in the previous section, except for the right hand side which is replaced by Eq. (4.3.49, 50) for the latter. The right-hand sides are programed in "RHSC20C22". C20 and C22 are so obtained by the programs "C20Numeric" and "C22Numeric", respectively.

4.4 - Electroviscous Potential

The electroviscous potential at $O(\epsilon^2)$, $\tilde{\psi}_2$, is given by

$$\tilde{\psi}_2 = \left(\frac{D_2 - D_1}{D_2 + D_1}\right)\tilde{c}_2 + \tilde{\phi} \tag{4.4.1}$$

in which $\tilde{c}_2$ has already been determined and $\tilde{\phi}$ satisfies the same equation and boundary condition as those for electroviscous ion concentrations at order Pe in which the coefficients of the boundary conditions, $\left(F_{cP}, F_{cW}\right)$ are replaced by $\left(F_{\phi P}, F_{\phi W}\right)$ defined by (1.3.61e). If we write

$$\tilde{\phi} = \Phi \cos\theta \tag{4.4.2}$$

Φ is determined with the same procedure as that for C_{21}. Therefore, at order Pe we have an analytical solution for the electroviscous potential also. Thus, if we expand the electroviscous potential as

$$\tilde{\psi}_2 = \cos\theta\psi_{21}\mathrm{Pe} + \frac{D_2 - D_1}{2D_2}\left(\psi_{20} + \cos 2\theta\psi_{22}\right)\mathrm{Pe}^2 + O\left(\mathrm{Pe}^3\right) \tag{4.4.3}$$

we have

$$\psi_{21} = \frac{D_2 - D_1}{D_2 + D_1}C_{21} + \Phi, \qquad \psi_{20} = C_{20}, \qquad \psi_{22} = C_{22} \tag{4.4.4}$$

The function Φ is programmed in "C21Psi21Analytic" for the analytical solution and in "PhiNumeric" for the numerical solution, from which $\tilde{\psi}_{21}$ is determined.

4.5 - Electroviscous Force on Sphere

The electroviscous force experienced by the particle is obtained from the integral

(3.6.1). Noting that the unit vector outward the solid surfaces for the particle is $-\vec{i}_\xi$ and for the wall is $\vec{i}_\xi$ the integrand of the force is determined by [c.f. (A.44), (A.43c)]

$$\tilde{\vec{B}}_P \cdot \tilde{\vec{\vec{\sigma}}}_P \cdot \tilde{\vec{S}}_P = -\left[\tilde{B}_{P\eta}\tilde{\sigma}_{P\eta\xi} + \tilde{B}_{P\theta}\tilde{\sigma}_{P\theta\xi}\right]\frac{c^2 \sin\eta}{(\cosh\alpha - \cos\eta)^2}d\eta d\theta \tag{4.5.1}$$

$$\tilde{\vec{B}}_W \cdot \tilde{\vec{\vec{\sigma}}}_W \cdot \tilde{\vec{S}}_W = \left[\tilde{B}_{W\eta}\tilde{\sigma}_{W\eta\xi} + \tilde{B}_{W\theta}\tilde{\sigma}_{W\theta\xi}\right]\frac{c^2 \sin\eta}{(1 - \cos\eta)^2}d\eta d\theta \tag{4.5.2}$$

in which [c.f. (2.6.30, 31, 3.6.2)]

$$\tilde{B}_{J\eta} = -2\lambda\frac{(\cos\xi - \cos\eta)}{c}\left[(G_J + H_J)\frac{\partial C_{21}}{\partial\eta} + (G_J - H_J)\frac{\partial\psi_{21}}{\partial\eta}\right]\cos\theta \qquad \text{on } S_J \tag{4.5.3}$$

$$\tilde{B}_{J\theta} = +2\lambda\frac{(\cos\xi - \cos\eta)}{c}\left[(G_J + H_J)C_{21} + (G_J - H_J)\psi_{21}\right]\sin\theta \qquad \text{on } S_J \tag{4.5.4}$$

where J = (W, P), and G_J and H_J are defined by (2.6.31).

4.5.1 - Stress Tensor for Translation Parallel to Wall

The flow field for translation of the sphere parallel to the wall with unit velocity is determined in § 4.2.3. The stress tensor is given by (A.58), from which the required components of the stress tensor, $\tilde{\sigma}_{\xi\eta}P$ and $\tilde{\sigma}_{\xi\theta}P$, where P stands for translation parallel to the wall, are determined by

$$\tilde{\sigma}_{\xi\eta}P = \frac{1}{c}\left[\sin\eta\,\tilde{u}_\xi T + \sinh\xi\,\tilde{u}_\eta T + (\cosh\xi - \cos\eta)\left(\frac{\partial\tilde{u}_\xi T}{\partial\eta} + \frac{\partial\tilde{u}_\eta T}{\partial\xi}\right)\right] \tag{4.5.5}$$

$$\tilde{\sigma}_{\xi\theta}P = \frac{1}{c}\left[\sinh\xi\,\tilde{u}_\theta T + (\cosh\xi - \cos\eta)\left(\frac{\partial\tilde{u}_\theta T}{\partial\xi} + \frac{1}{\sin\eta}\frac{\partial\tilde{u}_\xi T}{\partial\theta}\right)\right] \tag{4.5.6}$$

The flow field is given by (4.2.112, 145-147) from which, and upon excluding the term due to the moving coordinate system, the stress tensor is obtained as:

$$\tilde{\sigma}_{\xi\eta}P = -\frac{\cos\theta}{2c}\left[\sigma_{\xi\eta}PA + \sigma_{\xi\eta}PBC + \sigma_{\xi\eta}PDE + \sigma_{\xi\eta}PFG\right] \tag{4.5.7}$$

$$\tilde{\sigma}_{\xi\theta}P = \frac{\sin\theta}{2c}\left[\sigma_{\xi\theta}PA + \sigma_{\xi\theta}PBC + \sigma_{\xi\theta}PDE + \sigma_{\xi\theta}PFG\right] \tag{4.5.8}$$

where $\sigma_{\xi\eta}PA, \sigma_{\xi\eta}PBC, \sigma_{\xi\eta}PDE, \sigma_{\xi\eta}PFG$, $\sigma_{\xi\theta}PA, \sigma_{\xi\theta}PBC, \sigma_{\xi\theta}PDE$ and $\sigma_{\xi\theta}PFG$ are given in Appendix C, by the relationships (C.34-41), respectively. The stress tensor is determined in Program "SigmaParallel".

4.5.2 - Stress Tensor for Translation Normal to Wall

A novel solution for the flow field produced by translation of a sphere normal to and away from the wall is presented here upon the use of Jeffery's solution of the Laplace equation discussed in § 4.2. Because of the symmetry property around the z-axis, this flow field is independent of the azimuth angle θ, for which the suitable auxiliary functions are found as

$$\widetilde{p} = \frac{Q_0}{c}, \qquad \widetilde{u}_\rho = \frac{1}{2}\left[\frac{\rho}{c}Q_0 + U_1\right], \qquad \widetilde{u}_z = \frac{1}{2}\left[\frac{z}{c}Q_0 + 2W_0\right] \tag{4.5.9}$$

Introducing them in the two dimensional version of the Stokes equation results in

$$\frac{1}{\widetilde{\rho}}\frac{\partial}{\partial\widetilde{\rho}}\left[\widetilde{\rho}\frac{\partial W_0}{\partial\widetilde{\rho}}\right] + \frac{\partial^2 W_0}{\partial\widetilde{z}^2} = 0 \tag{4.5.10a}$$

$$\frac{1}{\widetilde{\rho}}\frac{\partial}{\partial\widetilde{\rho}}\left[\widetilde{\rho}\frac{\partial Q_0}{\partial\widetilde{\rho}}\right] + \frac{\partial^2 Q_0}{\partial\widetilde{z}^2} = 0 \tag{4.5.10b}$$

$$\frac{1}{\widetilde{\rho}}\frac{\partial}{\partial\widetilde{\rho}}\left[\widetilde{\rho}U_1\right] - \frac{U_1}{\widetilde{\rho}^2} + \frac{\partial^2 U_1}{\partial\widetilde{z}^2} = 0 \tag{4.5.10c}$$

$$3Q_0 + \widetilde{\rho}\frac{\partial Q_0}{\partial\widetilde{\rho}} + \widetilde{z}\frac{\partial Q_0}{\partial\widetilde{z}} + c\left(\frac{\partial U_1}{\partial\widetilde{\rho}} + \frac{U_1}{\widetilde{\rho}}\right) + 2c\frac{\partial W_0}{\partial\widetilde{z}} = 0 \tag{4.5.10d}$$

Thus, each of them satisfies Eq. (4.2.21) for which $\Phi = W_0$, Q_0, and U_1, corresponding to m = 0, 0, 1, respectively. Their solutions are [c.f., (4.2.49, 50, 64)]:

$$W_0 = \left(\cosh\xi - \mu\right)^{\frac{1}{2}}\sum_{n=1}^{\infty}\left[A_n \sinh\left(n+\frac{1}{2}\right)\xi\right]P_n(\mu) \tag{4.5.11}$$

$$Q_0 = \left(\cosh\xi - \mu\right)^{\frac{1}{2}}\sum_{n=1}^{\infty}\left[B_n \cosh\left(n+\frac{1}{2}\right)\xi + C_n \sinh\left(n+\frac{1}{2}\right)\xi\right]P_n(\mu) \tag{4.5.12}$$

$$U_1 = \left(\cosh\xi - \mu\right)^{\frac{1}{2}}\sin\eta\sum_{n=0}^{\infty}\left[D_n \cosh\left(n+\frac{1}{2}\right)\xi + E_n \sinh\left(n+\frac{1}{2}\right)\xi\right]P_n'(\mu) \tag{4.5.13}$$

The corresponding boundary conditions $\widetilde{u}_\rho = \widetilde{u}_z = 0$ on the wall $\left(\widetilde{z} = 0 \text{ or } \xi = 0\right)$, and

$\tilde{u}_\rho = 0$ and $\tilde{u}_z = 1$ on the sphere $(\xi = \alpha)$, in terms of auxiliary functions (4.5.9) are:

$$Q_0\big|_{\tilde{z}=0} = -\lim_{\tilde{z}=0} \frac{2c}{\tilde{z}} W_0 = -2\lim_{\xi=0} \frac{(\cosh\xi - \mu)}{\sinh\xi} W_0 \tag{4.5.14}$$

$$U_1\big|_{\tilde{z}=0} = \lim_{\tilde{z}=0} \frac{2\tilde{\rho}}{\tilde{z}} W_0 = \lim_{\xi=0} \frac{2\sin\eta}{\sinh\xi} W_0 \tag{4.5.15}$$

$$Q_0\big|_{\xi=\alpha} = 2\frac{c}{\tilde{z}}(1 - W_0)\big|_{\xi=\alpha} = 2\frac{(\cosh\xi - \mu)}{\sinh\xi}(1 - W_0)\big|_{\xi=\alpha} \tag{4.5.16}$$

$$U_1\big|_{\xi=\alpha} = 2\frac{\tilde{\rho}}{\tilde{z}}(W_0 - 1)\big|_{\xi=\alpha} = \frac{2\sin\eta}{\sinh\xi}(W_0 - 1)\big|_{\xi=\alpha} \tag{4.5.17}$$

The term $(\cosh\xi - \mu)W_0$ in B.C.s (4.5.14, 16), by the aid of (4.5.11), may be written as

$$(\cosh\xi - \mu)W_0 = (\cosh\xi - \mu)^{\frac{1}{2}} \sum_0^\infty A_n \left[\cosh\xi \sinh\left(n + \frac{1}{2}\right)\xi - \mu \sinh\left(n + \frac{1}{2}\right)\xi\right] P_n \tag{4.5.18}$$

Using the recurrence relationships [Macrobert (1967)]

$$\mu P_n(\mu) = \frac{n+1}{2n+1} P_{n+1} + \frac{n}{2n+1} P_{n-1} \text{ for } n \geq 1, \quad P_1(\mu) = \mu P_0 \text{ for } n = 0 \tag{4.5.19}$$

it may be expressed as

$$(\cosh\xi - \mu)W_0 = (\cosh\xi - \mu)^{\frac{1}{2}} \sum_0^\infty \left[\frac{-n}{2n-1} A_{n-1} \sinh\left(n - \frac{1}{2}\right)\xi \right.$$
$$\left. + A_n \cosh\xi \sinh\left(n + \frac{1}{2}\right)\xi - \frac{n+1}{2n+3} A_{n+1} \sinh\left(n + \frac{3}{2}\right)\xi\right] P_n \tag{4.5.20}$$

Imposing B.C. (4.5.14) results in

$$B_n = nA_{n-1} - (2n+1)A_n + (n+1)A_{n+1} \qquad n \geq 0 \tag{4.5.21}$$

Using the identity [Macrobert (1967)]

$$p_n = \frac{1}{2n+1}\left(P'_{n+1} - P'_{n-1}\right) \qquad n \geq 1 \tag{4.5.22}$$

the solution (4.5.11) may be written in terms of $P'_n(\mu)$ as:

$$W_0 = (\cosh\xi - \mu)^{\frac{1}{2}} \sum_1^\infty \left[\frac{A_{n-1}}{2n-1} \sinh\left(n - \frac{1}{2}\right)\xi - \frac{A_{n+1}}{2n+3} \sinh\left(n + \frac{3}{2}\right)\xi\right] P'_n \tag{4.5.23}$$

Now, imposing B.C. (4.5.15) results in

$$D_n = A_{n-1} - A_{n+1} \qquad n \geq 1 \tag{4.5.24}$$

The other sets of constant are determined by imposing the no-slip boundary condition on the sphere surface. Using identities (4.2.75, 76) and [Macrobert (1967)]

$$(\cosh\xi - \mu)^{\frac{1}{2}} = \sum_{1}^{n} \lambda_n P_n \ , \tag{4.5.25}$$

in which λ_n is defined by (4.2.135), B.C. (4.5.16) may be expressed as

$$\sinh\alpha\left[B_n \cosh\left(n+\frac{1}{2}\right)\alpha + C_n \sinh\left(n+\frac{1}{2}\right)\alpha\right] = 2\left\{\lambda_n - A_n \cosh\alpha \sinh\left(n+\frac{1}{2}\right)\alpha\right.$$
$$+\frac{n}{2n-1}A_{n-1}\left[\cosh\alpha \sinh\left(n+\frac{1}{2}\right)\alpha - \sinh\alpha \cosh\left(n+\frac{1}{2}\right)\alpha\right]$$
$$\left.+\frac{n+1}{2n+3}A_{n+1}\left[\cosh\alpha \sinh\left(n+\frac{1}{2}\right)\alpha + \sinh\alpha \cosh\left(n+\frac{1}{2}\right)\alpha\right]\right\} \tag{4.5.26}$$

Introducing (4.5.21) to (4.5.26) gives the set of C_n to be determined:

$$C_n = 2\,\mathrm{cosech}\alpha\,\mathrm{cosech}\left(n+\frac{1}{2}\right)\alpha\lambda_n - 2k_n\left[\frac{n}{2n-1}A_{n-1} - A_n + \frac{n+1}{2n+3}A_{n+1}\right] \tag{4.5.27}$$

for which $n \geq 0$ and k_n is defined by (4.2.82). The set of E_n is so obtained upon the use of B.C. (4.5.17):

$$E_n = 4\,\mathrm{cosech}\alpha\,\mathrm{cosech}\left(n+\frac{1}{2}\right)\alpha\lambda_n - 2k_n\left[\frac{A_{n-1}}{2n-1} - \frac{A_{n+1}}{2n+3}\right] \qquad n \geq 1 \tag{4.5.28}$$

It remains to determine the set of A_n by the use of the continuity equation. The terms in the continuity equation (4.5.10d) may be expressed in terms of P_n by the use of the identities (4.2.87) and (4.2.94) as

$$\tilde{\rho}\frac{\partial Q_0}{\partial\tilde{\rho}} + \tilde{z}\frac{\partial Q_0}{\partial\tilde{z}} = -\mu\sinh\xi\frac{\partial Q_0}{\partial\xi} - \sin\eta\frac{\partial Q_0}{\partial\eta} = \frac{1}{2}(\cosh\xi - \mu)^{\frac{1}{2}} \times$$
$$\sum_{0}^{\infty}\left\{\left[-nB_{n-1} - B_n + (n+1)B_{n+1}\right]\cosh\left(n+\frac{1}{2}\right)\xi\right.$$
$$\left.+\left[-nC_{n-1} - C_n + (n+1)C_{n+1}\right]\sinh\left(n+\frac{1}{2}\right)\xi\right\}P_n \tag{4.5.29}$$

$$c\left(\frac{\partial U_1}{\partial \tilde{\rho}}+\frac{U_1}{\tilde{\rho}}\right)=\left[-\sin\eta\sinh\xi\frac{\partial}{\partial\xi}+(\mu\cosh\xi-1)\frac{\partial}{\partial\eta}+\frac{(\cosh\xi-\mu)}{\sin\eta}\right]U_1=$$
$$\frac{1}{2}(\cosh\xi-\mu)^{\frac{1}{2}}\sum_0^\infty\left\{\left[n(n-1)D_{n-1}-2n(n+1)D_n+(n+1)(n+2)D_{n+1}\right]\cosh\left(n+\frac{1}{2}\right)\xi\right.$$
$$\left.+\left[n(n-1)E_{n-1}-2n(n+1)E_n+(n+1)(n+2)E_{n+1}\right]\sinh\left(n+\frac{1}{2}\right)\xi\right\}P_n$$

(4.5.30)

$$c\frac{\partial W_0}{\partial \tilde{z}}=\left[(1-\mu\cosh\xi)\frac{\partial}{\partial\xi}-\sin\eta\sinh\xi\frac{\partial}{\partial\eta}\right]W_0=$$
$$\frac{1}{2}(\cosh\xi-\mu)^{\frac{1}{2}}\sum_0^\infty\left[-nA_{n-1}+(2n+1)A_n-(n+1)A_{n+1}\right]\cosh\left(n+\frac{1}{2}\right)\xi\Big\}P_n$$

(4.5.31)

Now, to satisfy the continuity equation for all ranges of ξ and η, the summation of coefficients of cosh $(n+1/2)\xi$ and sinh $(n+1/2)\xi$ of all terms, contained in the continuity equation (4.5.10d), given by (4.5.12, 29-31), must be zero. Writing them in terms of A_n's by the use of (4.5.21, 24, 27, 28), for the coefficient of cosh $(n+1/2)\xi$ results in

$$3\left[nA_{n-1}-(2n+1)A_n+(n+1)A_{n+1}\right]+\frac{1}{2}\left\{-n\left[(n-1)A_{n-2}-(2n-1)A_{n-1}+nA_n\right]\right.$$
$$-\left[nA_{n-1}-(2n+1)A_n+(n+1)A_{n+1}\right]+(n+1)\left[(n+1)A_n-(2n+3)A_{n+1}+(n+2)A_{n+2}\right]$$
$$+n(n-1)\left[A_{n-2}-A_n\right]-2n(n+1)\left[A_{n-1}-A_{n+1}\right]+(n+1)(n+2)\left[A_n-A_{n+2}\right]$$
$$\left.+2\left[-nA_{n-1}+(2n+1)A_n-(n+1)A_{n+1}\right]\right\}=0$$

(4.5.32)

and for the coefficient of sinh $(n+1/2)\xi$:

$$\left[nk_{n-1}-\frac{n(2n-3)}{(2n-1)}k_n\right]A_{n-1}+\left[-\frac{n(2n-1)}{(2n+1)}k_{n-1}-5k_n+\frac{(n+1)(2n+3)}{(2n+1)}k_{n+1}\right]A_n$$
$$+\left[-\frac{(n+1)(2n+5)}{(2n+3)}k_n-(n+1)k_{n+1}\right]A_{n+1}=$$
$$\text{cosech}\,\alpha\left[n(2n-3)\,\text{cosech}\left(n-\frac{1}{2}\right)\alpha\lambda_{n-1}-(4n^2+4n-5)\,\text{cosech}\left(n+\frac{1}{2}\right)\alpha\lambda_n\right.$$
$$\left.+(n+1)(2n+5)\,\text{cosech}\left(n+\frac{3}{2}\right)\alpha\lambda_{n+1}\right]\qquad n\geq 0$$

(4.5.33)

Eq. (4.5.32) is automatically satisfied for all n's, which guarantees the correctness of the calculations. Eq. (4.5.33) represents n linear algebraic equations for n+1 unknowns, the solution of which by truncating at n = N, by letting $A_N = 0$, is determined in the program "CoefN".

This problem has been solved by Brenner (1961) with a different approach based on Stimson & Jeffery solution of the stream function for axisymmetric flow (1926). Because of this symmetry the hydrodynamic force experienced by the sphere has only one component (in the z-direction), $\widetilde{F}_z$. If we denote by k the correction which must be applied to Stokes' Law as a result of the presence of the solid wall then

$$\widetilde{F}_z = 6\pi k \tag{4.5.34}$$

The coefficient k is determined by Brenner (1961) as

$$k = \frac{4}{3}\sinh\alpha\sum_{1}^{\infty}\frac{n(n+1)}{(2n-1)(2n+3)}\left[\frac{2\sinh(2n+1)\alpha + (2n+1)\sinh 2\alpha}{4\sinh^2(n+\frac{1}{2})\alpha - (2n+1)^2\sinh^2\alpha} - 1\right] \tag{4.5.35}$$

Since the whole system is under statistical equilibrium the force the fluid exerts on the sphere is the same as the one exerted on the wall, but with opposite direction. It is more convenient to determine the force, upon the use of the cylindrical component of the stress tensor normal to the wall for which $\vec{i}_n = \vec{i}_z$. Thus, the force experienced by the sphere from the present solution is determined by [c.f., (A.5c, 22)]

$$\widetilde{F}_z = -\int_{S_w}\widetilde{\sigma}_{Wzz}d\widetilde{S} = -\int_0^{2\pi}\int_0^{\infty}\left[-\widetilde{p} + 2\frac{\partial\widetilde{u}_z}{\partial\widetilde{z}}\right]_{\widetilde{z}=0}\widetilde{\rho}\,d\theta\,d\widetilde{\rho} \tag{4.5.36}$$

The infinitesimal element of the surface on the wall may be written as [c.f., (A. 43c)]

$$\widetilde{\rho}\,d\theta\,d\widetilde{\rho} = \frac{c^2\sin\eta}{(\cosh\xi - \cos\eta)^2}\Big|_{\xi=0}d\theta\,d\eta = \frac{c^2}{(1-\mu)^2}d\theta\,d\mu \qquad -1 \le \mu \le 1 \tag{4.5.37}$$

and the stress tensor as [c.f., (4.5.9, 12)]

$$\begin{aligned}\left[-\widetilde{p} + 2\frac{\partial\widetilde{u}_z}{\partial\widetilde{z}}\right]_{\widetilde{z}=0} &= \left|-\frac{Q_0}{c} + 2\left(\frac{Q_0}{2c} + \frac{\widetilde{z}}{2c}\frac{\partial Q_0}{\partial\widetilde{z}} + \frac{\partial W_0}{\partial\widetilde{z}}\right)\right|_{\widetilde{z}=0} = 2\frac{\partial W_0}{\partial\widetilde{z}}\Big|_{\widetilde{z}=0} \\ &= \frac{1}{c}(1-\mu)^{\frac{3}{2}}\sum_{0}^{\infty}(2n+1)A_nP_n\end{aligned} \tag{4.5.38}$$

Thus, the hydrodynamic force is obtained as

$$\widetilde{F}_z = -c\int_0^{2\pi}\int_{-1}^{1}\sum_0^{\infty}(2n+1)A_n(1-\mu)^{-\frac{1}{2}}P_n = -4\sqrt{2}\pi c\sum_0^{\infty}A_n \tag{4.5.39}$$

where A_n are determined by (4.5.33). From this k for the present solution is obtained as

$$k = -\frac{2\sqrt{2}}{3}c\sum_0^{\infty}A_n \tag{4.5.40}$$

The correction coefficient, k, for both solutions is programed in "kEq4535Eq4540" and some examples of them are tabulated in Table B12, located in Appendix B . We see that, up to twelve digits of accuracy, these two solutions predict the same values for k, however, the smaller the gap width the larger the difference for the same truncated value of n. This is because the rates of convergence of the series in (4.5.35, 40) are different. The difference in the sign is due to the fact that Brenner (1961) considered the translation of the particle toward the wall, whereas the present solution is for translation of the particle away from the wall.

The bipolar component of the velocity is obtained from (4.5.9, 11-13), by the aid of the relation (A.51, 52), as:

$$\begin{aligned}\widetilde{u}_\xi = \frac{1}{2}(\cosh\xi-\mu)^{-\frac{1}{2}}\Bigg\{&-\mu\sinh\xi\sum_0^{\infty}\left[B_n\cosh\left(n+\frac{1}{2}\right)\xi + C_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n\\ &-\sin^2\eta\sinh\xi\sum_1^{\infty}\left[D_n\cosh\left(n+\frac{1}{2}\right)\xi + E_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n'\\ &+2(1-\mu\cosh\xi)\sum_0^{\infty}A_n\sinh\left(n+\frac{1}{2}\right)\xi P_n\end{aligned} \tag{4.5.41}$$

and

$$\begin{aligned}\widetilde{u}_\eta = \frac{1}{2}\sin\eta(\cosh\xi-\mu)^{-\frac{1}{2}}\Bigg\{&-\cosh\xi\sum_0^{\infty}\left[B_n\cosh\left(n+\frac{1}{2}\right)\xi + C_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n\\ &-(1-\mu\cosh\xi)\sum_1^{\infty}\left[D_n\cosh\left(n+\frac{1}{2}\right)\xi + E_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n'\\ &-2\sinh\xi\sum_0^{\infty}A_n\sinh\left(n+\frac{1}{2}\right)\xi P_n\end{aligned} \tag{4.5.42}$$

from which the only non-zero component of the stress tensor in (4.5.1, 2), $\widetilde{\sigma}_{\xi\eta}$, is obtained, upon the use of the relation (A.58):

$$\widetilde{\sigma}_{\xi\eta}N = \frac{1}{2c}\left[\sigma_{\xi\eta}NA + \sigma_{\xi\eta}NBC + \sigma_{\xi\eta}NDE\right] \tag{4.5.43}$$

where N denotes translation normal to the wall and where $\sigma_{\xi\eta}NA$, $\sigma_{\xi\eta}NBC$, $\sigma_{\xi\eta}NDE$ are given in Appendix C by the relations (C.42-44), respectively. This is programmed in "SigmaNormal".

4.5.3 - Force Parallel to Wall

In the integrand of the force, given by (1.5.1, 2), two components of the stress tensor, namely $\widetilde{\sigma}_{\xi\eta}$ and $\widetilde{\sigma}_{\xi\theta}$, are involved. Thus, if we write the tangent component of the force as the sum of the contribution of each of them, denoted by $\widetilde{F}_{\xi\eta}$ and $\widetilde{F}_{\xi\theta}$, that is

$$\widetilde{F}_x = \lambda\left(\widetilde{F}_{\xi\eta} + \widetilde{F}_{\xi\theta}\right) \tag{4.5.44}$$

$\widetilde{F}_{\xi\eta}$ and $\widetilde{F}_{\xi\theta}$ are determined by the aid of (4.5.3, 4) as

$$\widetilde{F}_{\xi\eta} = Pe\left\{-\int_0^{2\pi}\int_\pi^0\left[\left(G_p + H_p\right)\frac{\partial C_{21}}{\partial\eta}\bigg|_{S_W} + \left(G_p - H_p\right)\frac{\partial\psi_{21}}{\partial\eta}\bigg|_{S_W}\right]\widetilde{\sigma}_{\xi\eta}P\big|_{S_W} \times \right.$$
$$\frac{c\sin\eta}{(1-\cos\eta)}\left(\frac{1+\text{co}2\theta}{2}\right)d\eta d\theta + \int_0^{2\pi}\int_\pi^0\left[\left(G_p + H_p\right)\frac{\partial C_{21}}{\partial\eta}\bigg|_{S_P} + \left(G_p - H_p\right)\frac{\partial\psi_{21}}{\partial\eta}\bigg|_{S_P}\right]\times$$
$$\left.\widetilde{\sigma}_{\xi\eta}P\big|_{S_P}\frac{c\sin\eta}{(\cosh\alpha - \cos\eta)}\left(\frac{1+\text{co}2\theta}{2}\right)d\eta d\theta\right\} \tag{4.5.45}$$

and

$$\widetilde{F}_{\xi\theta} = Pe\left\{\int_0^{2\pi}\int_\pi^0\left[\left(G_p + H_p\right)C_{21}\big|_{S_W} + \left(G_p - H_p\right)\psi_{21}\big|_{S_W}\right]\widetilde{\sigma}_{\xi\theta}P\big|_{S_W} \times \right.$$
$$\frac{c}{(1-\cos\eta)}\left(\frac{1-\text{co}2\theta}{2}\right)d\eta\, d\theta - \int_0^{2\pi}\int_\pi^0\left[\left(G_p + H_p\right)C_{21}\big|_{S_P} + \left(G_p - H_p\right)\psi_{21}\big|_{S_P}\right]\times$$
$$\left.\widetilde{\sigma}_{\xi\eta}P\big|_{S_P}\frac{c}{(\cosh\alpha - \cos\eta)}\left(\frac{1-\text{co}2\theta}{2}\right)d\eta\, d\theta\right\} \tag{4.5.46}$$

in which $\tilde{\sigma}_{\xi\eta}P$ and $\tilde{\sigma}_{\xi\theta}P$ are determined by (4.5.7, 8).

The force is obtained by the program "ForceParallelAnalytic" for analytical solution of electroviscous ion concentrations and potential, and by the program "ForceParallelLowPe" for the corresponding numerical solution, upon the integration of (4.5.45, 6).

The analytical and numerical solution of the dimensionless force, $\tilde{F}_z/\lambda$, for different mesh sizes, particle-wall distances, ratio of diffusivity of ions, ratio of the angular and linear velocity, and different ζ-potentials, for a univalent electrolyte are tabulated in Table B13 in Appendix B. It shows that the numerical solution is reasonably mesh independent and it is in fair agreement with the analytical solution.

4.5.4 - Force Normal to Wall

For the lift component of the force only C_{20} and ψ_{20} contributes to the integral of the force and the stress tensor is given by (4.5.43), from which the force is determined upon the use of (3.4.1, 4.4.4, 5, 2.6.32):

$$\frac{\tilde{F}_z}{\lambda} = Pe^2\left\{-\left(G_W + SH_W\right)\int_0^{2\pi}\int_{\pi}^{0}\left[\frac{\partial C_{20}}{\partial\eta}\sigma_{\xi\eta}N\right]_{S_W}\frac{c\sin\eta}{\left(1-\cos\eta\right)}d\eta\, d\theta \right.$$
$$\left. +\left(G_p + SH_p\right)\int_0^{2\pi}\int_{\pi}^{0}\left[\frac{\partial C_{20}}{\partial\eta}\sigma_{\xi\eta}N\right]_{S_p}\frac{c\sin\eta}{\left(\cosh\alpha-\cos\eta\right)}d\eta\, d\theta\right\} \tag{4.5.47}$$

where S is defined as the ratio of diffusivity of counterions to diffusivity of coions:

$$S = \frac{D_1}{D_2} \tag{4.5.48}$$

This is programmed in "ForceNormalLowPe"

4.6 - Electroviscous Force for Arbitrary Peclet Numbers

4.6.1 - Electroviscous ion concentrations

In this section the restriction on the Peclet numbers is released, so that the electroviscous ion concentration satisfies a single equation, given by (1.3.60), which may be written in the bipolar coordinate system as

$$\left(\cosh\xi - \cos\eta\right)\left(\frac{\partial^2\tilde{c}_2}{\partial\xi^2} + \frac{\partial^2\tilde{c}_2}{\partial\eta^2} + \frac{1}{\sin^2\eta}\frac{\partial^2\tilde{c}_2}{\partial\theta^2}\right) - \left(\frac{1+S}{2}cPe\tilde{u}_\xi + \sinh\xi\right)\frac{\partial\tilde{c}_2}{\partial\xi}$$
$$-\left(\frac{1+S}{2}cPe\tilde{u}_\eta + \frac{\cosh\xi\cos\eta - 1}{\sin\eta}\right)\frac{\partial\tilde{c}_2}{\partial\eta} - \frac{1+S}{2\sin\eta}cPe\tilde{u}_\theta\frac{\partial\tilde{c}_2}{\partial\theta} = 0 \tag{4.6.1}$$

with the boundary condition

$$\left.\frac{\partial\tilde{c}_2}{\partial\xi}\right|_{S_J} = PeF_{cJ}\left(\cosh\xi - \cos\eta\right)\frac{\partial}{\partial\xi}\left[\left(\cosh\xi - \cos\eta\right)\frac{\partial}{\partial\xi}\right]\tilde{u}_\xi, \quad J = \left(P, W\right) \tag{4.6.2a}$$

$$\tilde{c}_2 \to 0 \qquad \text{as}\left(\xi, \eta\right) \to 0 \tag{4.6.2b}$$

The corresponding finite difference equation is

$$A_0\tilde{c}_2 = A_1\tilde{c}_2(1) + A_2\tilde{c}_2(2) + A_3\tilde{c}_2(3) + A_4\tilde{c}_2(4) + A_5\tilde{c}_2(5) + A_6\tilde{c}_2(6) \tag{4.6.3}$$

in which A_i (i = 0, 1, 2, 3, 4, 5, 6) are weighted functions and $C_{21}(i)$ (i = 1, 2, 3, 4, 5, 6) are the value of C_{21} at six immediate neighborhood nodes, located on the coordinate curves passing at the point under consideration, C_{21}. Here, node (1) is taken to be located in increasing direction of η, node (2) is its reflection with respect to ξ coordinate, node (3) is in the increasing direction of ξ, node (4) is its reflection with respect to η coordinate, node (5) is in the increasing direction of θ coordinate, and node (6) is its reflection with respect to (ξ, η)-plane. The weighted functions are determined upon expanding the finite difference equation by a Taylor series, then equating it to the analytical equation, and collecting the terms of the same order:

$$A_0 = \left(\cosh\xi - \mu\right)\left(\frac{2}{h_\eta^2} + \frac{2}{h_\xi^2} + \frac{2}{h_\eta^2\sin^2\eta}\right) \tag{4.6.4a}$$

$$A_1 = \frac{\cosh\xi - \mu}{h_\eta^2} + \frac{\mu\cosh\xi - 1}{2h_\eta\sin\eta} - \frac{1+S}{2h_\eta}cPe\tilde{u}_\eta \tag{4.6.4b}$$

$$A_2 = \frac{\cosh\xi - \mu}{h_\eta^2} - \frac{\mu\cosh\xi - 1}{2h_\eta\sin\eta} + \frac{1+S}{2h_\eta}cPe\tilde{u}_\eta \tag{4.6.4c}$$

$$A_3 = \frac{\cosh\xi - \mu}{h_\xi^2} - \frac{\sinh\xi}{h_\xi\sin\eta} - \frac{1+S}{2h_\xi}cPe\tilde{u} \tag{4.6.4d}$$

$$A_4 = \frac{\cosh\xi - \mu}{h_\xi^2} + \frac{\sinh\xi}{h_\xi \sin\eta} + \frac{(1+S)cPe\tilde{u}_\xi}{2h_\xi} \tag{4.6.4e}$$

$$A_5 = \frac{\cosh\xi - \mu}{h_\theta^2 \sin^2\eta} - \frac{1+S}{2h_\theta \sin\eta} cPe\tilde{u}_\theta \tag{4.6.4f}$$

$$A_6 = \frac{\cosh\xi - \mu}{h_\theta^2 \sin^2\eta} + \frac{1+S}{2h_\theta \sin\eta} cPe\tilde{u}_\theta \tag{4.6.4g}$$

Using the symmetry property with respect to the (x, z)-plane, only calculations for half the domain are required, that is only the part of the domain bounded by $\xi = 0$, $\xi = \alpha$, $\eta = 0$, $\eta = \pi$, $\theta = 0$ and $\theta = \pi$ is considered in the calculation. This is done by the program "c2ArbitraryPe". The domain is divided between $(K+1)(L+1)^2$ nodes, where K is the number of intervals on the ξ-coordinate and L is the number of intervals on both η and θ-coordinate. Thus, we have L+1 planes bounded by the plane $\theta = 0$ and $\theta = \pi$, separated by an angle $h_\theta = \pi/L$. Each plane consists of the matrix of nodes with (K+1)(L+1) elements. The finite difference equation for each node located on the solid surfaces is determined with the same procedure as that discussed in § 4.3.3 for low Pe. For nodes on the boundaries $\theta = 0$ and $\theta = \pi$, the symmetry property is used, for which the finite difference equation is determined by

$$A_0\tilde{c}_2 = A_1\tilde{c}_2(1) + A_2\tilde{c}_2(2) + A_3\tilde{c}_2(3) + A_4\tilde{c}_2(4) + \left(A_5 + A_6\right)\tilde{c}_2(5) \tag{4.6.5a}$$

for nodes on the plane $\theta = 0$, and

$$A_0\tilde{c}_2 = A_1\tilde{c}_2(1) + A_2\tilde{c}_2(2) + A_3\tilde{c}_2(3) + A_4\tilde{c}_2(4) + \left(A_5 + A_6\right)\tilde{c}_2(6) \tag{4.6.5b}$$

for those on the plane $\theta = \pi$.

4.6.2 - Electroviscous potential

The electroviscous potential is determined by

$$\tilde{\psi}_2 = \left(\frac{D_2 - D_1}{D_2 + D_1}\right)\tilde{c}_2 + \tilde{\phi} \tag{4.6.6}$$

where $\tilde{\phi}$ satisfies the Laplace equation written in the bipolar coordinate system:

$$\left(\cosh\xi - \cos\eta\right)\left(\frac{\partial^2\tilde{\phi}}{\partial\xi^2} + \frac{\partial^2\tilde{\phi}}{\partial\eta^2} + \frac{1}{\sin^2\eta}\frac{\partial^2\tilde{\phi}}{\partial\theta^2}\right) - \sinh\xi\frac{\partial\tilde{\phi}}{\partial\xi} + \frac{\cosh\xi\cos\eta - 1}{\sin\eta}\frac{\partial\tilde{\phi}}{\partial\eta} = 0 \tag{4.6.7}$$

with boundary conditions [c.f., (A.44)]

$$\frac{\partial\tilde{\phi}}{\partial\xi}|_{\xi=0} = \mathrm{PeF_{\phi W}BCWTR}, \qquad \frac{\partial\tilde{\phi}}{\partial\xi}|_{\xi=\alpha} = \mathrm{PeF_{\phi P}BCSTR} \tag{4.6.8}$$

$$\tilde{\phi} \to 0 \qquad \text{as}\left(\xi, \eta\right) \to 0 \tag{4.6.9}$$

Its finite difference equation is the same as that for $\tilde{c}_2$, given by (4.6.3), from which and from the analytical equation, given by (4.6.7), the weighted functions for $\tilde{\phi}$ are determined as:

$$A_0 = \left(\cosh\xi - \mu\right)\left(\frac{2}{h_\eta^2} + \frac{2}{h_\xi^2} + \frac{2}{h_\eta^2\sin^2\eta}\right) \tag{4.6.10a}$$

$$A_1 = \frac{\cosh\xi - \mu}{h_\eta^2} + \frac{\mu\cosh\xi - 1}{2h_\eta\sin\eta} \tag{4.6.10b}$$

$$A_2 = \frac{\cosh\xi - \mu}{h_\eta^2} - \frac{\mu\cosh\xi - 1}{2h_\eta\sin\eta} \tag{4.6.10c}$$

$$A_3 = \frac{\cosh\xi - \mu}{h_\xi^2} - \frac{\sinh\xi}{h_\xi\sin\eta} \tag{4.6.10d}$$

$$A_4 = \frac{\cosh\xi - \mu}{h_\xi^2} + \frac{\sinh\xi}{h_\xi\sin\eta} \tag{4.6.10e}$$

$$A_5 = A_6 = \frac{\cosh\xi - \mu}{h_\theta^2\sin^2\eta} \tag{4.6.10f}$$

The value of $\tilde{\phi}$ for each node is obtained by Program "PhiArbitraryPe" from which $\tilde{\psi}_2$, given by (4.6.6), is determined in Program "ForceParallelArbitraryPe".

4.6.2 - Electroviscous Force

The tangential and normal component of the force are determined by Programs

ForceParallelArbitrayPe" and "ForceNormalArbitraryPe" with the same procedure as that discussed for low Pe. However, for low Pe the integration over θ is performed analytically between 0-2π, whilst for arbitrary Pe the integration is performed numerically between 0-π, and the results are multiplied by a factor of two.

4.7 - Results and Conclusions

The exact and numerical solutions of a sphere-wall interactions are obtained by the use of a bipolar coordinate system (ξ, η, θ) described in AppendixA. For low Peclet numbers and arbitrary particle-wall distances the numerical solutions of electroviscous ion concentrations and potential are determined by the aid of Programs "C21Numeric", "C22Numeric", "C20Numeric", and "PhiNumeric", from which the tangential and normal component of the electroviscous force are obtained by Programs "ForceParallelNumericLowPe" and "ForceNormaLowPe". The boundary conditions and the flow field involved in the numerical calculation of the electroviscous ion concentrations and potential, or in general the hydrodynamic part of the problem is determined analytically. The stress tensor involved in the calculation of the force are determined analytically by the Programs "SigmaParallel" and "SigmaNormal, for the tangential and normal components of the force, respectively. The electroviscous ion concentration and potential at order Pe are also determined analytically, programmed by "C21Psi21Analytic" which agrees with the numerical solution within 98% percent accuracy, illustrated by Table B11 in Appendix B. The tangential component of the force is determined from the analytical solution by Program "ForceParallelAnalytic". Table B13 shows not only that the numerical and analytical solutions of the force are in fair agreement with each other, but also indicates that the problem is mesh independent.

For arbitrary Peclet numbers and arbitrary particle-wall distances the electroviscous ion concentrations and potential are obtained numerically by the aid of Programs "c2ArbitraryPe" and "PsiArbitraryPe", from which the tangential and normal components of the electroviscous force are determined by Programs "ForceParallelArbitraryPe" and "ForceNormalArbitraryPe"

The inputs of the force programs for both low and arbitrary Peclet numbers are:

- determination of mesh size, K×L for low Pe and K×L×L for arbitrary Pe (with K is the number of intervals on the ξ-coordinate and L is the number of intervals on either the η-coordinate or θ-coordinate).

- dimensionless particle-wall distances defined by relation (3.2.2c).
- ζ-potential of particle and wall surfaces, denoted by ZetaP and ZetaW, respectively made dimensionless by the relation (1.3.10).
- Peclet number defined by relation (3.2.2.d).
- ratio of angular velocity to the linear velocity, r, defined by relation (4.2.147).
- ratio of diffusivity of ions, defined by relation (4.5.48).

The outputs are the dimensionless force divided by λ [λ is defined by the relation (3.2.2.e)], denoted by *Integral*. Thus, the dimensional force is determined by

$$F_x = \frac{1}{2}\frac{(\varepsilon_r\varepsilon_0)^2(kT)^3}{a(z_1e)^4 c_\infty}\text{Integral}_x, \quad F_z = \frac{1}{2}\frac{(\varepsilon_r\varepsilon_0)^2(kT)^3}{a^2(z_1e)^4 c_\infty}\text{Integral}_z \tag{4.7.1}$$

where $(\varepsilon_r\varepsilon_0)$ is the permitivity of the medium, (kT) the thermal energy, (z_1e) charge of a counterion , c_∞ the number ion bulk concentration and a the particle radius.

The numerical solution and also the analytical one (for the tangential component) for small particle wall distances ($\delta << 1$) and for small and intermediate Peclet numbers ($Pe << \delta^{-1/2}$) can be approximated by the following formulas:

$$\frac{\tilde{F}_x}{\lambda} = -\pi Pe\delta^{-2}\left\{\left[\left(\frac{28}{3}G_P + \frac{41}{30}G_W\right)(G_P + G_W) + S\left(\frac{28}{3}H_P + \frac{41}{30}H_W\right)(H_P + H_W)\right]\times (q+r) - \frac{1}{3}\left[\left(\frac{28}{3}G_P + \frac{41}{30}G_W\right)(G_P - G_W) + S\left(\frac{28}{3}H_P + \frac{41}{30}H_W\right)(H_P - H_W)\right](q-r)\right\} \tag{4.7.2}$$

$$\frac{\tilde{F}_z}{\lambda} = \frac{\pi}{450}Pe^2\delta^{-2}\times\left\{\left[\frac{283}{10}(G_P + SH_P) + \frac{88}{3}(G_W + SH_W)\right]^2 (q+r)^2 - \frac{1}{3}\left[\left(\frac{283}{10}\right)^2 (G_P + SH_P)^2 - \left(\frac{88}{3}\right)^2 (G_W + SH_W)^2\right](q^2 - r^2)\right\} \tag{4.7.3}$$

in which q is equal to zero in the absence of translation, otherwise it is equal to one; the parameters G and H are defined by (2.6.70), and r and S by

$$r = \frac{a\Omega}{U}, \qquad S = \frac{D_1}{D_2} \tag{4.7.4}$$

The orders of the force in Pe and δ agree with the inner solution presented in Chapter 3. In fact the dependence of the force on Pe, δ, the angular and linear velocity, the ratio of diffusivities of ions, and on the ζ-potentials is deduced from the analytical solution, but the coefficients are determined numerically and approximated in a fraction form, 9.3292≈28/3, 1.3663≈41/30, 28.3005≈283/10, 29.3325≈88/3. It is observed that the second terms in square brackets on the right-hand side of either component of the force has a coefficient of -1/3 in addition to the change in the sign. Assuming there is a similarity between the inner solution and the complete one, the inner solution for arbitrary ζ-potentials can be approximated by the following relations [c.f., (3.6.23a, 26a)]:

$$F_x = -\frac{8\pi}{25}\frac{(\varepsilon_r\varepsilon_0)^2(kT)^3}{c_\infty(z_1e)^4}\frac{a}{h^2}\times$$
$$\left\{\left[\frac{(7G_P+2G_W)(G_P+G_W)}{D_1}+\frac{(7H_P+2H_W)(H_P+H_W)}{D_2}\right](U+a\Omega)\right.$$
$$\left.-\frac{1}{3}\left[\frac{(7G_P+2G_W)(G_P-G_W)}{D_1}+\frac{(7H_P+2H_W)(H_P-H_W)}{D_2}\right](U-a\Omega)\right\} \tag{4.7.5}$$

$$F_z = \frac{12\pi}{25}\frac{(\varepsilon_r\varepsilon_0)^2(kT)^3}{c_\infty(z_1e)^4}\frac{a^2}{h^2}\left[\left(\frac{G_P}{D_1}+\frac{H_P}{D_2}\right)+\left(\frac{G_W}{D_1}+\frac{H_W}{D_2}\right)\right]^2(U+a\Omega)^2$$
$$-\frac{1}{3}\left[\left(\frac{G_P}{D_1}+\frac{H_P}{D_2}\right)^2-\left(\frac{G_W}{D_1}+\frac{H_W}{D_2}\right)^2\right](U^2-a^2\Omega^2) \tag{4.7.6}$$

However, comparison of (4.7.2) with (4.7.5), and (4.7.3) with (4.7.6), shows that the similarity for the tangential component is very weak, whereas for the normal component the similarity is strong, that is the ratio of the contribution of the wall to the force to that of the particle for tangential component in formula (4.7.2) is 0.1464 and in formula (4.7.5) is 0.2857, almost two times, whereas for normal component that ratio is 1.0365 in formula

(4.7.3) and 1 in formula (4.7.6) which is very close. Tables B14 and B15, located in Appendix B, compare the tangential and normal components of the force obtained from different methods for different conditions with the formulas (4.7.2, 3). It also shows that the contribution from the inner region is more than half the force. It is interesting to note that for large particle-wall distances the effects of wall interaction diminishes resulting in a tangential component of the force comparable with the drag force experienced by an isolated sphere obtained by Oshima *et al.* (1984). In the example of Table B14, for $\delta = 100$, the tangential component of the force is obtained as $\widetilde{F}_x / \lambda$, =- 0.1518, -0.1503, and -0.1480, determined, respectively, by the analytical method, numerical method for low Pe and numerical method for arbitrary Pe. For the same Pe, ratio of diffusivity of ions, and particle ζ-potential, formula (1.3.74) predicts an electroviscous drag of magnitude, $\widetilde{F}_x / \lambda$, = -0.1592 for an isolated sphere.

Representative numerical results are illustrated in Fig.s 4.3-9. The tangential components, $\widetilde{F}_x / \lambda$, are calculated by Program "ForceParallelArbitraryPe", and the normal components, $\widetilde{F}_z / \lambda$, by Program "ForceNormalArbitraryPe". The ion valency is taken to be one and the temperature of the medium is room temperature. The dependence of the force on Peclet number is illustrated in Fig. 4.3 for three particle-wall distances, δ =0 .1, δ =1, δ =10. In this example ζ_P = -50 mV, ζ_W=-100 mV, S (=D_1/D_2) =1and r (=$a\Omega/U$) =1/3. Fig. 4.3.a, b show that in general the force increases as Pe (=Ua/D_1) increases, because the higher the Pe the more pronounced the effect of the flow field on the system. The tangential component of the force depends almost linearly on the Peclet number for the whole rang of Pe. This is because most (more than 98 %) of the contribution to the tangential component of the force comes from the parameter ϕ in the equation of the electroviscous potential, given by (1.3.61), and the equation and boundary conditions (1.3.61b-d) indicates that ϕ linearly depends on Pe for arbitrary Peclet numbers. For the same reason formula (4.7.2) works for arbitrary Pe. Fig. 4.3b indicates that for different particle-wall distances the normal component of the force depends linearly on Pe^2 when Pe is small, and for small δ the linear part extends up to Pe being smaller than $\delta^{-1/2}$, which agrees with the analytical solution of the inner region. The dependence of the force on the dimensionless gap width is plotted in Fig.

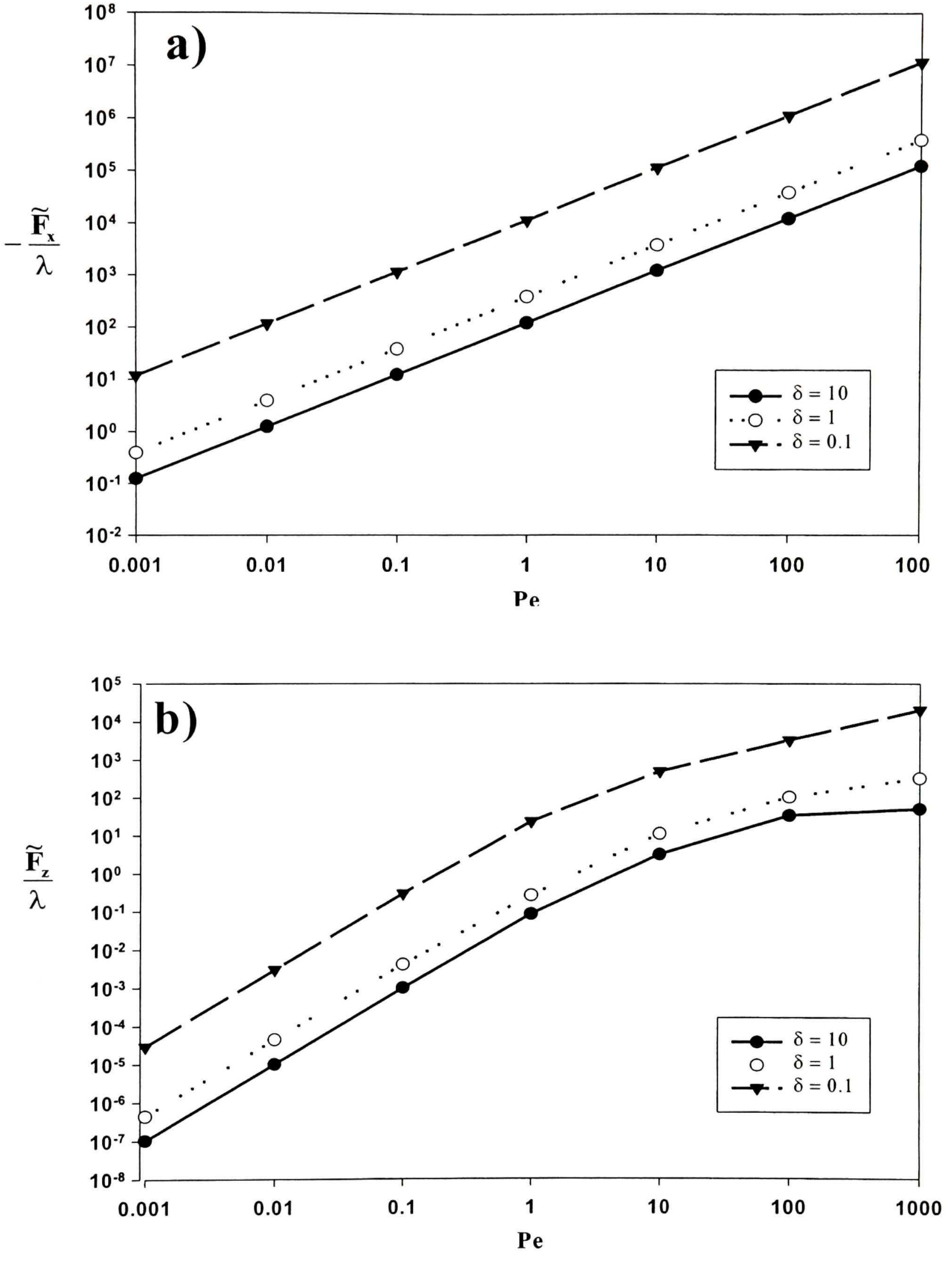


Fig. 4.3 -Tangential (a) and normal (b) components of force vs Peclet number.

[ζ_P = -50 mV, ζ_W=-100 mV, S (=D_1/D_2) =1, r (=$a\Omega/U$) =1/3]

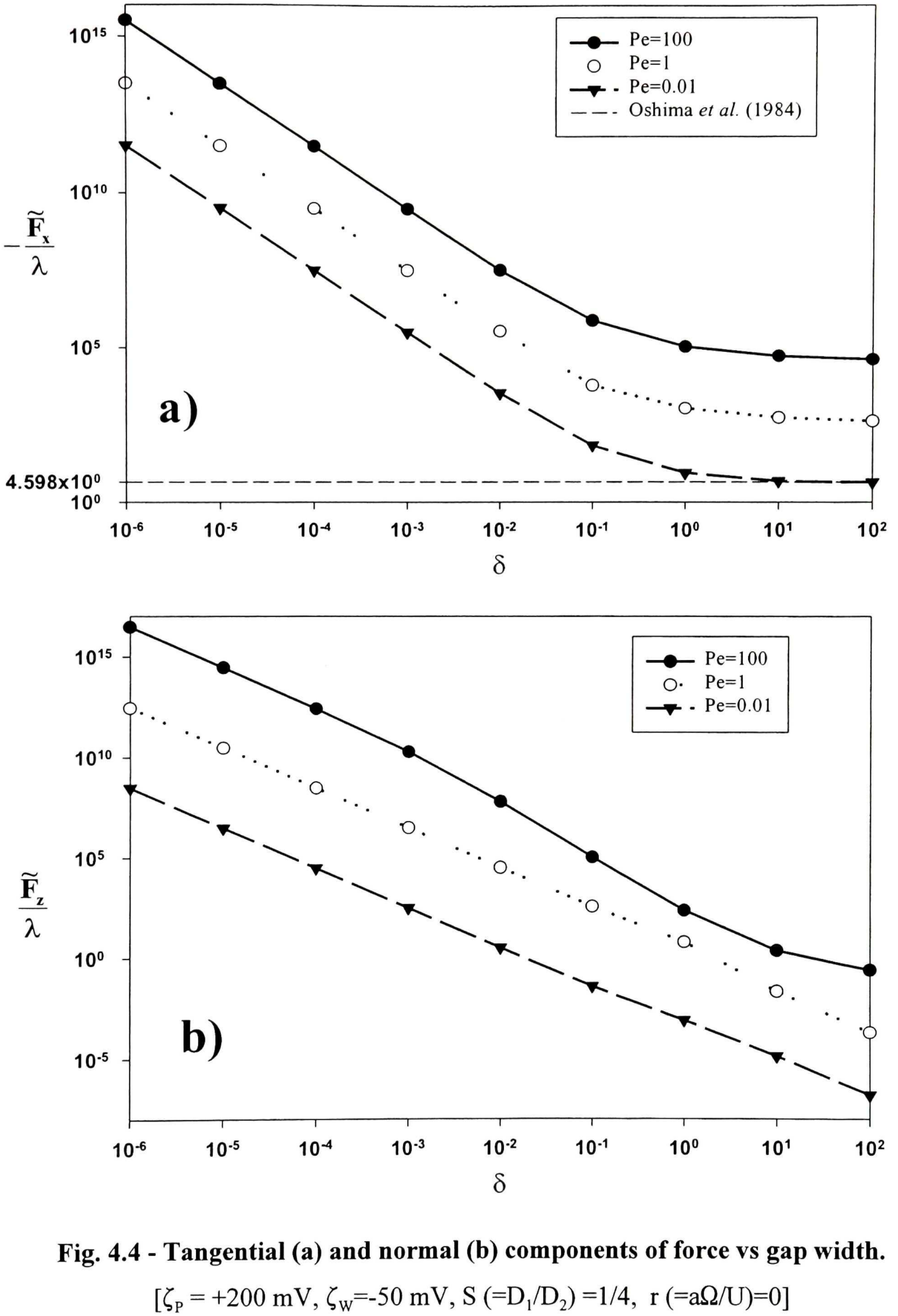


Fig. 4.4 - Tangential (a) and normal (b) components of force vs gap width.

[ζ_P = +200 mV, ζ_W=-50 mV, S (=D_1/D_2) =1/4, r (=aΩ/U)=0]

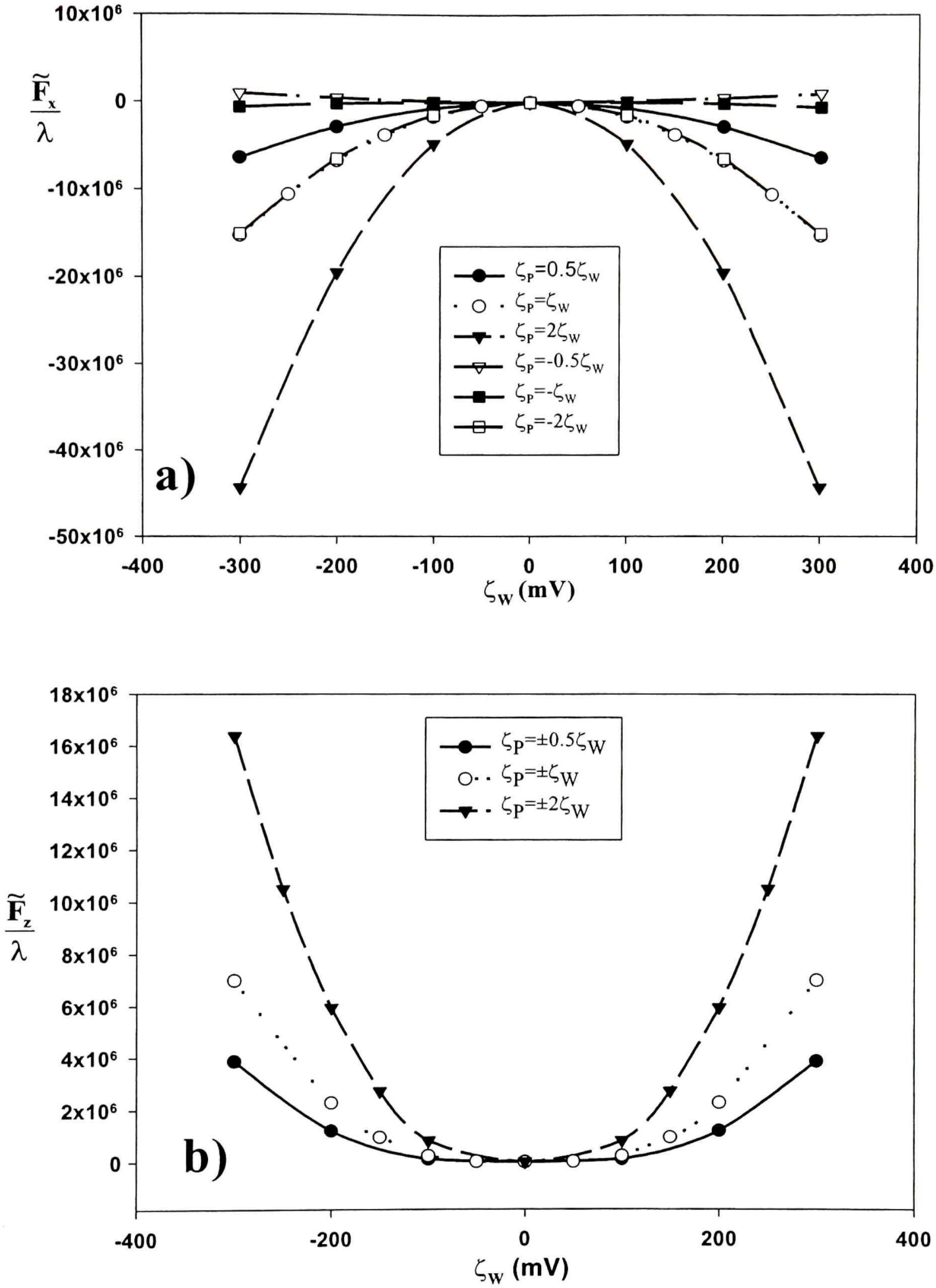
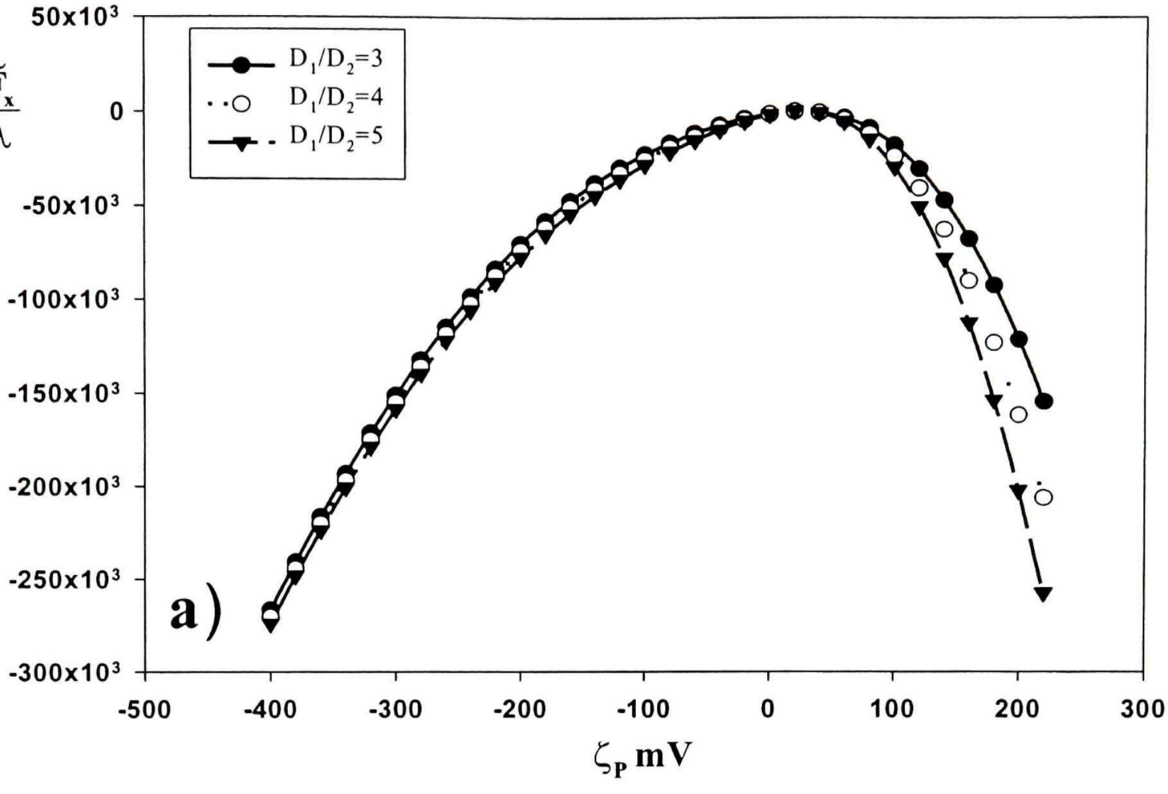


Fig. 4.5 - Tangential (a) and normal (b) components of force vs wall Zeta-potential with constant ratio of diffusivity.

[$\delta(=h/a) = 0.1$, $Pe(=aU/D_1)=100$, $S\ (=D_1/D_2)=1$, $r\ (=a\Omega/U)=0$]



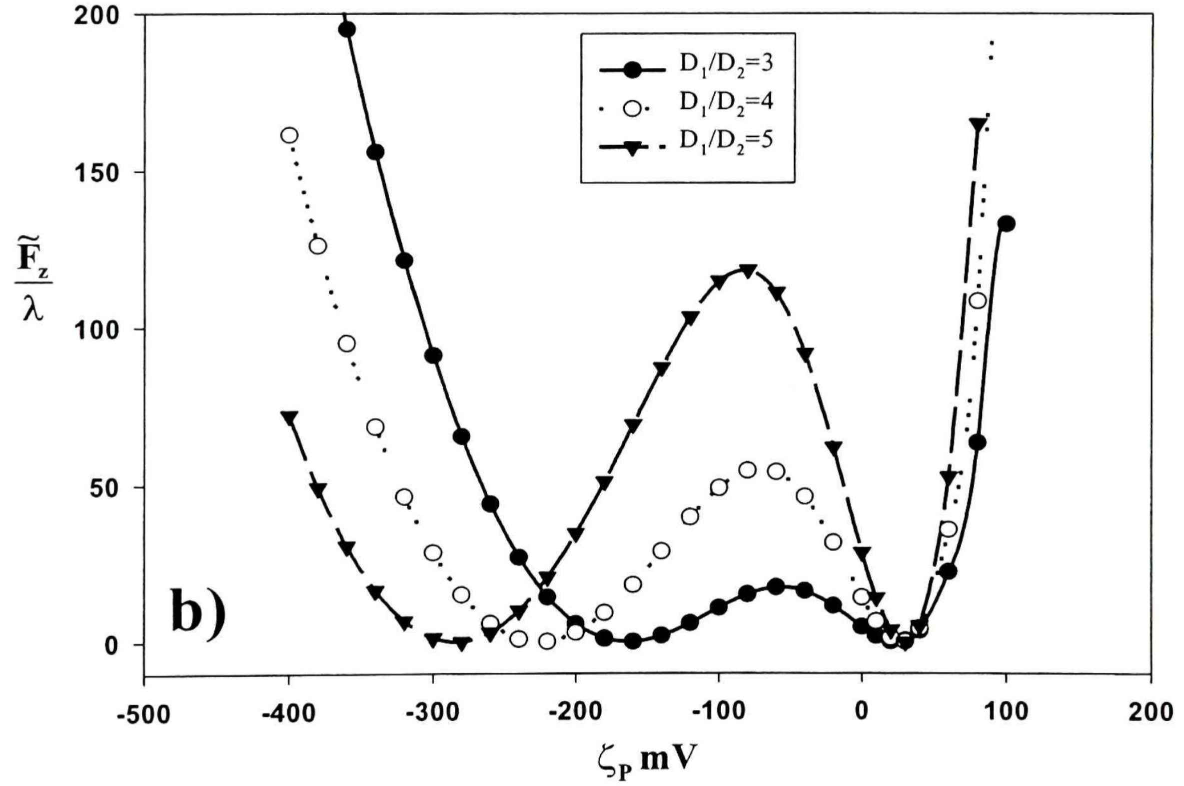


Fig. 4.6 - Tangential (a) and normal (b) components of force vs particle Zeta-potential with constant wall Zeta potential.

[ζ_W=-50 mV, δ(=h/a) = 0.01, Pe(=aU/D_1)=0.01, r (=aΩ/U) =2/3]

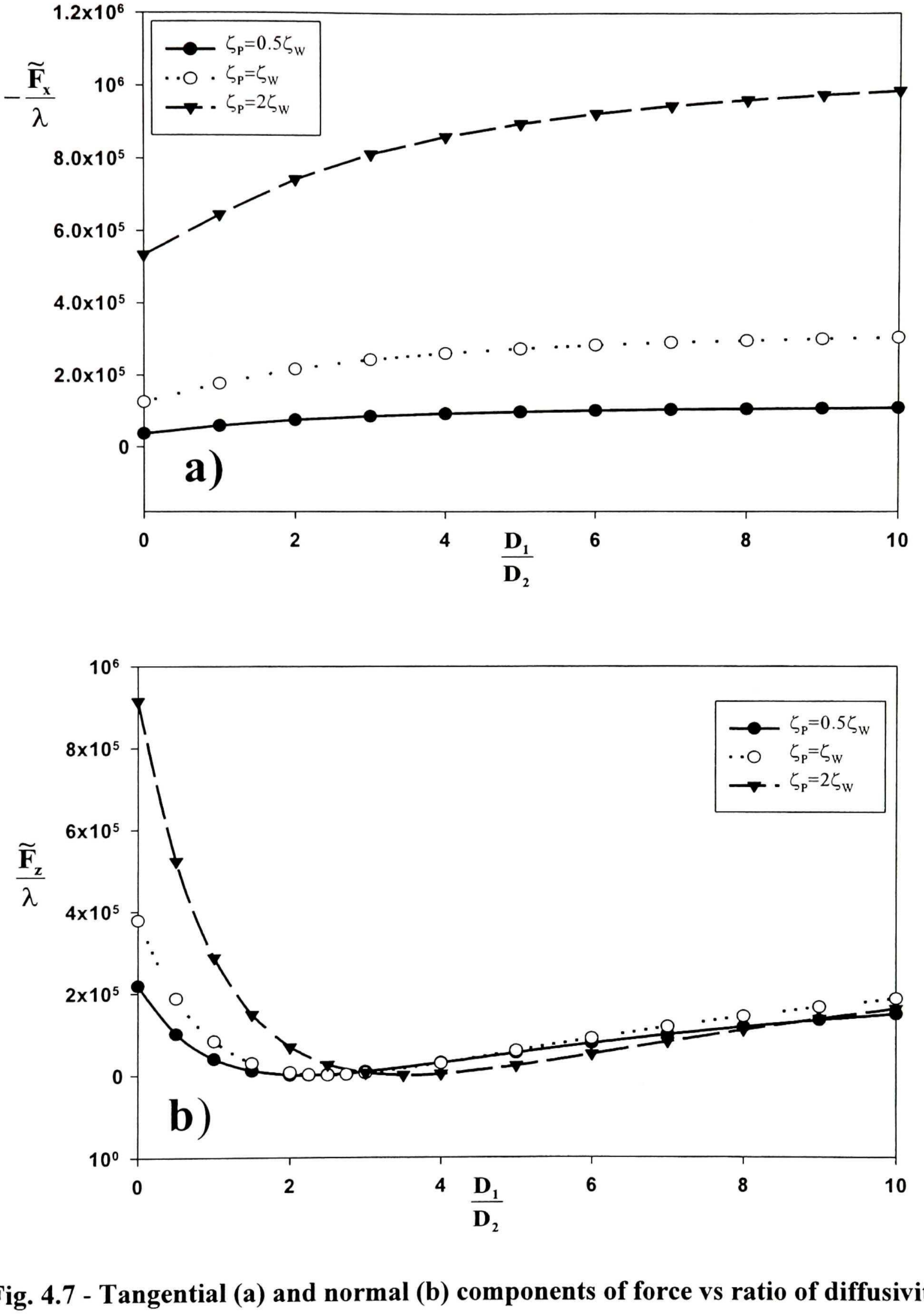


Fig. 4.7 - Tangential (a) and normal (b) components of force vs ratio of diffusivity of counter-ions to co-ions for rotation of particle.

[Pe($=a^2\,\Omega/D_1$) =10, δ=(h/a)=0.1, ζ_W=-100 mV, q=0, r=1]

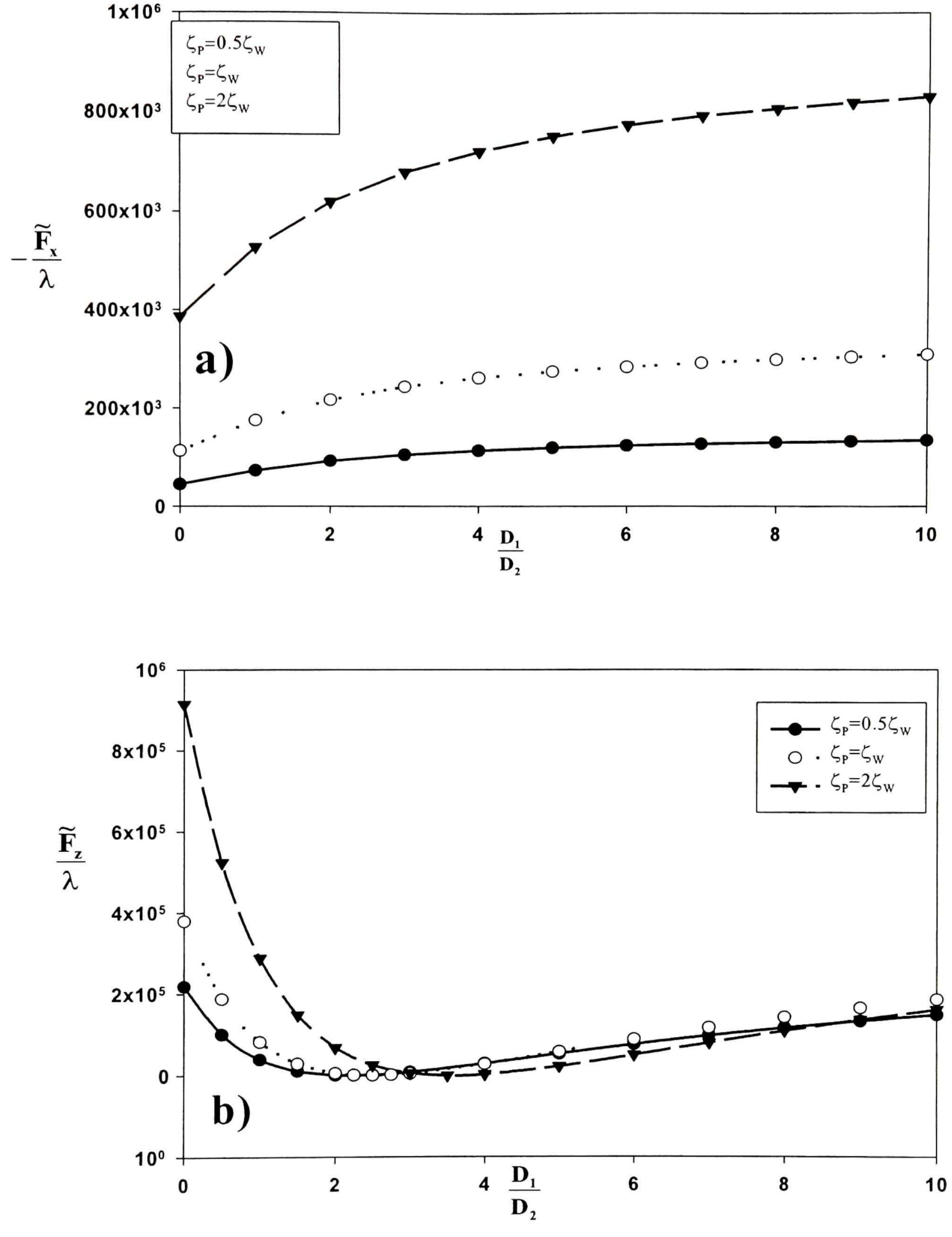
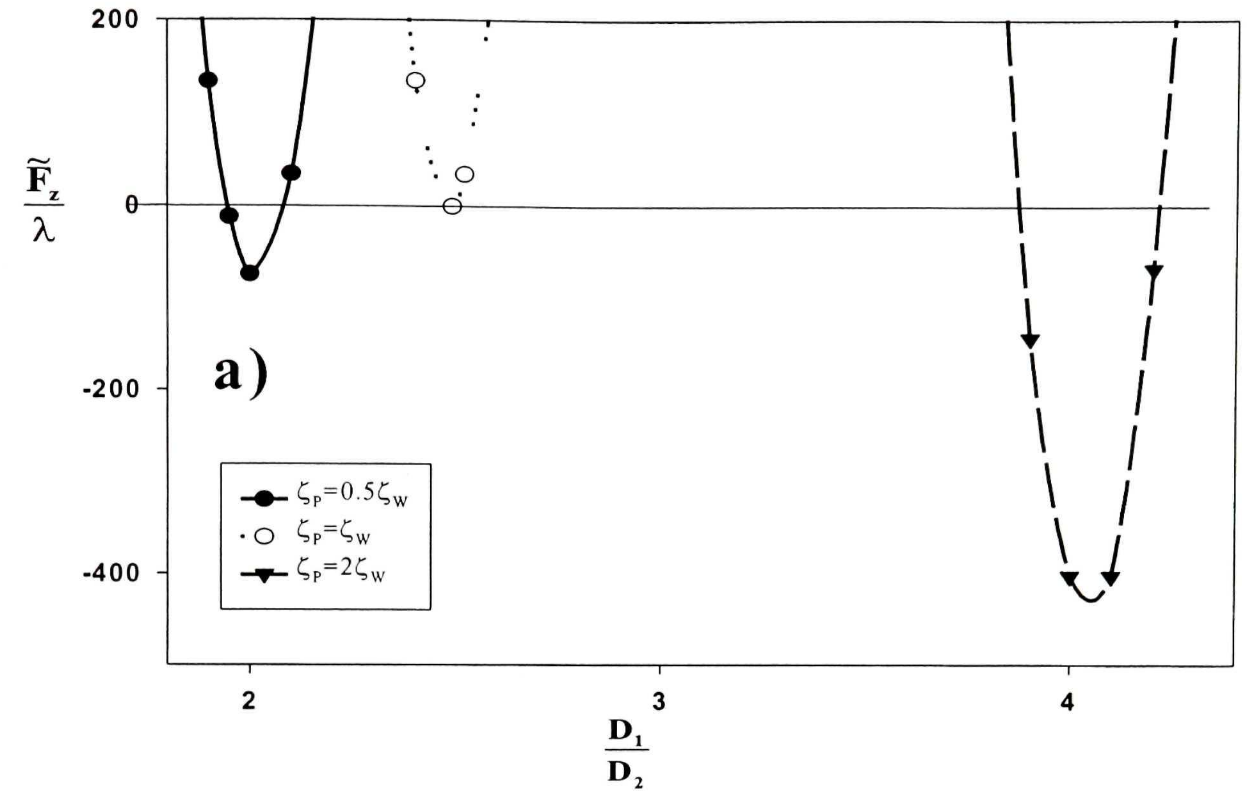
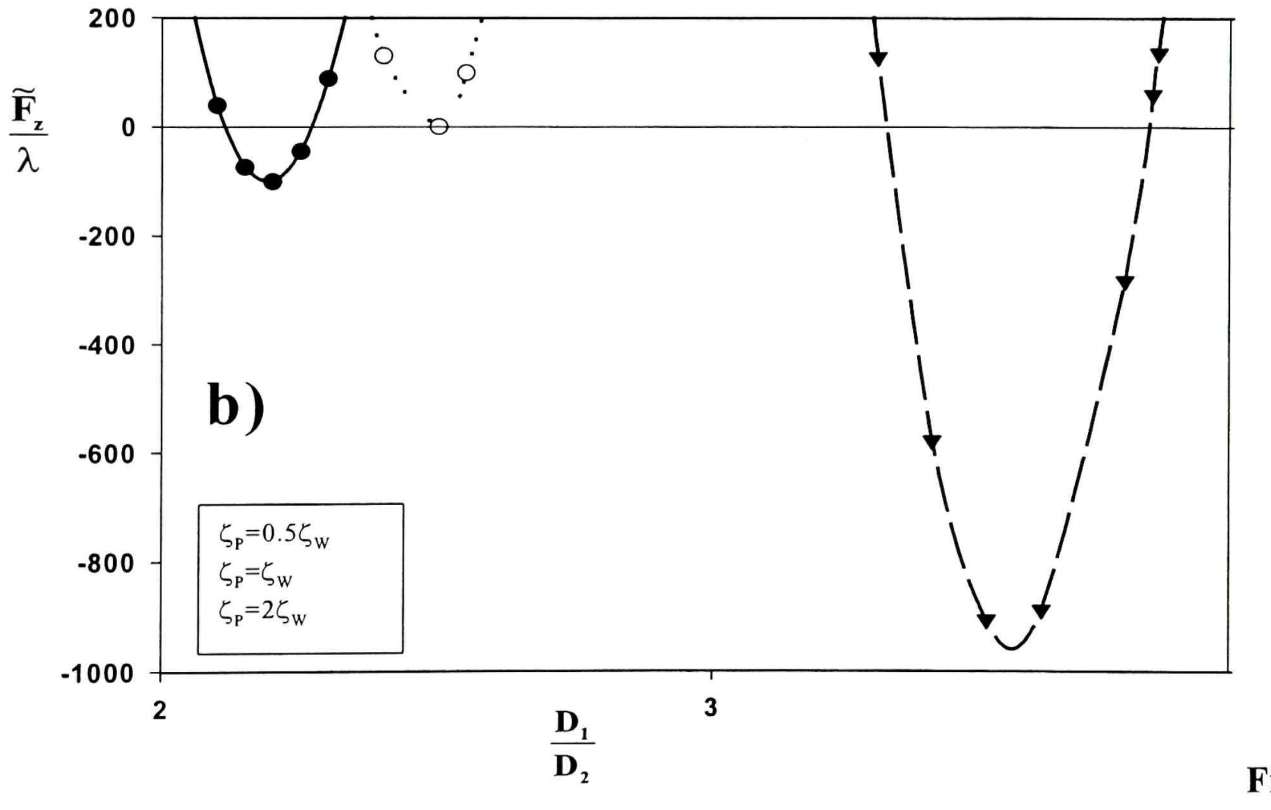


Fig. 4.8 - Tangential (a) and normal (b) components of force vs ratio of diffusivity of counter-ions to co-ions for translation of particle.

[Pe(=a U/D_1) =10, δ=(h/a)=0.1, ζ_W=-100 mV, q=1, r = 0]





Figg. 4.9 - Magnifying location of minima of (a) Fig. 4.7b for rotation and (b) Fig. 4.8b for translation of particle.

[Pe(=a U/D_1) =10, δ=(h/a)=0.1, ζ_W=-100 m)]

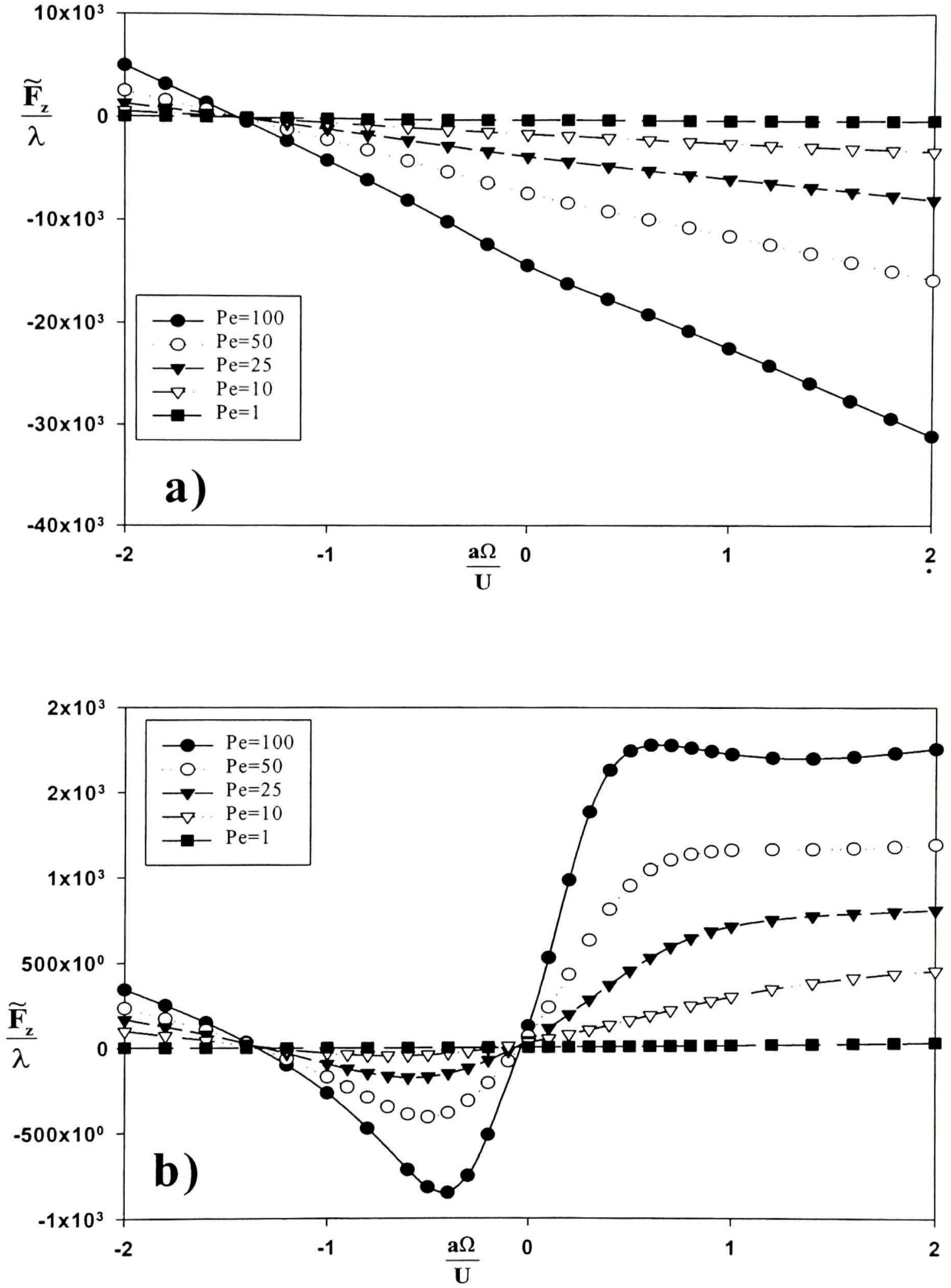


Fig. 4.10 - Tangential (a) and normal (b) components of force vs ratio of angular velocity to linear velocity.

[ζ_P=-50 mV, ζ_W=-25 mV δ(=h/a)=1, S (=D_1/D_2) =1/2, q=1]

4.4, for low Pe (Pe=0.01), intermediate Pe (Pe=1) and high Pe (Pe=100). For this figure, ζ_P = +200 mV, ζ_W=-50 mV, S (=D_1/D_2) =1/4, r (=$a\Omega/U$)=0 (only translation). As the particle-wall distance increases the effect of the wall interaction diminishes resulting in a lower magnitude of the force for both normal and tangential components, and hence at large distances from the wall, the drag component is comparable to Oshima *et al.*'s theory(1984) for sedimentation of an isolated sphere . When δ is small the tangential component of the force depends linearly on δ^{-2} for low, intermediate and high Pe, whereas the normal component depends linearly on δ^{-2} for Pe smaller than $\delta^{-1/2}$, and hence for high Pe the linear part of the normal component occurs at extremely small δ, in agreement with the analytical results. The dependence of the force on ζ-potentials is illustrated in Figs. 4.5, 6. In Fig. 4.6, the force is plotted versus the wall ζ-potential, ζ_W , for varius particle ζ-potentials, ζ_P , ζ_P= $\pm0.5\zeta_W$, ζ_P= $\pm\zeta_W$, and ζ_P= $\pm2\zeta_W$. In this example δ = 0.1, Pe =100, r=0 (only translation of particle), and S=1. At zero charge there is no electric field so that we do not expect any force to be experienced by the particle. The dependence of the force on ζ-potentials is non linear. This figure shows that there is a symmetry property with respect to ζ-potentials for both tangential and normal components of the force. For the tangential component by reversing the signs of both particle and wall ζ-potentials, and for the normal component by reversing the sign of one or both of ζ-potentials the magnitude of the force remains unaltered. Thus, the normal component is independent of the signs of the particle and wall charges, that is even the charges of the particle and wall are different (positive and negative) the particle experiences the same force (lift force) as that for the cases of both charges are of the same signs (negative or positive), but with the same magnitude. However, the above symmetry properties are only for identical diffusivity of ions (S=1), as can easily be observed from the formula (4.7.2, 3), that is by reversing the signs of ζ-potentials, the parameters G and H [c.f., definitions (2.6.70)] are replaced with each other and for only S =1 does this result in the symmetry properties. Fig. 4.5a also shows that the tangential component of the force can be positive (decreasing the hydrodynamic drag), as it happens for the case ζ_P= $-0.5\zeta_W$. The dependence of the force on particle ζ-potentials is illustrated in Fig. 4.6 for three ratios of diffusivity of ions, D_1/D_2= 3, 4, 5. For this example ζ_W=- 50 mV, δ = 0.01, Pe =0.01,and r=2/3. For the tangential component the curve has only one maximum, whereas for the normal component, there is one maximum and two minima. One of the minima occurs when the ζ-potentials of particle and wall are of a different sign, and the other when they are of the same sign. Both minima have negative values. The dependence of the force on ratio of diffusivity of ions is illustrated in Fig.4.7 for the rotation and in Fig. 4.8 for the translation of the particle, for three cases $\zeta_P = 0.5\zeta_W$, $\zeta_P = \zeta_W$, and $\zeta_P = 2\zeta_W$. These curves are obtained for Pe =10, δ=0.1, ζ_W=-100 mV, and q=0, r=1 for only rotation and q=1, r=0 for only translation of the particle. For only rotation, Pe is defined as $a^2\Omega/D_1$. For both rotation and translation, the normal component of the force has a minimum, depending on the magnitude of ζ-potentials. For identical ζ- potentials the minimum is zero, otherwise it is negative, the same as those observed for the analytical solutions of cylinder-wall and sphere-wall interactions. The location of the minima is magnified in Fig. 4.9a for the rotation of the particle and in Fig. 4.9b for its translation. This property is an interesting results, since it allows one to obtain a desired force, either positive, zero or negative, by a suitable combination of ζ-potentials and ratio of diffusivity of ions. The dependence of the force on the ratio of the angular velocity to the transnational velocity is illustrated in Fig.4.10. The data for this example are: ζ_P=-50 mV, ζ_W=-25 mV δ(=h/a)=1, S (=D_1/D_2) =1/2, q=1. Although for just translation or just rotation of the particle the drag component is negative (act in the opposite direction of the flow) and the normal component is positive (lift force) regardless of the direction of the flow, when both translation and rotation are present, but with the opposite direction, there would be a range of the ratio of the angular velocity to linear velocity that the former remains unaltered, and the latter changes the direction from positive to negative (attractive force). For this example, that range for the tangential component is (-1.47 to 0) and for the normal component (-1.42 to 0). The tangential component depends almost linearly on the ratio of the angular velocity to the linear velocity with a constant slope for low and intermediate Pe, and with a change in the slope of the curve for high Pe. In this example it happens at Pe $\geq$50. For the normal component also there is a change in the behavior of the force with respect to Pe. For low and intermediate Pe, each curve has only one minimum with a negative value (attractive force), but for high Pe (Pe>50) the curves have one maximum and two minima, one with a negative value, and the other with a positive one.

An experiment on a spherical particle of radius 2.6 μm in a shear flow was conducted by Wu, Warszynski & van de Ven (1996) demonstrated in Fig 4.11. The experiment was carried out in a surface collision apparatus with forward and backward movement. The variations in particle-wall separation distances with time are measured by a video tape resulting in an empirical expression:

$$\frac{h}{a} = p\left(1 - e^{-bt}\right) + c \tag{4.7.7}$$

in which p, b, and c are three adjustable parameters determined from the best fit. The force balance on the particle in the z-direction may be written as

$$F_{net} = \frac{6\pi\eta a u_z}{f_1(h/a)} \tag{4.7.8a}$$

where $f_1(h/a)$ is the correction coefficient to Stokes law due to the presence of the wall. F_{net} is composed of bouncy force, electrostatic force and electroviscous force during the shear and only bouncy and electrostatic force in the absence of shear. For the former it may be written as

$$F_{net} = F_{lift} + \frac{2\pi a B}{\kappa} e^{-kh} - \frac{4}{3}\pi a^3\left(\rho_f - \rho_p\right)g \tag{4.7.8b}$$

in which g is gravitation acceleration, ρ_f and ρ_p are fluid and particle densities, κ the reciprocal double layer thickness and B is determined by

$$B = 32\tanh^2\left(\frac{ze\zeta}{4kT}\right) \in \kappa^2\left(\frac{kT}{ze}\right)^2 \tag{4.7.8c}$$

The force was determined upon combination Eq.s (4.6.7, 8). The electrolyte is KCl with conductivity 5μS/m, and the medium is 96% glycerole-water solution. The shear rate is 19.1 s^{-1}. The present theory and the one by Bike & Prieve (1990) as an example of previous theories, given by (1.2.31), are compared with the experiments. The force from the present theory is obtained by Program "ForceNormalArbitraryPe". The linear and angular velocity in a simple shear flow is obtained by linear interpolation of the data obtained by Goldmann, Cox & Brenner (1967). In this experiment only the particle ζ-potential was measured, ζp =-

45 mV. The wall ζ-potential is taken to be between -75 and -125 mV. However, the shear flow can be decomposed into three individual flows, translation of particle, rotation of particle and shear for the whole medium, excluding the sphere. The present theory consists of the translation and the rotation of the particle. Therefore, no solid conclusion can be drawn, as far as the there is uncertainty in the wall ζ-potential and the contribution of the shear flow, which is not taken into account. But, since we expect the contribution to the force from the shear to be of the same order as that of the translation or the rotation of the particle, at least it can be concluded that the present theory predicts the right order for the force, whereas the pervious theories underestimate the force by more than two orders of magnitude.

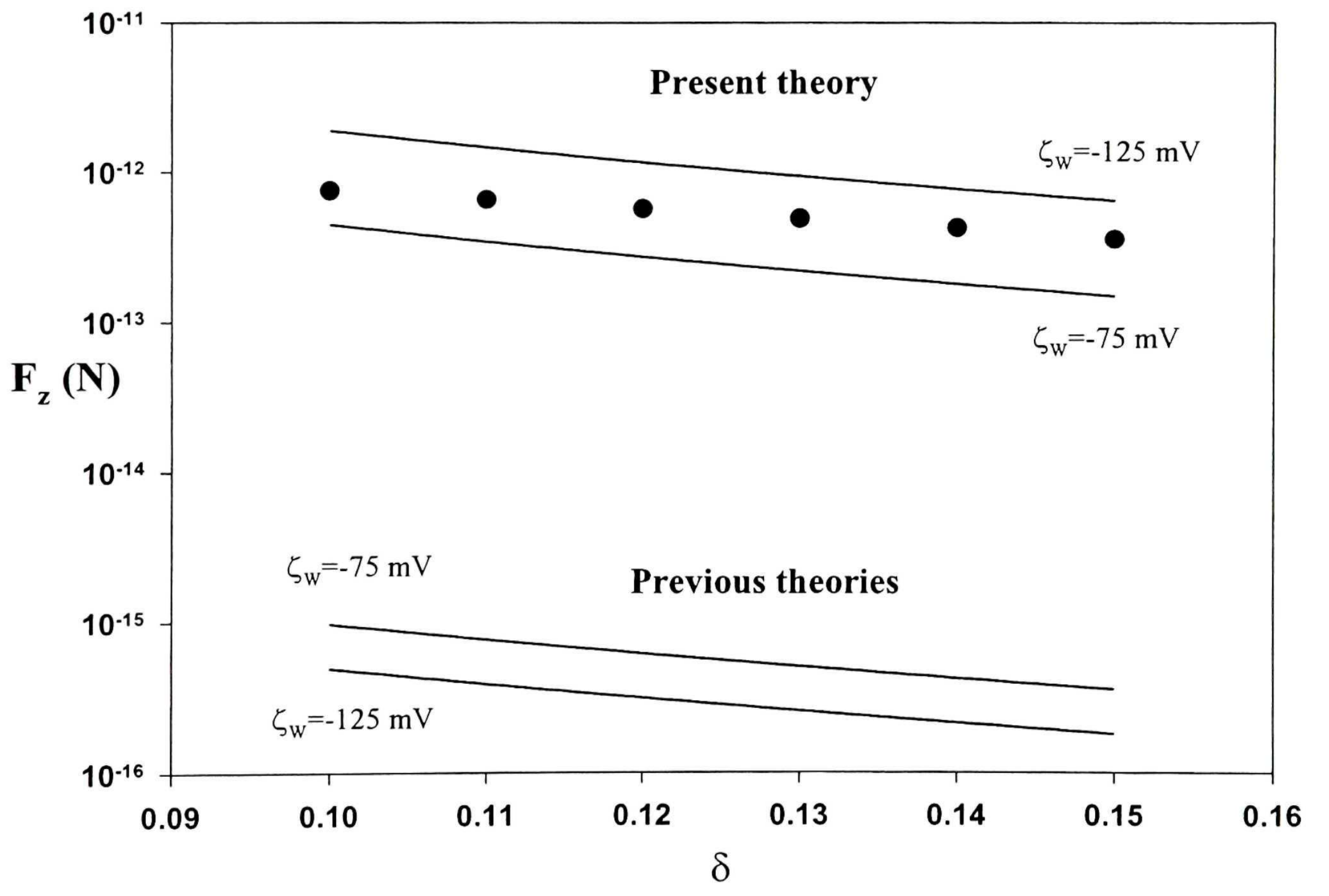


Fig. 4.11 - Comparison of theories with experiment.

[Symbols are experimental observations of Wu *et al.* (1996). Previous theories refers to Bike & Prieve (1990).]

Chapter Five

Conclusions

5.1 - Summary of Results and Conclusions

Electroviscous particle-wall interactions in systems in which the double layer thickness is thin, are evaluated as a solution of three partial differential equations, derived from Cox's general theory (1997), for electroviscous ion concentrations, electroviscous potential and electroviscous flow field, given by (1.3.59-61). The electroviscous cylinder-wall interactions and sphere-wall interactions for the translation and rotation of the particle close and parallel to a charged plane wall are analyzed by the use of the matched asymptotic expansion technique. The inner solutions of the force experienced by the particles are determined, upon the use of the Lorentz reciprocal theorem, discussed in §1.3.6. These solutions are obtained under the assumption of small particle wall distances, δ, ($\delta \ll 1$) but for low and intermediate Peclet numbers, Pe, ($Pe \ll \delta^{-1/2}$). For sphere-wall interactions the problem is extended to arbitrary particle-wall distances and arbitrary Pe.

For cylinder-wall interactions, the tangential component of the electroviscous force is of order $\left(\epsilon^4\ \delta^{-5/2}Pe\right)$ and the normal component of order $\left(\epsilon^4\ \delta^{-5/2}Pe^2\right)$, where ϵ is the ratio of double layer thickness to the cylinder radius, δ the dimensionless gap width, and Pe the Peclet number. These parameters are defined by (2.2.4a). The tangential component of the force per unit length of the cylinder is obtained as

$$F_x = -2\sqrt{2}\pi\eta\sqrt{\frac{a}{h}}U - \frac{\sqrt{2}\pi}{2}\frac{(\varepsilon_r\varepsilon_0)^2(kT)^3}{(z_1e)^4 c_\infty}\frac{\sqrt{a}}{h^2\sqrt{h}} \times$$
$$\left\{\left[\frac{(3G_P+G_W)}{D_1}(G_P+G_W)+\frac{(3H_P+H_W)}{D_2}(H_P+H_W)\right](U+a\Omega) + \left[\frac{2G_P}{D_1}(G_P-G_W)+\frac{2H_P}{D_2}(H_P-H_W)\right](U-a\Omega)\right\} \tag{5.1.1}$$

and the normal component as

$$F_z = \frac{\sqrt{2}\pi}{8}\frac{(\varepsilon_r\varepsilon_0)^2(kT)^3}{(z_1e)^4 c_\infty}\frac{\sqrt{a}}{h^2\sqrt{h}}\left\{5\left[\left(\frac{G_P}{D_1}+\frac{H_P}{D_2}\right)+\left(\frac{G_W}{D_1}+\frac{H_W}{D_2}\right)\right]^2(U+a\Omega)^2 + 4\left[\left(\frac{G_P}{D_1}+\frac{H_P}{D_2}\right)^2-\left(\frac{G_W}{D_1}+\frac{H_W}{D_2}\right)^2\right](U^2-a^2\Omega^2)\right\} \tag{5.1.2}$$

in which $(\varepsilon_r \varepsilon_0)$ is the permitivity of the medium, (kT) the thermal energy, $(z_1 e)$ charge of a counter-ion, c_∞ the number ion bulk concentrations, D_1 and D_2 the diffusivity of counter-ions and co-ions, respectively; a is the particle radius, h the clearance between the particle and wall, and U is the translation velocity of the particle and Ω its rotation with the clockwise direction taken to be the positive direction, as shown in Fig. 2.1. The parameters G and H are functions of ζ-potentials defined by

$$G_J = \ln \frac{1 + e^{-\frac{z_1 e \zeta_J}{2kT}}}{2}, \qquad H_J = \ln \frac{1 + e^{\frac{z_1 e \zeta_J}{2kT}}}{2} \qquad J = (P, W) \tag{5.1.3}$$

The first term in (5.1.1) is the purely hydrodynamic force. Because of the symmetry, the hydrodynamic force, at the first approximation, is independent of the rotation of the particle.

Upon comparison of results with the existing theories, it is found that Cox's theory for the drag component of the electroviscous force, given by (1.2.32d), is valid for both translation and rotation of a cylinder parallel to the wall, but its normal component, reported in Wu, *et al.* (1996), given by (1.2.32a), is valid only for translation of a cylinder. The expression by Warszynski & van de Ven's theory (2000), given by (1.2.33), is valid only for a charged wall, but with an uncharged cylinder under translation parallel to a wall.

For sphere-wall interactions the inner solution of the electroviscous force is similarly obtained analytically for the cases of identical particle and wall ζ-potentials. The tangential component of the force is of order $(\epsilon^4 \delta^{-2} Pe)$ and the normal component of order $(\epsilon^4 \delta^{-2} Pe^2)$, an $O(\delta^{1/2})$ smaller than those of the cylinder-wall interactions. The tangential component is obtained as

$$F_x = -\frac{144\pi}{25} \frac{(\varepsilon_r \varepsilon_0)^2 (kT)^3}{c_\infty (z_1 e)^4} \frac{a}{h^2} \left[\frac{G^2}{D_1} + \frac{H^2}{D_2} \right] (U + a\Omega) \tag{5.1.4}$$

and the normal component as

$$F_z = \frac{48\pi}{25} \frac{(\varepsilon_r \varepsilon_0)^2 (kT)^3}{c_\infty (z_1 e)^4} \frac{a^2}{h^2} \left[\frac{G}{D_1} + \frac{H}{D_2} \right]^2 (U + a\Omega)^2 \tag{5.1.5}$$

For both cylinder-wall interactions and sphere-wall interactions, the tangential component of the electroviscous force depends linearly on the ratio of diffusivity of ions, and the normal component is proportional to the second power of that ratio, which leads to the existence of a minimum for the magnitude of the normal component of the force at a specified ratio of diffusivity of ions. This is illustrated in Figs. 2.3, 4 and Fig. 3.2. The location of the minimum depends on the ζ-potentials of particle and wall. For identical ζ-potentials the minimum is zero, otherwise it is negative (attractive force). The tangential component of the force also can be either negative or positive depending on the magnitude and signs of the ζ-potentials and the ratio of diffusivity of ions. For small, but equal ζ-potentials and for equal mobilities of ions, as a first approximation, the tangential component of the electroviscous force is proportional to the viscosity of medium, η, ion radius, a_i, and ζ^2, whereas the normal component is proportional to η^2, a_i^2 and ζ^4. For identical ζ-potentials, the ratio of the force experienced by a sphere to that experienced by a cylinder, for both tangential and normal components, is proportional to $\sqrt{2ab}$. The Derjaguin scaling approximation, given by (3.7.5) predicts the same proportionality to the geometry of the problem for the ratio of the force, but with a different coefficient. In both cases it overestimates those ratios.

The problem of sphere-wall interactions is extended to the cases of arbitrary particle-wall distances, and arbitrary Peclet numbers, by the use of a bipolar coordinate system. For arbitrary particle-wall distances, but for low Pe the force is obtained both analytically and numerically for the tangential component and numerically for the normal component, and for arbitrary Pe they are determined numerically. Comparison of the analytical solution with the numerical one is illustrated in Tables B11, 13, located in Appendix B. It is found that for small particle-wall distances (δ <<1) the tangential component can be approximated as

$$F_x = -\frac{\pi}{2}\frac{(\varepsilon_r\varepsilon_0)^2 (kT)^3}{(z_1 e)^4 c_\infty}\frac{a}{h^2}\times$$
$$\left\{\left[\left(\frac{28}{3}G_P+\frac{41}{30}G_W\right)\frac{(G_P+G_W)}{D_1}+\left(\frac{28}{3}H_P+\frac{41}{30}H_W\right)\frac{(H_P+H_W)}{D_2}\right](U+a\Omega)\right.$$
$$\left.-\frac{1}{3}\left[\left(\frac{28}{3}G_P+\frac{41}{30}G_W\right)\frac{(G_P-G_W)}{D_1}+\left(\frac{28}{3}H_P+\frac{41}{30}H_W\right)\frac{(H_P-H_W)}{D_2}\right](U-a\Omega)\right\} \tag{5.1.6}$$

an expression valid for arbitrary Pe, and the normal component as

$$F_z = \frac{\pi}{900} \frac{(\varepsilon_r \varepsilon_0)^2 (kT)^3}{(z_1 e)^4 c_\infty} \frac{a}{h^2} \times$$

$$\left\{ \left[\frac{283}{10} \left(\frac{G_P}{D_1} + \frac{H_P}{D_2} \right) + \frac{88}{3} \left(\frac{G_W}{D_1} + \frac{H_W}{D_2} \right) \right]^2 (U + a\Omega)^2 \right.$$

$$\left. - \frac{1}{3} \left[\left(\frac{283}{10} \right)^2 \left(\frac{G_P}{D_1} + \frac{H_P}{D_2} \right)^2 - \left(\frac{88}{3} \right)^2 \left(\frac{G_W}{D_1} + \frac{H_W}{D_2} \right)^2 \right] \left(U^2 - a^2 \Omega^2 \right) \right\} \tag{5.1.7}$$

valid for low and intermediate Pe, Pe << $\delta^{-1/2}$. The accuracy of the formulas (5.1.6, 7) is illustrated in Tables B14, 15. Upon comparison of the drag component of the electroviscous force with that of an isolated sphere [formulas (5.1.6) and (1.3.74)] it is observed that the ratio of the force satisfies the following relations:

$$\frac{F_{\text{Sphere-wall}}}{F_{\text{Sphere}}} = \frac{107}{240} \delta^{-2} \qquad \delta = \frac{h}{a} \tag{5.1.8}$$

valid for small δ (δ<<1). For the inner solution, the ratio of the force is given by the relation (3.7.4), which is similar to (5.1.8) but differs from it by a numerical factor.

Representative numerical results for arbitrary Pe and arbitrary particle wall distances are illustrated in Fig. 4.3-10. The dependence of the dimemsionless force $\left(\tilde{F}_x/\lambda , \tilde{F}_z/\lambda \right)$ [$\tilde{\vec{F}}$ and λ are defined by (3.2.2)] on Pe is illustrated in Fig. 4.3, on δ in Fig. 4.4, on the ζ-potentials in Fig. 4.5 and Fig. 4. 6, on the ratio of diffusivity of ions in Figs. 4.7, 8, 9. and on the ratio of angular velocity to the linear velocity in Fig. 4.10. The results are in complete agreement with the formulas (5.1.6, 7), for the range of their validity. Of special interest is the existence of a minimum for the normal component of the force at a specified ratio of the diffusivity of ions regardless of the magnitude of Pe and δ. The location of minimum depends only on the ζ-potentials, and its magnitude is equal to zero for identical ζ-potentials, otherwise it is negative, the same as that observed for the analytical solutions of the inner region. The force is compared with the experimental observations of Wu, Warszynski &, van de Ven (1996) in Fig. 4.11, and a fair agreement is found.

In summary, although in most cases the tangential component of the electroviscous force is negative (increasing the drag above the purely hydrodynamic drag) and the normal component is positive (lift force), there are some situations that the former is positive (electroviscous drag reduction) and the latter is negative (attractive force). This is an interesting result since it allows one to tune the force to a desirable magnitude (attractive, neutral or repulsive), by suitable combinations of ζ-potentials and ratio of diffusivity of ions.

5.2 - Contributions to Knowledge

This dissertation has the following contributions to the knowledge:

1. Analytical solution of the electroviscous equations (electroviscous ion concenterations, electroviscous potential and electroviscous flow field), for the inner region at order Pe (Peclet number) in an expansion of this parameter, resulting in an analytical expression for the tangential component of the electroviscous force experienced by a cylinder-wall interactions, valid for small particle-wall distances, but low and intermediate Pe.
2. Inner solution of the electroviscous equations, at order Pe^2 resulting in an analytical expression for the normal component of the electroviscous force experienced by a cylinder-wall interactions, valid for small particle-wall distances, but low and intermediate Pe.
3. Outer solution of the electroviscous ion concentrations and potentials, for cylinder-wall interactions at order Pe.
4. Explaining the discrepancy between the Cox' theory reported in Wu *et al.*'s paper (1996) and Warszynski & van de Ven's theory (2000).
5. Inner solution of the electroviscous equations for sphere-wall interactions of identical particle and wall ζ-potentials, at order Pe, resulting in an analytical expression for the tangential component of the electroviscous force experienced by the particle, valid for small particle-wall distances, but low and intermediate Pe.
6. Inner solution of the electroviscous equations for sphere-wall interactions of identical particle and wall ζ-potentials, at order Pe^2, resulting in an analytical expression for

the normal component of the electroviscous force experienced by the particle, valid for small particle-wall distances, but low and intermediate Pe.

7. Observing that, for the electroviscous force, the Derjaguin approximation overestimates the ratio of the force experienced by the sphere-wall interactions to that of the cylinder-wall interactions.

8. An exact analytical solution for the hydrodynamics of the motion of a sphere normal and away from a plane wall for arbitrary particle-wall distances.

9. An analytical solution of the electroviscous equations, for the whole domain of interest, at order Pe, resulting in a analytical solution for the tangential component of the force on a sphere-wall interactions valid for Low Pe, but arbitrary particle-wall distances.

10. An analytical-numerical solution of the electroviscous equations, for the whole domain of interest, at order Pe, resulting in a numerical solution for the tangential component of the force on a sphere-wall interactions, valid for Low Pe, but arbitrary particle-wall distances.

11. An analytical-numerical solution of the electroviscous equations, for the whole domain of interest, at order Pe^2, resulting in a numerical solution for the normal component of the force on a sphere-wall interaction, valid for Low Pe, but arbitrary particle-wall distances.

12. An analytical-numerical solution of the electroviscous equations, for the whole domain of interest, resulting in a numerical solution for the tangential and normal components of the force on a sphere-wall interactions, valid for arbitrary Pe and arbitrary particle-wall distances.

13. Obtaining a model for the tangential component of the force valid for arbitrary Pe, but small particle wall distances.

14. Obtaining a model for the normal component of the force valid for small particle wall distances, but small and intermediate Pe.

15. Observing that the normal component of the force can be negative and the tangential component can be positive under certain circumstances.

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Appendix A
Orthogonal Curvilinear Coordinate Systems

A.1 - Cylinderical Coordinate System

The transformation from Cartesian to cylindrical coordinates is defined by:

$$x = \rho\cos\theta, \qquad y = \rho\sin\theta, \qquad z = z \tag{A.1}$$

Using the chain rule we have

$$\frac{\partial}{\partial x} = \cos\theta\frac{\partial}{\partial\rho} - \frac{\sin\theta}{\rho}\frac{\partial}{\partial\theta}, \qquad \frac{\partial}{\partial y} = \sin\theta\frac{\partial}{\partial\rho} + \frac{\cos\theta}{\rho}\frac{\partial}{\partial\theta} \tag{A.2}$$

or alternatively

$$\frac{\partial}{\partial\rho} = \cos\theta\frac{\partial}{\partial x} + \sin\theta\frac{\partial}{\partial y}, \qquad \frac{\partial}{\partial\theta} = -\rho\sin\theta\frac{\partial}{\partial x} + \rho\cos\theta\frac{\partial}{\partial y} \tag{A.3}$$

The metrical coefficients h_K (k=1, 2,3) for any orthogonal coordinate systems (q_1, q_2, q_3) are determined by

$$\frac{1}{h_k^{\,2}} = \left(\frac{\partial x}{\partial q_k}\right)^2 + \left(\frac{\partial y}{\partial q_k}\right)^2 + \left(\frac{\partial z}{\partial q_k}\right)^2 \tag{A.4a}$$

from which and relationship (A.1) the metrical coefficients for cylinder coordinates (h_ρ, h_θ, h_z) are obtained as

$$h_\rho = 1, \qquad h_\theta = \frac{1}{\rho}, \qquad h_z = 1 \tag{A.5a}$$

Thus, the metrical coefficients in each coordinate system can be interpreted as a reciprocal weighted function to be multiplied by each coordinate to convert it to a length dimension, and hence for the cylindrical coordinate system $h_\rho = h_z = 1$, but $h_\theta = 1/\rho$, that is $\rho\theta$ is the arch length of a sector whose angle and radius are θ and ρ, respectively. Therefore, an infinitesimal length, dl_i, surface, dS_i, and volume, dV, for any coordinate system, may be written as

$$dl_k = \frac{dq_k}{h_k} \qquad k = (1, 2, 3) \tag{A.4b}$$

$$dS_1 = dl_2 dl_3 = \frac{dq_2 dq_3}{h_2 h_3}, dS_2 = dl_1 dl_3 = \frac{dq_1 dq_3}{h_1 h_3}, dS_3 = dl_1 dl_2 = \frac{dq_1 dq_2}{h_1 h_2} \tag{A.4c}$$

and

$$dV = dl_1 dl_2 dl_3 = \frac{q_1 q_2 q_3}{h_1 h_2 h_3} \tag{A.4d}$$

In relation (A.4c) dS_i are infinitesimal surfaces normal to coordinates q_i. Thus, for a cylindrical coordinate system we have

$$dl_\rho = d\rho, \qquad dl_\theta = \rho\, d\theta, \qquad dl_z = dz, \tag{A.5b}$$

$$dS_\rho = \rho\, d\theta\, dz, \quad dS_\theta = d\rho\, dz, \quad dS_z = \rho\, d\rho\, d\theta, \quad dV = \rho\, d\rho\, d\theta\, dz \tag{A.5c}$$

The unit vector $\vec{i}_k$ for the orthogonal coordinate system (q_1, q_2, q_3) may be written in terms of Cartesian unit vectors $(\vec{i}, \vec{j}, \vec{k})$ according to the following relationships

$$\vec{i}_k = h_k \left(\vec{i} \frac{\partial x}{\partial q_k} + \vec{j} \frac{\partial y}{\partial q_k} + \vec{k} \frac{\partial z}{\partial q_k} \right) \tag{A.6}$$

From this, the unit vectors of the cylindrical coordinates may be expressed as

$$\vec{i}_\rho = \cos\theta\, \vec{i} + \sin\theta\, \vec{j}, \qquad \vec{i}_\theta = -\sin\theta\, \vec{i} + \cos\theta\, \vec{j} \tag{A.7}$$

or

$$\vec{i} = \cos\theta\, \vec{i}_\rho - \sin\theta\, \vec{i}_\theta, \qquad \vec{j} = \sin\theta\, \vec{i}_\rho + \cos\theta\, \vec{i}_\theta \tag{A.8}$$

Then, if we write the velocity $\vec{u}$ as

$$\vec{u} = u_\rho \vec{i}_\rho + u_\theta \vec{i}_\theta + u_z \vec{i}_z = u_x \vec{i} + u_y \vec{j} + u_z \vec{k} \tag{A.9}$$

the relationship between the cylindrical and the Cartesian components of the velocity may be written as

$$u_\rho = u_x \cos\theta + u_y \sin\theta, \quad u_\theta = -u_x \sin\theta + u_y \cos\theta, \quad u_z = u_z \tag{A.10}$$

or alternatively

$$u_x = u_\rho \cos\theta - u_\theta \sin\theta, \quad u_y = u_\rho \sin\theta + u_\theta \cos\theta, \quad u_z = u_z \tag{A.11}$$

A sphere with unit radius ($r = 1$) above plane $z = 0$ which its center is on the z-axis at location $z = 1 + \delta$ (δ is the clearance between sphere and wall) may be described in the Cartesian coordinate system as

$$z - \delta - 1 = \pm\sqrt{1 - x^2 - y^2} \tag{A.12}$$

with the sign + and - for the upper and lower parts of sphere, respectively. The unit vector normal to it $\left(\vec{n}_P\right)$ in cylindrical coordinates may be derived from the relationship between the spherical unit vector, $\vec{i}_r$, and Cartesian ones which may be written as:

$$\vec{n}_p = \vec{i}_r = \frac{x\vec{i} + y\vec{j} + (z - 1 - \delta)\vec{k}}{r} \qquad \text{(A.13)}$$

Letting r = 1 and introducing (A.7) into (A.13) gives the unit vector in terms of cylindrical coordinates as

$$\vec{n}_P = \rho\,\vec{i}_\rho + (z - 1 - \delta)\vec{i}_z \quad \text{on } S_P, \qquad \vec{n}_W = \vec{i}_z \quad \text{on } S_W \qquad \text{(A.14)}$$

in which $\vec{n}_W$ is the unit vector normal to the plane S_W.

The gradient, ∇, and Laplacian, ∇^2, for the orthogonal coordinate systems (q_1, q_2, q_3) are defined by

$$\nabla = \vec{i}_1 h_1 \frac{\partial}{\partial q_1} + \vec{i}_2 h_2 \frac{\partial}{\partial q_2} + \vec{i}_3 h_3 \frac{\partial}{\partial q_3} \qquad \text{(A.15)}$$

and

$$\nabla^2 = h_1 h_2 h_3 \left[\frac{\partial}{\partial q_1}\left(\frac{h_1}{h_2 h_3}\frac{\partial}{\partial q_1}\right) + \frac{\partial}{\partial q_2}\left(\frac{h_2}{h_1 h_3}\frac{\partial}{\partial q_2}\right) + \frac{\partial}{\partial q_3}\left(\frac{h_3}{h_2 h_1}\frac{\partial}{\partial q_3}\right)\right] \qquad \text{(A.16)}$$

Thus, for the cylindrical polar coordinate system (ρ, θ, z) with metrical coefficients $h_1 = h_\rho$, $h_2 = h_\theta$, and $h_3 = h_z$, they may be obtained as

$$\nabla = \vec{i}_\rho \frac{\partial}{\partial \rho} + \vec{i}_\theta \frac{1}{\rho}\frac{\partial}{\partial \theta} + \vec{i}_z \frac{\partial}{\partial z} \qquad \text{(A.17)}$$

and

$$\nabla^2 = \frac{1}{\rho}\frac{\partial}{\partial \rho}\left(\rho \frac{\partial}{\partial \rho}\right) + \frac{1}{\rho^2}\frac{\partial^2}{\partial \theta^2} + \frac{\partial^2}{\partial z^2} \qquad \text{(A.18)}$$

Noting that all partial derivatives of unit vectors in cylindrical coordinates are zero except that $\partial\vec{i}_\rho/\partial\theta = \vec{i}_\theta$ and $\partial\vec{i}_\theta/\partial\theta = -\vec{i}_\rho$, the Laplacian and divergence of the vector $\vec{u}$ may be expressed as:

$$\nabla^2\vec{u} = \vec{i}_\rho\left(\nabla^2 u_\rho - \frac{2}{\rho^2}\frac{\partial u_\theta}{\partial\theta} - \frac{u_\rho}{\rho^2}\right) + \vec{i}_\theta\left(\nabla^2 u_\theta - \frac{2}{\rho^2}\frac{\partial u_\rho}{\partial\theta} - \frac{u_\theta}{\rho^2}\right) + \vec{i}_z\nabla^2 z \qquad \text{(A.19)}$$

and

$$\nabla\cdot\vec{u} = \frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho u_\rho\right) + \frac{1}{\rho}\frac{\partial u_\theta}{\partial\theta} + \frac{\partial u_z}{\partial z} \qquad \text{(A.20)}$$

The stress tensor, σ_{ij}, is a symmetric tensor and may be determined by the rate of strain tensor (e_{11}, e_{12}, e_{13}...) as

$$\begin{aligned} e_{11} &= h_1\frac{\partial u_1}{\partial q_1} + h_1 h_2 u_2\frac{\partial h_1}{\partial q_1} + h_1 h_3 u_3\frac{\partial h_1}{\partial q_2}, \\ e_{23} &= \frac{1}{2}\left[\frac{h_2}{h_3}\frac{\partial}{\partial q_2}\left(h_3 u_3\right) + \frac{h_3}{h_2}\frac{\partial}{\partial q_3}\left(h_2 u_2\right)\right], \\ \sigma_{ij} &= -p\delta_{ij} + 2e_{ij}, \qquad \delta_{ij} = \begin{cases} 1 & \text{if} \quad i = j \\ 0 & \text{if} \quad i \neq j \end{cases} \end{aligned} \qquad \text{(A.21)}$$

Thus for cylindrical coordinates we have

$$\begin{aligned} &\sigma_{\rho\rho} = -p + 2\frac{\partial u_\rho}{\partial\rho}, \quad \sigma_{\rho\theta} = \frac{\partial u_\theta}{\partial\rho} + \frac{1}{\rho}\frac{\partial u_\rho}{\partial\theta} - \frac{u_\theta}{\rho}, \quad \sigma_{\rho z} = \frac{\partial u_z}{\partial\rho} + \frac{\partial u_\rho}{\partial z} \\ &\sigma_{\theta\theta} = -p + \frac{2}{\rho}\frac{\partial u_\theta}{\partial\rho}, \quad \sigma_{z\theta} = \frac{\partial u_\theta}{\partial z} + \frac{1}{\rho}\frac{\partial u_z}{\partial\theta}, \quad \sigma_{zz} = -p + 2\frac{\partial u_z}{\partial z} \end{aligned} \qquad \text{(A.22)}$$

A.2 - Tangent Circle Coordinate System

The transformation from the Cartesian coordinate (x, z) to the tangent circle coordinate (ζ, μ) is defined by

$$x = \frac{2\mu}{\zeta^2 + \mu^2}, \qquad z = \frac{2\zeta}{\zeta^2 + \mu^2}, \qquad 0 \le \zeta \le 1, \qquad -\infty < \mu < +\infty \qquad \text{(A.23)}$$

Eliminating μ results in

$$\left(z - \frac{1}{\zeta}\right)^2 + x^2 = \frac{1}{\zeta^2} \qquad \text{(A.24)}$$

which represents a family of non-intersection circles in the (x, y)-plane with radius $1/\zeta$ where centers are located on the z-axis at the points $z = 1/\zeta$. Thus, any sphere ζ = constant, ζ_0 say, is tangent to the x-axis with radius $r = 1/\zeta_0$, as shown in Fig. A.1. Therefore, a circle tangent to the x-axis at the origin with unit radius is denoted by $\zeta = 1$, and $\zeta = 0$ is a circle of an infinity radius which is the x-axis. Eliminating ζ leads to the following relationship for μ:

$$\left(x \pm \frac{1}{\mu}\right)^2 + z^2 = \frac{1}{\mu^2} \tag{A.25}$$

This represents a family of non-intersecting circles tangent to the z-axis and normal to the ζ-coordinate which radius are equal to $1/\mu$ and located on the x-axis with - sign for those constructed on the positive direction of the x-axis and + sign their reflection with respect to the z-axis for negative values of μ. Infinity is determined by $\zeta = \mu = 0$, the z-axis above the sphere by $\mu = 0$ and the contact point by ($\zeta = 0, \mu = \pm\infty$). Thus, a circle with unit radius tangent to the x-axis at the origin may be described in these coordinates by

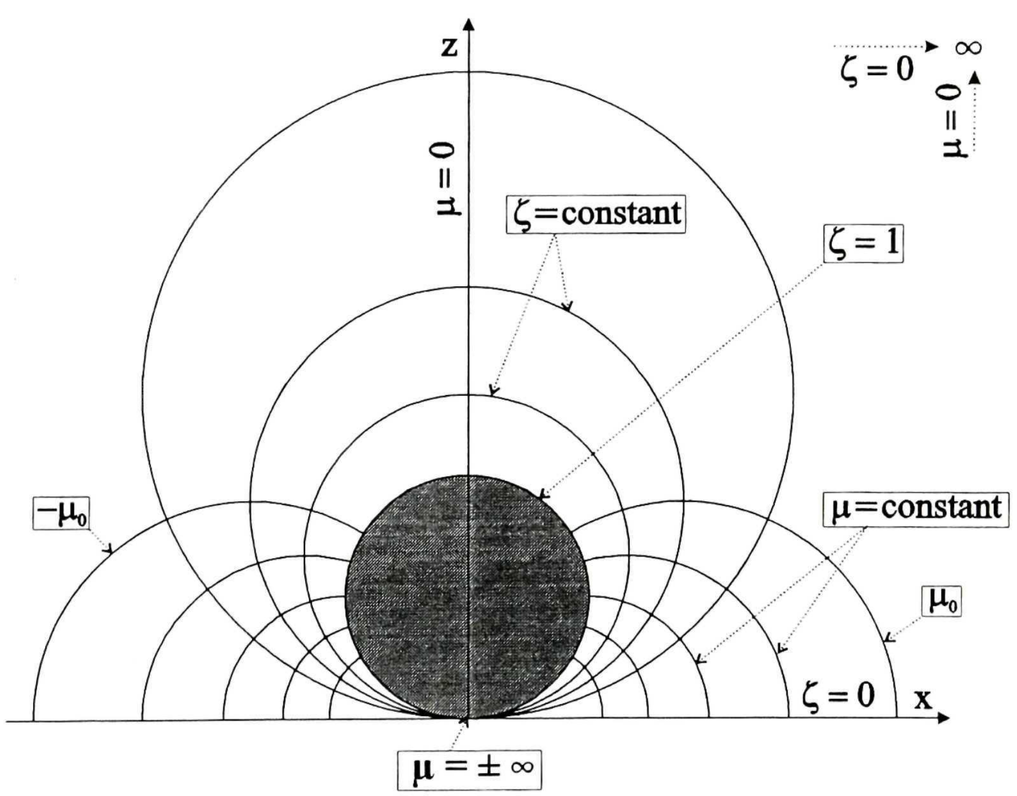

Fig. A.1- Tangent circle coordinate system (ζ, μ)

$$\left(0 \le \zeta \le 1, -\infty < \mu < +\infty\right).$$

$$\zeta = 1, \tag{A.26}$$

and the plane by

$$\zeta = 0, \tag{A.27}$$

From relationships (A1, 4, 13), upon applying the chain rule, its metrical coefficients are determined by

$$h_\zeta = h_\mu = \frac{\zeta^2 + \mu^2}{2}, \tag{A.28}$$

Therefore, applying relationships (A.15, 16), its gradient and Laplacian of any scalar may be obtained as

$$\nabla = \frac{\zeta^2 + \mu^2}{2}\left[\vec{i}_\zeta \frac{\partial}{\partial \zeta} + \vec{i}_\mu \frac{\partial}{\partial \mu}\right] \tag{A.29}$$

$$\nabla^2 = \left(\frac{\zeta^2 + \mu^2}{2}\right)^2 \left[\frac{\partial^2}{\partial \zeta^2} + \frac{\partial^2}{\partial \mu^2}\right] \tag{A.30}$$

The base unit vectors $\left(\vec{i}_\zeta, \vec{i}_\mu\right)$ may be determined in terms of those of the cylindrical coordinates, according to the relationships [Happel & Brenner (1965)]

$$\vec{i}_\rho = \sum_{k=1}^{2} \vec{i}_k h_k \frac{\partial \rho}{\partial q_k}, \qquad \vec{i}_z = \sum_{k=1}^{2} \vec{i}_k h_k \frac{\partial z}{\partial q_k}, \tag{A.31}$$

They are obtained as

$$\vec{i}_\rho = \frac{2}{\zeta^2 + \mu^2}\left[-\zeta\mu \vec{i}_\zeta - \frac{\zeta^2 - \mu^2}{2}\vec{i}_\mu\right] \tag{A.32}$$

and

$$\vec{i}_z = \frac{2}{\zeta^2 + \mu^2}\left[\frac{\zeta^2 - \mu^2}{2}\vec{i}_\zeta - \zeta\mu \vec{i}_\mu\right] \tag{A.33}$$

Now, the relationship between tangent circle component of velocity and cylindrical one is straight forward, that is

$$u_\zeta = \frac{-2\zeta\mu}{\zeta^2+\mu^2} u_\rho - \frac{\zeta^2-\mu^2}{\zeta^2+\mu^2} u_z \tag{A.34}$$

and

$$u_\mu = -\frac{\zeta^2-\mu^2}{\zeta^2+\mu^2} u_\rho - \frac{2\zeta\mu}{\zeta^2+\mu^2} u_z \tag{A.35}$$

Since the coordinates ζ and μ are orthogonal to each other, unit vector outward from each surface is

$$\vec{n}_P = -\vec{i}_\zeta \qquad \text{on } S_P, \qquad \vec{n}_W = \vec{i}_\zeta \qquad \text{on } S_W \tag{A.36}$$

A.3 - Bipolar Coordinate System

Bipolar coordinates (ξ, η, θ) transform to the cylindrical coordinates according to the relationship

$$\rho = c\frac{\sin\eta}{\cosh\xi - \cos\eta}, \qquad z = c\frac{\sinh\xi}{\cosh\xi - \cos\eta}, \qquad \theta = \theta \tag{A.37}$$

The range of coordinates is given by by

$$-\infty < \xi < \infty, \qquad 0 \le \eta \le \pi, \qquad 0 \le \theta \le 2\pi$$

In which c is a positive constant (a geometry constant) and is determined from the dimensions of the system. The coordinates ξ and η describe families of orthogonal circles in the plane formed by the ρ and z-axes. This is illustrated in Fig. A.2. The coordinates ξ describes non-intersection circles which lie entirely above or below the plane z = 0. Therefore, $\xi = \pm\,\alpha_i$ describes two circles of a specific diameter which are reflections of each other in the plane $z = 0$, and their centers lie on the z-axis. Plane z = 0 is described by ξ = 0 and $\xi = +\infty$ represents a circle with zero radius above the plane z = 0 and $\xi = -\infty$ represents its reflection with respect to the plane. The coordinate η describes a family of circles which are orthogonal to all ξ circles and their centers lie on the ρ-axis in the plane $z = 0$. In the limits, $\eta = \pi$ represents the darkened line segment on the z-axis, and $\eta = 0$ represents the remainder of the z-axis.

Upon rotating the bipolar coordinate system shown in Fig. A.2 through the azimuthal angle θ=2π, one obtains a family of coaxial spheres described by the coordinate ξ = constant,

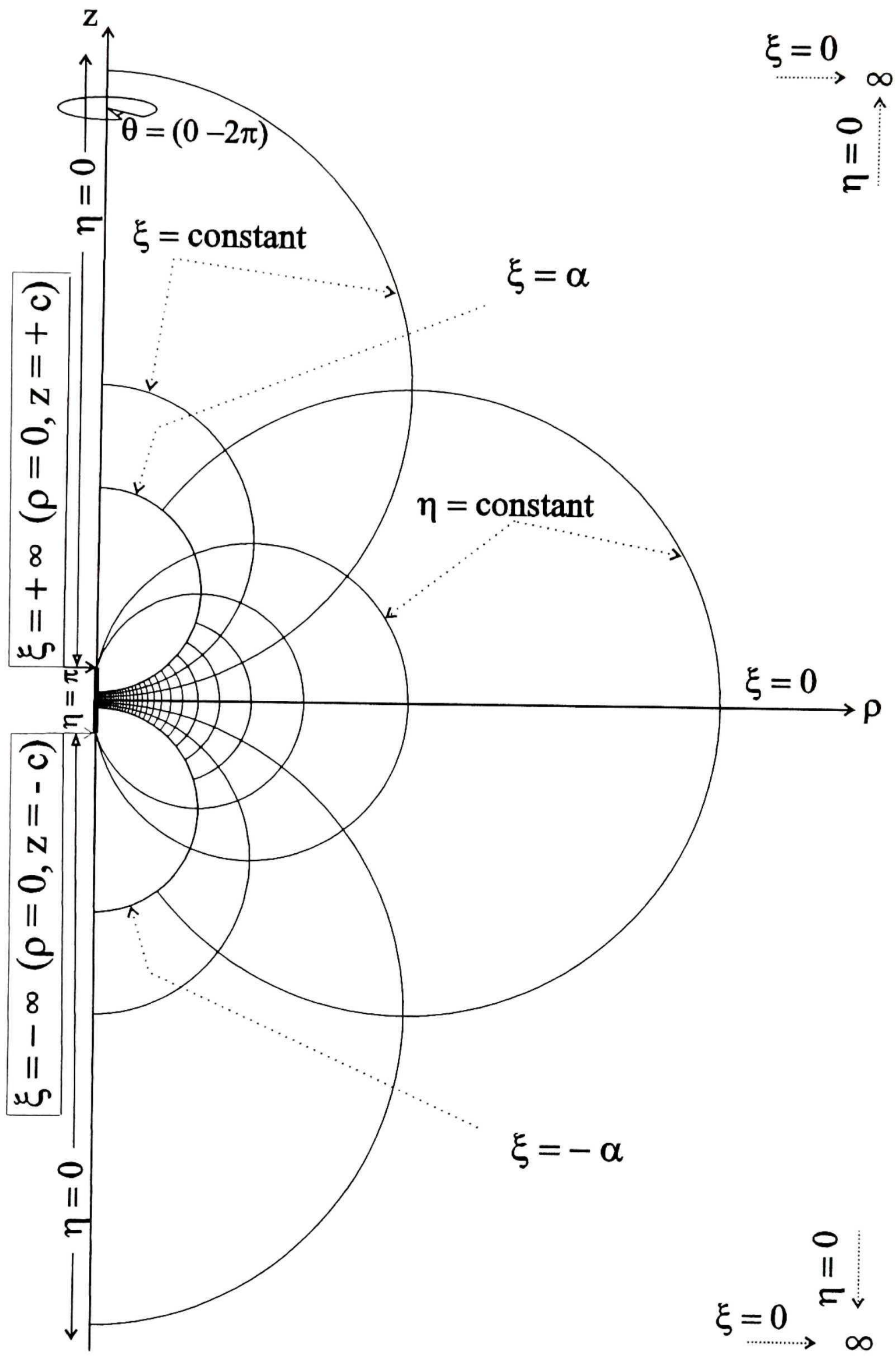

Fig. A.2- Bipolar coordinate system (ξ, θ, η)

$\left(-\infty < \xi < \infty, \mathbf{0} \leq \eta \leq \pi, \mathbf{0} \leq \theta \leq \mathbf{2}\pi\right)$.

and a family of spindle-like surfaces of revolution described by η = constant. It is apparent that one may describe the sphere-plane system shown in Fig 4.1 by restricting the rang of the ξ coordinate to $0 \le \xi \le \infty$. In this case, the sphere is described by the single coordinate, $\xi = \alpha$, and the plane is described by the single coordinate, $\xi = 0$. Thus, the coordinates of each surface are

$$\xi = \alpha, \qquad 0 \le \eta \le \pi, \qquad 0 \le \theta \le 2\pi, \qquad \text{on} \quad S_P \tag{A.38}$$

and

$$\xi = 0, \qquad 0 \le \eta \le \pi, \qquad 0 \le \theta \le 2\pi, \qquad \text{on} \quad S_W \tag{A.39}$$

The value of α in relationship (A.38) and c in transformation function (A.37) may be determined by eliminating η in relationship (A.37). Thus, adding $\cos^2 \eta$ obtained from Eq. (A.37b) and $\sin^2 \eta$ derived from Eq.s (A.37a, b) leads to the following relationship

$$(z - c \coth \xi)^2 + \rho^2 = (c \operatorname{csch} \xi)^2 \tag{A.40}$$

Eq. (A.40) describes a family of spheres, each with a radius of c csch ξ and its center on the z-axis and at point $z = c \coth \xi$. Since the sphere has the dimensionless radius of unity and its center at $z = 1 + \delta$, then the sphere described by $\xi = \alpha$ satisfies the following relationships

$$c \operatorname{csch} \alpha = 1, \qquad\qquad c \coth \alpha = 1 + \delta$$

or

$$c = \sinh \alpha, \qquad \text{and} \qquad 1 + \delta = \cosh \alpha \tag{A.41}$$

from them it follows that

$$\alpha = \ln\left[1 + \delta + \sqrt{(1+\delta)^2 - 1}\right] \tag{A.42}$$

The metrical coefficients of the coordinate systems of revolution (q_1, q_2, θ) may be determined by the following expression (Happel & Brenner 1965)

$$\frac{1}{h_1^2} = \left(\frac{\partial \rho}{\partial q_1}\right)^2 + \left(\frac{\partial z}{\partial q_1}\right)^2, \quad \frac{1}{h_2^2} = \left(\frac{\partial \rho}{\partial q_2}\right)^2 + \left(\frac{\partial z}{\partial q_2}\right)^2, \quad h_3 = \frac{1}{\rho(q_1, q_2)}$$

from them the metrical coefficients of the bipolar coordinate system (ξ, η, θ), h_ξ, h_η, and h_θ, are determined, upon using Eq. (A.37), as

$$h_\xi = h_\eta = \frac{\cosh\xi - \cos\eta}{c}, \qquad h_\theta = \frac{\cosh\xi - \cos\eta}{c\sin\eta} \tag{A.43a}$$

Therefore, an infinitesimal length (dl_i), surface (dS_i) and volume (dV), given by (A.4b-d), for bipolar coordinate system are determined by

$$dl_\xi = \frac{c}{\cosh\xi - \cos\eta}d\xi,\ dl_\eta = \frac{c}{\cosh\xi - \cos\eta}d\eta,\ dl_\theta = \frac{c\sin\eta}{\cosh\xi - \cos\eta}d\theta \tag{A.43b}$$

$$dS_\xi = \frac{c^2\sin\eta\, d\eta d\theta}{(\cosh\xi - \cos\eta)^2},\ dS_\eta = \frac{c^2\sin\eta\, d\xi d\theta}{(\cosh\xi - \cos\eta)^2},\ dS_\theta = \frac{c^2\, d\xi d\eta}{(\cosh\xi - \cos\eta)^2} \tag{A.43c}$$

$$dV = \frac{c^3\sin\eta}{(\cosh\xi - \cos\eta)^3}d\xi d\eta d\theta \tag{A.43d}$$

The gradient, ∇, and Laplacian, ∇^2, defined by relations. (A.15, 16) may be expressed in this coordinates as

$$\nabla = \frac{\cosh\xi - \cos\eta}{c}\left(\vec{i}_\xi\frac{\partial}{\partial\xi} + \vec{i}_\eta\frac{\partial}{\partial\eta} + \vec{i}_\theta\frac{1}{\sin\eta}\frac{\partial}{\partial\theta}\right) \tag{A.44}$$

$$\begin{aligned}\nabla^2 = \frac{1}{c^2}\Bigg[&(\cosh\xi - \cos\eta)^2\left(\frac{\partial^2}{\partial\xi^2} + \frac{\partial^2}{\partial\eta^2} + \frac{1}{\sin^2\eta}\frac{\partial^2}{\partial\theta^2}\right) \\ &+ (\cosh\xi - \cos\eta)\left(-\sinh\xi\frac{\partial}{\partial\xi} + \frac{\cosh\xi\cos\eta - 1}{\sin\eta}\frac{\partial}{\partial\eta}\right)\Bigg]\end{aligned} \tag{A.45}$$

Unit vectors in cylindrical coordinates transform to the unit vectors in coordinate systems of revolution (q_1, q_2, θ) according to the relationships (Happel & Brenner 1965)

$$\vec{i}_\rho = \sum_{k=1}^{2}\vec{i}_k h_k\frac{\partial\rho}{\partial q_k}, \qquad \vec{i}_z = \sum_{k=1}^{2}\vec{i}_k h_k\frac{\partial z}{\partial q_k}, \qquad \vec{i}_\theta = \vec{i}_\theta \tag{A.46}$$

Thus, the relationships between the unit vectors of the cylindrical coordinate system and the bipolar coordinate system are obtained as

$$\vec{i}_\rho = \frac{1}{\cosh\xi - \cos\eta}\left[-\sinh\xi\sin\eta\,\vec{i}_\xi + (\cosh\xi\cos\eta - 1)\,\vec{i}_\eta\right] \tag{A.47}$$

$$\vec{i}_z = \frac{1}{\cosh\xi - \cos\eta}\left[\left(1 - \cosh\xi\cos\eta\right)\vec{i}_\xi - \sinh\xi\sin\eta\;\vec{i}_\eta\right] \tag{A.48}$$

The unit normal vector outward to each surface may also be written as

$$\vec{n} = -\vec{i}_\xi \quad \text{on } S_p \qquad \text{and} \qquad \vec{n} = \vec{i}_\xi \quad \text{on } S_w \tag{A.49}$$

The velocity vector, $\vec{u}$, may be expressed in each coordinate system as

$$\vec{u} = u_\rho\vec{i}_\rho + u_\theta\vec{i}_\theta + u_z\vec{i}_z = u_\xi\vec{i}_\xi + u_\theta\vec{i}_\theta + u_\eta\vec{i}_\eta \tag{A.50}$$

Combining Eqs. (A.47, 48, 50) leads to the following relationships between the cylindrical and bipolar components of the velocity

$$u_\xi = \frac{-\sinh\xi\sin\eta}{\cosh\xi - \cos\eta}u_\rho + \frac{1 - \mathrm{conh}\,\xi\cos\eta}{\cosh\xi - \cos\eta}u_z \tag{A.51}$$

$$u_\eta = \frac{\mathrm{conh}\,\xi\cos\eta - 1}{\cosh\xi - \cos\eta}u_\rho + \frac{-\sinh\xi\sin\eta}{\cosh\xi - \cos\eta}u_z \tag{A.52}$$

The relationship between the cylindrical partial derivatives and those of any coordinate systems of revolution (q_1, q_2, θ) is given by (Happel & Brenner 1965):

$$\frac{\partial}{\partial\rho} = \sum_{k=1}^{2} h_k^2 \frac{\partial\rho}{\partial q_k}\frac{\partial}{\partial q_k}, \qquad \frac{\partial}{\partial z} = \sum_{k=1}^{2} h_k^2 \frac{\partial z}{\partial q_k}\frac{\partial}{\partial q_k} \tag{A.53}$$

From them and in view of (A.37, 43) the first derivatives with respect to the ρ and z are determined as

$$\frac{\partial}{\partial\rho} = -\frac{1}{c}\left[\sin\eta\sinh\xi\frac{\partial}{\partial\xi} + \left(1 - \cos\eta\cosh\xi\right)\frac{\partial}{\partial\eta}\right] \tag{A.54}$$

$$\frac{\partial}{\partial z} = \frac{1}{c}\left[\left(1 - \cos\eta\cosh\xi\right)\frac{\partial}{\partial\xi} - \sin\eta\sinh\xi\frac{\partial}{\partial\eta}\right] \tag{A.55}$$

The second derivatives $\partial^2/\partial\rho^2 = \partial/\partial\rho\,(\partial/\partial\rho)$ and $\partial^2/\partial z^2 = \partial/\partial z(\partial/\partial z)$ are obtained from the first derivatives as

$$\frac{\partial^2}{\partial \rho^2} = \frac{\sin\eta \sinh\xi}{c^2}\left[\sin\eta\cosh\xi\frac{\partial}{\partial\xi} + \sin\eta\sinh\xi\frac{\partial^2}{\partial\xi^2} - \cos\eta\sinh\xi\frac{\partial}{\partial\eta} + \left(1-\cos\eta\cosh\xi\right)\frac{\partial^2}{\partial\xi\partial\eta}\right] + \frac{1-\cos\eta\cosh\xi}{c^2}\left[\cos\eta\sinh\xi\frac{\partial}{\partial\xi} + \sin\eta\sinh\xi\frac{\partial^2}{\partial\xi\partial\eta} + \sin\eta\cosh\xi\frac{\partial}{\partial\eta} + \left(1-\cos\eta\cosh\xi\right)\frac{\partial^2}{\partial\eta^2}\right] \tag{A.56}$$

and

$$\frac{\partial^2}{\partial z^2} = \frac{1-\cos\eta\cosh\xi}{c^2}\left[-\cos\eta\sinh\xi\frac{\partial}{\partial\xi} + \left(1-\cos\eta\cosh\xi\right)\frac{\partial^2}{\partial\xi^2} - \sin\eta\cosh\xi\frac{\partial}{\partial\eta} - \sin\eta\sinh\xi\frac{\partial^2}{\partial\xi\partial\eta}\right] - \frac{\sin\eta\sinh\xi}{c^2}\left[\sin\eta\cosh\xi\frac{\partial}{\partial\xi} + \left(1-\cos\eta\cosh\xi\right)\frac{\partial^2}{\partial\xi\partial\eta} - \cos\eta\sinh\xi\frac{\partial}{\partial\eta} - \sin\eta\sinh\xi\frac{\partial^2}{\partial\eta^2}\right] \tag{A.57}$$

From the relation (A.21), the $\sigma_{\xi\eta}$ and $\sigma_{\xi\theta}$ components of the stress tensor are obtained as

$$\begin{aligned} \sigma_{\xi\eta} &= \frac{1}{c}\left[\sin\eta\, U_\xi + \sinh\xi\, U_\xi + \left(\cosh\xi - \cos\eta\right)\left(\frac{\partial U_\xi}{\partial\eta} + \frac{\partial U_\eta}{\partial\xi}\right)\right] \\ \sigma_{\xi\theta} &= \frac{1}{c}\left[\sinh\xi\, U_\theta + \left(\cosh\xi - \cos\eta\right)\left(\frac{\partial U_\theta}{\partial\xi} + \frac{1}{\sin\eta}\frac{\partial U_\xi}{\partial\theta}\right)\right] \end{aligned} \tag{A.58}$$

Appendix B
Tables

Table B1 - Distribution of $\widetilde{u}_{\rho T}$ ($\delta = 0.05$) on the nodes demonstrated in Fig. 4.1.

⇓ Nodes number	⇓ Wall Surface	⇓ Medium	⇓ Medium	⇓ Sphere Surface
1(origin)-4	-1.00000000000000	-0.80303405944808	--0.47096507303833	-0.00000000000000
5-8	-1.00000000000000	-0.80158001969678	-0.46949113075993	-0.00000000000000
9-12	-1.00000000000000	-0.79723409872698	-0.46508588146849	0.00000000000000
13-16	-1.00000000000000	-0.79004472436729	-0.45779889293584	-0.00000000000000
17-20	-1.00000000000000	-0.78009205554582	-0.44771223090067	-0.00000000000000
21-24	-1.00000000000000	-0.76748716035002	-0.43493964902042	-0.00000000000000
25-28	-1.00000000000000	-0.75237088405299	-0.41962547679030	-0.00000000000000
29-32	-1.00000000000000	-0.73491242652041	-0.40194322854049	0
33-36	-1.00000000000000	-0.71530765509977	-0.38209396500967	-0.00000000000000
37-40	-1.00000000000000	-0.69377718701281	-0.36030444949996	0.00000000000000
41-44	-1.00000000000000	-0.67056428522018	-0.33682515421267	-0.00000000000000
45-48	-1.00000000000000	-0.64593262504817	-0.31192819112357	-0.00000000000000
49-52	-1.00000000000000	-0.62016400784049	-0.28590526913173	-0.00000000000000
53-56	-1.00000000000000	-0.59355612647764	-0.25906582102703	-0.00000000000000
57-60	-1.00000000000000	-0.56642053286572	-0.23173551024980	-0.00000000000000
61-64	-1.00000000000000	-0.53908103250198	-0.20425543681646	0.00000000000000
65-68	-1.00000000000000	-0.51187286083065	-0.17698254813088	-0.00000000000000
69-72	-1.00000000000000	-0.48514322747127	-0.15029208875756	-0.00000000000000
73-76	-1.00000000000000	-0.45925423125619	-0.12458352578437	-0.00000000000000
77-80	-1.00000000000000	-0.43458987809986	-0.10029254660524	-0.00000000000000
81-84	-1.00000000000000	-0.41157014148742	-0.07791405952292	0.00000000000000
85-88	-1.00000000000000	-0.39067715869259	-0.05804592033258	0.00000000000000
89-92	-1.00000000000000	-0.37250491445298	-0.04147306171343	0.00000000000000
93-96	-1.00000000000000	-0.35787183563926	-0.02933480962732	-0.00000000000000
97-100	-1.00000000000000	-0.34815571921365	-0.02349281566758	-0.00000000000000
101-104	-1.00000000000000	-0.34640462703587	-0.02753058610774	0.00000000000000
105-108	-1.00000000000000	-0.36060561655999	-0.05000734661333	-0.00000000000000
109-112	-1.00000000000000	-0.41066910210973	-0.11412196098471	-0.00000000000000
113-116	-1.00000000000000	-0.53472057193136	-0.27166181179843	-0.00000000000000
117-120	-1.00000000000000	-0.76755415258590	-0.55272808954765	-0.00000000000000
121(infinity)-124	-1.00000000000000	-0.96552559541135	-0.73797466771637	-0.00000000000000

Table B2 - Distribution of $\widetilde{u}_{zT}$ ($\delta = 0.05$) on the nodes demonstrated in Fig. 4.1.

⇓ Nodes number	⇓ Wall Surface	⇓ Medium	⇓ Medium	⇓ Sphere Surface
1(origin)-4	0	-0.00000000000000	-0.00000000000000	-0.0000000000000
5-8	0	-0.00197396385159	-0.00395456214716	0.00000000000000
9-12	0	-0.00391012937049	-0.00783314387456	0.00000000000000
13-16	0	-0.00577093646598	-0.01156024934659	-0.01156024934659
17-20	0	-0.00751929221763	-0.01506133351920	-0.0000000000000
21-24	0	-0.00911878078454	-0.01826323134864	-0.0000000000000
25-28	0	-0.01053384376409	-0.02109452943269	0.00000000000000
29-32	0	-0.01172991907385	-0.02348585709050	-0.00000000000000
33-36	0	-0.01267352429086	-0.02537007006119	0.00000000000000
37-40	0	-0.01333226716629	-0.02668229424448	-0.00000000000000
41-44	0	-0.01367476124997	-0.02735978834422	0.000000000000000
45-48	0	-0.01367041743029	-0.02734157173197	0.000000000000000
49-52	0	-0.01328907148881	-0.02656774528380	0.000000000000000
53-56	0	-0.01250039149244	-0.02497840516124	-0.00000000000000
57-60	0	-0.01127298367136	-0.02251200742161	0.000000000000000
61-64	0	-0.00957307559056	-0.01910297664414	0.000000000000000
65-68	0	-0.00736259082423	-0.01467825034653	-0.00000000000000
69-72	0	-0.00459632415383	-0.00915229140261	-0.00000000000000
73-76	0	-0.00121776542510	-0.00241986407156	-0.00000000000000
77-80	0	0.00284707750759	0.00565440500637	-0.00000000000000
81-84	0	0.00769863942222	0.01525073848874	-0.00000000000000
85-88	0	0.01347649239702	0.02661380897602	-0.00000000000000
89-92	0	0.02037959050675	0.04007907648860	-0.00000000000000
93-96	0	0.02871769957379	0.05612859516381	-0.00000000000000
97-100	0	0.03909638283057	0.07560972579874	-0.00000000000000
101-104	0	0.05301155228883	0.10058131424333	-0.00000000000000
105-108	0	0.07408386255548	0.13649500621316	-0.00000000000000
109-112	0	0.10823731903626	0.19307124170241	-0.00000000000000
113-116	0	0.15443868239879	0.26324073470589	-0.00000000000000
117-120	0	0.16757398998821	0.24698573512430	-0.00000000000000
121(infinity)-124	0	0	0	0

Table B3 - Distribution of $\widetilde{u}_{\xi T}$ ($\delta = 0.05$) on the nodes demonstrated in Fig. 4.1.

⇓ Nodes number	⇓ Wall Surface	⇓ Medium	⇓ Medium	⇓ Sphere Surface
1(origin)-4	0	0.00000000000000	0.00000000000000	-0.00000000000000
5-8	0	0.00249518687909	0.00126598142504	0.00000000000000
9-12	0	0.00500416910953	0.00253895371721	0.00000000000000
13-16	0	0.00754104940237	0.00382606318201	-0.00000000000000
17-20	0	0.01012055988400	0.00513477459237	-0.00000000000000
21-24	0	0.01275841476709	0.00647304954419	-0.00000000000000
25-28	0	0.01547171215047	0.00784954961806	-0.00000000000000
29-32	0	0.01827940778895	0.00927387590617	-0.00000000000000
33-36	0	0.02120289030963	0.01075685975234	-0.00000000000000
37-40	0	0.02426669727816	0.01231092454147	-0.00000000000000
41-44	0	0.02749942628152	0.01395054586111	0.00000000000000
45-48	0	0.03093491727471	0.01569284846956	0.00000000000000
49-52	0	0.03461381588256	0.01755839530613	-0.00000000000000
53-56	0	0.03858567887433	0.01957224969960	0.00000000000000
57-60	0	0.04291186412523	0.02176543279430	0.00000000000000
61-64	0	0.04766957832242	0.02417696431309	0.00000000000000
65-68	0	0.05295767322848	0.02685678513119	0.00000000000000
69-72	0	0.05890515202340	0.02987004823595	0.00000000000000
73-76	0	0.06568398525997	0.03330358047629	0.00000000000000
77-80	0	0.07352891883356	0.03727580837610	-0.00000000000000
81-84	0	0.08276877898708	0.04195212384597	0.00000000000000
85-88	0	0.09387731058854	0.04756888521901	0.00000000000000
89-92	0	0.10756190981601	0.05447465459851	0.00000000000000
93-96	0	0.12494896158868	0.06322676895179	0.00000000000000
97-100	0	0.14807355566899	0.07490541860594	0.00000000000000
101-104	0	0.18131221557061	0.09216760617042	0.00000000000000
105-108	0	0.23519944403874	0.12201776489752	0.00000000000000
109-112	0	0.33417921342535	0.17901847976281	0.00000000000000
113-116	0	0.52233438119949	0.26920413107879	0.00000000000000
117-120	0	0.76497805346238	0.28889753606587	0.00000000000000
121(infinity)-124	0	0	0	0

Table B4 - Distribution of $\widetilde{u}_{\eta T}$ ($\delta = 0.05$) on the nodes demonstrated in Fig. 4.1.

⇓ Nodes number	⇓ Wall Surface	⇓ Medium	⇓ Medium	⇓ Sphere Surface
1(origin)-4	1.00000000000000	0.80303405944808	0.47096507303833	0.00000000000000
5-8	1.00000000000000	0.80157856667504	0.46950607846442	0.00000000000000
9-12	1.00000000000000	0.79722798218341	0.46514491182673	0.00000000000000
13-16	1.00000000000000	0.79002981132499	0.45792884488615	0.00000000000000
17-20	1.00000000000000	0.78006264437466	0.44793606637032	0.00000000000000
21-24	1.00000000000000	0.76743528477505	0.43527479083781	0.00000000000000
25-28	1.00000000000000	0.75228554097381	0.42008202117476	0.00000000000000
29-32	1.00000000000000	0.73477869382997	0.40252197415607	0.00000000000000
33-36	1.00000000000000	0.71510565450484	0.38278418008061	0.00000000000000
37-40	1.00000000000000	0.69348083028330	0.36108126826596	0.00000000000000
41-44	1.00000000000000	0.67013971771734	0.33764644940944	0.00000000000000
45-48	1.00000000000000	0.64533624360293	0.31273070279284	-0.00000000000000
49-52	1.00000000000000	0.61933987421436	0.28659966985505	-0.00000000000000
53-56	1.00000000000000	0.59243251130606	0.25953024369137	0.00000000000000
57-60	1.00000000000000	0.56490518862022	0.23180682285938	0.00000000000000
61-64	1.00000000000000	0.53705457328118	0.20371716074586	-0.00000000000000
65-68	1.00000000000000	0.50917925944094	0.17554767577087	0.00000000000000
69-72	1.00000000000000	0.48157580963132	0.14757796786584	0.00000000000000
73-76	1.00000000000000	0.45453442769466	0.12007406950065	0.00000000000000
77-80	1.00000000000000	0.42833394226042	0.09327958678322	0.00000000000000
81-84	1.00000000000000	0.40323514186876	0.06740330111059	0.00000000000000
85-88	1.00000000000000	0.37946977314156	0.04260076119613	0.00000000000000
89-92	1.00000000000000	0.35721936475725	0.01894358008504	0.00000000000000
93-96	1.00000000000000	0.33657794641144	-0.00365047104510	0.00000000000000
97-100	1.00000000000000	0.31751402186856	-0.02564997635127	0.00000000000000
101-104	1.00000000000000	0.29988709674277	-0.04878182365560	0.00000000000000
105-108	1.00000000000000	0.28320672822095	-0.07901447010421	0.00000000000000
109-112	1.00000000000000	0.26208525707139	-0.13510259159216	0.00000000000000
113-116	1.00000000000000	0.19220871698397	-0.26575357045243	0.00000000000000
117-120	1.00000000000000	-0.17896646890782	-0.53202303332182	0.00000000000000
121(infinity)-124	1.00000000000000	-0.96552559541135	-0.73797466771637	0.00000000000000

Table B5 - Distribution of $\widetilde{p}_T$ ($\delta = 0.05$) on the nodes demonstrated in Fig. 4.1.

⇓ Nodes number	⇓ Wall Surface	⇓ Medium	⇓ Medium	⇓ Sphere Surface
1(origin)-4	0.00000000000000	0.00000000000000	0.00000000000000	0.00000000000000
5-8	2.56683126460221	2.50489993442630	2.54107234013403	2.67712152950532
9-12	5.06404206577036	4.94266596845149	5.01462393992073	5.28344062347382
13-16	7.42458823742511	7.24863429056500	7.35560849728765	7.75074673204120
17-20	9.58647071406446	9.36297838860926	9.50382565855289	10.01589938292411
21-24	11.49499398730029	11.23287494355764	11.40609113150217	12.02310095476723
25-28	13.10472044412745	12.81437865537711	13.01811560422546	13.72586352994599
29-32	14.38103993974254	14.07392880473506	14.30601523422136	15.08859039908391
33-36	15.30129055377915	14.98942623056694	15.24739235449095	16.08770808608646
37-40	15.85538582312015	15.55083790896266	15.83194355407044	16.71230423787189
41-44	16.04592499406338	15.76030664723196	16.06157262372460	16.96424779451904
45-48	15.88778506546034	15.63176467258456	15.95000713271661	16.85779010894405
49-52	15.40721563352735	15.19007117077438	15.52193869248578	16.41866806513056
53-56	14.64047882789031	14.46971418848033	14.81172734060274	15.68275155185052
57-60	13.63209601622328	13.51313586539680	13.86172905899788	14.69429704244176
61-64	12.43277960135191	12.36875589799380	12.72032141933486	13.50388588818905
65-68	11.09714142064867	11.08878076566148	11.43971502247043	12.16613937494904
69-72	9.68127847713881	9.72689503874103	10.07364719247197	10.73731187931117
73-76	8.24034178974969	8.33593566387165	8.67505890210303	9.27286819016280
77-80	6.82619494138144	6.96565008698245	7.29385617885482	7.82515097265814
81-84	5.48526361473268	5.66063335305729	5.97485454702668	6.44124126175602
85-88	4.25665728921488	4.45852530909417	4.75600314642702	5.16111931588135
89-92	3.17058994143488	3.38852497296632	3.66698800663818	4.01627263094401
93-96	2.24704144847708	2.47025923243755	2.72830737158633	3.02899565740887
97-100	1.49465852723310	1.71308745630983	1.95081762639781	2.21265807266163
101-104	0.91061053592599	1.11611598944693	1.33541775411246	1.57260220465705
105-108	0.48360700500082	0.66940126540957	0.87208950749518	1.10505613981956
109-112	0.20110265474448	0.35640116111268	0.53830032864728	0.78809246521702
113-116	0.05117303095520	0.15657411766398	0.30116367814816	0.56157689181553
117-120	0.00384191971613	0.04719083197523	0.12978973336354	0.32118158346124
121(infinity)-124	0.00000000000000	0	0	0

Table B6 - Distribution of $\widetilde{u}_{\rho T}$ on the nodes constructed for $\delta = 2$.

⇓ Nodes number	⇓ Wall Surface	⇓ Medium	⇓ Medium	⇓ Sphere Surface
1(origin)-4	-1.00000000000000	-0.87514451361309	-0.58856295653182	-0.00000000000001
5-8	-1.00000000000000	-0.87386468921777	-0.58673340512381	0.00000000000000
9-12	-1.00000000000000	-0.87005004114578	-0.58127773839553	0.00000000000000
13-16	-1.00000000000000	-0.86377517075531	-0.57229528328935	-0.00000000000000
17-20	-1.00000000000000	-0.85516482206919	-0.55995281975983	0.00000000000000
21-24	-1.00000000000000	-0.84439445202442	-0.54448649847410	0.00000000000000
25-28	-1.00000000000000	-0.83169093808133	-0.52620463516070	-0.00000000000000
29-32	-1.00000000000000	-0.81733331898155	-0.50549144066845	0.00000000000000
33-36	-1.00000000000000	-0.80165341662936	-0.48281168478404	-0.00000000000000
37-40	-1.00000000000000	-0.78503612800100	-0.45871616290233	0
41-44	-1.00000000000000	-0.76791910597691	-0.43384761380163	0.00000000000000
45-48	-1.00000000000000	-0.75079146933532	-0.40894639823666	-0.00000000000000
49-52	-1.00000000000000	-0.73419109949077	-0.38485476803643	0.00000000000000
53-56	-1.00000000000000	-0.71870000198881	-0.36251791923664	0.00000000000000
57-60	-1.00000000000000	-0.70493714316153	-0.34297923670114	-0.00000000000000
61-64	-1.00000000000000	-0.69354812546423	-0.32736624647290	0.00000000000000
65-68	-1.00000000000000	-0.68519104330942	-0.31686290340778	-0.00000000000000
69-72	-1.00000000000000	-0.68051785698359	-0.31266315615731	-0.00000000000000
73-76	-1.00000000000000	-0.68015060189133	-0.31590057537960	0.00000000000000
77-80	-1.00000000000000	-0.68465163174830	-0.32754968215944	-0.00000000000000
81-84	-1.00000000000000	-0.69448671130670	-0.34829710526175	0.00000000000000
85-88	-1.00000000000000	-0.70997882818907	-0.37838556360207	0.00000000000000
89-92	-1.00000000000000	-0.73124861181435	-0.41744158284636	-0.00000000000000
93-96	-1.00000000000000	-0.75813365052612	-0.46430903316173	0.00000000000000
97-100	-1.00000000000000	-0.79007364616757	-0.51692408743832	-0.00000000000000
101-104	-1.00000000000000	-0.82594365531974	-0.57227991772814	-0.00000000000000
105-108	-1.00000000000000	-0.86382459860619	-0.62653503445383	0.00000000000000
109-112	-1.00000000000000	-0.90074923757116	-0.67530829146311	-0.00000000000000
113-116	-1.00000000000000	-0.93260175680685	-0.71416736810511	0.00000000000000
117-120	-1.00000000000000	-0.95456071995419	-0.73925562157885	0.00000000000000
121(infinity)-124	--1.00000000000000	-0.96244632852818	-0.74793197691388	-0.00000000000001

Table B7 - Distribution of $\widetilde{u}_{\rho T}$ ($\delta = 10^{-6}$) on the nodes constructed for $\delta = 10^{-6}$.

⇓ Nodes number	⇓ Wall Surface	⇓ Medium	⇓ Medium	⇓ Sphere Surface
1(origin)-4	-1.00011917730444	-0.80011509856558	-0.46816765549011	-0.02102174452739
5-8	-1.00000202311708	-0.79854116794786	-0.46523118766413	-0.00035389025675
9-12	-0.99999461613334	-0.79416759792548	-0.46077222415079	0.00094147196069
13-16	-1.00000323561653	-0.78695156203867	-0.45365554359705	-0.00056570854940
17-20	-1.00000102975901	-0.77694650215562	-0.44362506160905	-0.00018015443857
21-24	-0.99999652724364	-0.76427017815877	-0.43089683511789	0.00060717602173
25-28	-1.00000234481558	-0.74907350817375	-0.41576722139871	-0.00041007557593
29-32	-1.00000080333848	-0.73150612082100	-0.39818205672782	-0.00014054600615
33-36	-0.99999715173908	-0.71176550260861	-0.37839933900977	0.00049805347226
37-40	-1.00000199933129	-0.69007805250294	-0.35676775965840	-0.00034950560075
41-44	-1.00000070483657	-0.66666741791414	-0.33334221797122	-0.00012357458763
45-48	-0.99999743091757	-0.64179405923642	-0.30843109897978	0.00044921622612
49-52	-1.00000184198143	-0.61573971703183	-0.28242761688307	-0.00032233470120
53-56	-1.00000066417851	-0.58877718044096	-0.25545148417586	-0.00011629564688
57-60	-0.99999753758311	-0.56120533417561	-0.22784359147772	0.00043054381968
61-64	-1.00000179879135	-0.53333516645944	-0.20002252931590	-0.00031433699769
65-68	-1.00000065981294	-0.50545983252232	-0.17213406314841	-0.00011534945224
69-72	-0.99999751627911	-0.47788797828252	-0.14452600028017	0.00043413531967
73-76	-1.00000184285454	-0.45093073128373	-0.11761862382991	-0.00032231389196
77-80	-1.00000068804366	-0.42487107384659	-0.09154564779601	-0.00012036580301
81-84	-0.99999736073369	-0.39999769766291	-0.06663394677162	0.00046138776815
85-88	-1.00000199797796	-0.37659278657520	-0.04328251550032	-0.00034945261723
89-92	-1.00000076198194	-0.35489957335813	-0.02157507193624	-0.00013346933702
93-96	-0.99999699834734	-0.33515894664743	-0.00179111938633	0.00052490374947
97-100	-1.00000234456820	-0.31759830933879	0.01570778979658	-0.00040995924064
101-104	-1.00000093079871	-0.30239495944988	0.03092733729136	-0.00016274797963
105-108	-0.99999614941407	- 0.28971884435305	0.04365823934495	0.00067326353746
109-112	-1.00000323299355	-0.27972370063435	0.05357108373755	-0.00056534623764
113-116	-1.00000144460137	-0.27250056958928	0.06081326753792	-0.00025252721025
117-120	-0.99999240399234	-0.26814114946819	0.06526720074362	0.00132809963134
121(infinity)-124	-0.99999933246095	-0.96573198816636	-0.73752125961111	-0.00040738874699

Table B8 - Distribution of $\widetilde{u}_{\rho R}$ (for $\theta=\pi$) on the nodes demonstrated in Fig. 4.1.

⇓ Nodes number	⇓ Wall Surface	⇓ Medium	⇓ Medium	⇓ Sphere Surface
1(origin)-4	0.00000000000000	-0.45667681301488	--0.78869047485863	-1.00000000000000
5-8	-0.00000000000000	-0.45522875263913	-0.78718389002079	-0.99986221034354
9-12	0.00000000000000	-0.45090005913025	-0.78267916169799	-0.99944591662036
13-16	0.00000000000000	-0.44373701113462	-0.77522114843458	-0.99874221375189
17-20	0.00000000000000	-0.43381612664348	-0.76488387948690	-0.99773581391756
21-24	-0.00000000000000	-0.42124324652654	-0.75176944645978	-0.99640434148731
25-28	0.00000000000000	-0.40615225728937	-0.73600643819033	-0.99471726952774
29-32	-0.00000000000000	-0.38870345758458	-0.71774790139313	-0.99263441064152
33-36	-0.00000000000000	-0.36908157225031	-0.69716879800408	-0.99010383245452
37-40	-0.00000000000000	-0.34749341491064	-0.67446291214022	-0.98705900842639
41-44	-0.00000000000000	-0.32416519438368	-0.64983913158736	-0.98341492837071
45-48	0.00000000000000	-0.29933944963453	-0.62351698517204	-0.97906276531224
49-52	0.00000000000000	-0.27327158011235	-0.59572124933196	-0.97386250234932
53-56	-0.00000000000000	-0.24622590870199	-0.56667533005195	-0.96763262626268
57-60	0.00000000000000	-0.21847116619785	-0.53659295581301	-0.96013552918690
61-64	0.00000000000000	-0.19027520794436	-0.50566744257635	-0.95105651629516
65-68	-0.00000000000000	-0.16189864760287	-0.47405734440938	-0.93997310709889
69-72	-0.00000000000000	-0.13358689420584	-0.44186656813516	-0.92630930829855
73-76	-0.00000000000000	-0.10555977406960	-0.40911581960108	-0.90926613386873
77-80	0.00000000000000	-0.07799748983952	-0.37570027355548	-0.88771378290959
81-84	0.00000000000000	-0.05102123061632	-0.34132522825010	-0.86002062704471
85-88	-0.00000000000000	-0.02466710815494	-0.30540689887781	-0.82377610785200
89-92	0.00000000000000	0.00114313568389	-0.26692017283704	-0.77533332444798
93-96	0.00000000000000	0.02660942798014	-0.22417569351228	-0.70904622882451
97-100	-0.00000000000000	0.05194139367094	-0.17454669687966	-0.61601208541887
101-104	0	0.07685544645262	-0.11435677479839	-0.48214266439190
105-108	-0.00000000000000	0.09917759774669	-0.03976870053604	-0.28598017585474
109-112	-0.00000000000000	0.11234925849755	0.04928822716086	-0.00000000000000
113-116	0.00000000000000	0.10413120596956	0.14092699059691	0.38853438153656
117-120	-0.00000000000000	0.06464789452361	0.20877439479179	0.80263330164336
121(infinity)-124	-0.00000000000000	0.02656381138936	0.23240008363428	1.00000000000000

Table B9 - Distribution of $\widetilde{u}_{zR}$ (for $\theta=\pi$) on the nodes demonstrated in Fig. 4.1.

⇓ Nodes number	⇓ Wall Surface	⇓ Medium	⇓ Medium	⇓ Sphere Surface
1(origin)-4	0	-0.00000000000000	-0.00000000000000	-0.00000000000000
5-8	0	-0.00373940538488	-0.01115297227831	-0.01660000984717
9-12	0	-0.00745101720776	-0.02226875469910	-0.03328452719956
13-16	0	-0.01110746390396	-0.03331137894460	-0.05013970951222
17-20	0	-0.01468221642837	-0.04424733190434	-0.06725507881398
21-24	0	-0.01815000594596	-0.05504681482100	-0.08472536966717
25-28	0	-0.02148723756199	-0.06568504377983	-0.10265258741638
29-32	0	-0.02467239927810	-0.07614361135281	-0.12114836693231
33-36	0	-0.02768646571040	-0.08641193478030	-0.14033674130060
37-40	0	-0.03051329638573	-0.09648882349743	-0.16035745659093
41-44	0	-0.03314002842592	-0.10638420826597	-0.18137000484545
45-48	0	-0.03555746270395	-0.11612108559943	-0.20355859495278
49-52	0	-0.03776044024139	-0.12573774384728	-0.22713834224527
53-56	0	-0.03974819996577	-0.13529034887069	-0.25236303333092
57-60	0	-0.04152469641937	-0.14485597152681	-0.27953490943532
61-64	0	-0.04309882939498	-0.15453612140715	-0.30901699437495
65-68	0	-0.04448448214009	-0.16446077765246	-0.34124852810065
69-72	0	-0.04570015147092	-0.17479270301358	-0.37676393850722
73-76	0	-0.04676772397112	-0.18573132676340	-0.41621520611270
77-80	0	-0.04770948699701	-0.19751431825046	-0.46039574241337
81-84	0	-0.04854146602029	-0.21041226904337	-0.51025926846812
85-88	0	-0.04925877404112	-0.22470532492641	-0.56691527068180
89-92	0	-0.04980218209064	-0.24061352143323	-0.63155224328669
93-96	0	-0.04997806859189	-0.25810715014230	-0.70516199939428
97-100	0	-0.04926888300675	-0.27641274704872	-0.78773670132723
101-104	0	-0.04644677320823	-0.29282972797987	-0.87609271836552
105-108	0	-0.03908413023816	-0.30041074273894	-0.95823553420759
109-112	0	-0.02393845404476	-0.28535152104114	-1.00000000000000
113-116	0	-0.00081279036348	-0.22979356939568	-0.92143422682468
117-120	0	0.01784110097952	-0.12820618621149	-0.59647278487210
121(infinity)-124	0	0	0	0

Table B10 - Distribution of $\widetilde{u}_{\theta R}$ (for $\theta=\pi/2$)on the nodes demonstrated in Fig. 4.1.

⇓ Nodes number	⇓ Wall Surface	⇓ Medium	⇓ Medium	⇓ Sphere Surface
1(origin)-4	-0.00000000000000	0.45667681301488	0.78869047485863	1.00000000000000
5-8	0.00000000000000	0.45661018233330	0.78857408452067	0.99986221034354
9-12	-0.00000000000000	0.45640881756512	0.78822237513956	0.99944591662036
13-16	-0.00000000000000	0.45606823107182	0.78762761390726	0.99874221375189
17-20	0.00000000000000	0.45558070624066	0.78677651107054	0.99773581391756
21-24	0.00000000000000	0.45493492116465	0.78564958332667	0.99640434148731
25-28	0.00000000000000	0.45411537813137	0.78422019026559	0.99471726952774
29-32	0.00000000000000	0.45310158854460	0.78245316069106	0.99263441064152
33-36	-0.00000000000000	0.45186693755514	0.78030288422342	0.99010383245452
37-40	0.00000000000000	0.45037711638444	0.77771068458891	0.98705900842639
41-44	0.00000000000000	0.44858795684336	0.77460120450001	0.98341492837071
45-48	-0.00000000000000	0.44644242204969	0.77087740237837	0.97906276531224
49-52	-0.00000000000000	0.44386638421353	0.76641356337041	0.97386250234931
53-56	-0.00000000000000	0.44076262982243	0.76104542097665	0.96763262626268
57-60	0	0.43700223599276	0.75455600675536	0.96013552918689
61-64	0.00000000000000	0.43241200142929	0.74665509241410	0.95105651629515
65-68	0.00000000000000	0.42675591308226	0.73694890741732	0.93997310709889
69-72	-0.00000000000000	0.41970760381373	0.72489499376134	0.92630930829854
73-76	-0.00000000000000	0.41080940304362	0.70973436862966	0.90926613386872
77-80	0.00000000000000	0.39941223534530	0.69038956738587	0.88771378290958
81-84	0.00000000000000	0.38459067972731	0.66531348956002	0.86002062704471
85-88	0.00000000000000	0.36503323527105	0.63227404974155	0.82377610785199
89-92	0.00000000000000	0.33893032627800	0.58807545423987	0.77533332444797
93-96	0.00000000000000	0.30394641037017	0.52828119226613	0.70904622882451
97-100	-0.00000000000000	0.25750983762542	0.44719449896697	0.61601208541886
101-104	-0.00000000000000	0.19791196959716	0.33881895516736	0.48214266439189
105-108	0.00000000000000	0.12690231698505	0.20039348969443	0.28598017585473
109-112	0.00000000000000	0.05370214685627	0.04063944174139	-0.00000000000000
113-116	-0.00000000000000	-0.00330227415246	-0.10963302976832	-0.38853438153656
117-120	0.00000000000000	-0.02680653327642	-0.20522792234966	-0.80263330164336
121(infinity)-124	0.00000000000000	-0.02656381138936	-0.23240008363428	-1.00000000000000

Table B11 - Comparison of Numerical and Analytical solutions, Pe =0.01, δ=0.1.								
Node	Analytic	Numeric	Analytic	Numeric	Analytic	Numeric	Analytic	Numeric
1(origin)-4	-0.0000	0.0003	-0.0000	0.0003	-0.0000	0.0002	-0.0000	0.0002
5-8	-29.8909	-29.6491	-26.8998	-26.6808	-25.1019	-24.8945	-24.4400	-24.2321
9-12	-59.3302	-58.8966	-53.3814	-52.9911	-49.8060	-49.4370	-48.4896	-48.1189
13-16	-87.8735	-87.2688	-79.0335	-78.4925	-73.7211	-73.2106	-71.7651	-71.2514
17-20	-115.0903	-114.3297	-103.4583	-102.7814	-96.4692	-95.8319	-93.8955	-93.2537
21-24	-140.5718	-139.6682	-126.2780	-125.4781	-117.6915	-116.9403	-114.5293	-113.7722
25-28	-163.9366	-162.9022	-147.1413	-146.2305	-137.0551	-136.2021	-133.3403	-132.4799
29-32	-184.8375	-183.6845	-165.7294	-164.7195	-154.2586	-153.3155	-150.0332	-149.0815
33-36	-202.9678	-201.7083	-181.7616	-180.6648	-169.0375	-168.0164	-164.3496	-163.3187
37-40	-218.0662	-216.7126	-195.0009	-193.8293	-181.1695	-180.0827	-176.0729	-174.9752
41-44	-229.9222	-228.4871	-205.2584	-204.0245	-190.4794	-189.3395	-185.0326	-183.8810
45-48	-238.3806	-236.8768	-212.3976	-211.1143	-196.8427	-195.6628	-191.1088	-189.9169
49-52	-243.3448	-241.7854	-216.3383	-215.0188	-200.1894	-198.9833	-194.2356	-193.0175
53-56	-244.7806	-243.1785	-217.0590	-215.7168	-200.5073	-199.2889	-194.4041	-193.1745
57-60	-242.7175	-241.0856	-214.5998	-213.2483	-197.8435	-196.6274	-191.6643	-190.4390
61-64	-237.2512	-235.6019	-209.0631	-207.7160	-192.3065	-191.1077	-186.1274	-184.9227
65-68	-228.5431	-226.8884	-200.6147	-199.2855	-184.0668	-182.9007	-177.9659	-176.7992
69-72	-216.8206	-215.1711	-189.4830	-188.1848	-173.3565	-172.2388	-167.4141	-166.3037
73-76	-202.3746	-200.7397	-175.9575	-174.7029	-160.4685	-159.4153	-154.7672	-153.7326
77-80	-185.5562	-183.9428	-160.3857	-159.1870	-145.7544	-144.7822	-140.3796	-139.4415
81-84	-166.7696	-165.1823	-143.1691	-142.0381	-129.6220	-128.7469	-124.6625	-123.8423
85-88	-146.4635	-144.9046	-124.7586	-123.7074	-112.5310	-111.7687	-108.0800	-107.3992
89-92	-125.1205	-123.5927	-105.6504	-104.6919	-94.9889	-94.3533	-91.1433	-90.6218
93-96	-103.2547	-101.7673	-86.3865	-85.5352	-77.5453	-77.0464	-74.4008	-74.0543
97-100	-81.4327	-80.0099	-67.5609	-66.8325	-60.7812	-60.4225	-58.4203	-58.2568
101-104	-60.3318	-59.0180	-49.8288	-49.2389	-45.2891	-45.0646	-43.7586	-43.7737
105-108	-40.8191	-39.6728	-33.9040	-33.4652	-31.6327	-31.5247	-30.9090	-31.0800
109-112	-23.9775	-23.0502	-20.5195	-20.2392	-20.2733	-20.2520	-20.2215	-20.5005
113-116	-10.9738	-10.2955	-10.3289	-10.1998	-11.4473	-11.4757	-11.7889	-12.0982
117-120	-2.7877	-2.3957	-3.6976	-3.6748	-4.9722	-5.0237	-5.3109	-5.5466
121(∞)-124	-0.0000	0	0	-0.0000	0	-0.0000	0	-0.0001

Table B12-Correction coefficient to Stokes law, k, due to the presence of a wall		
δ	k Brenner (1961)'s solution	k Present solution
10	1.11350323390571	-1.11350323390571
1	2.12553556676004	-2.12553556676004
0.1	11.45915720340954	-11.45915720340951
0.01	1.018961723245513e+002	-1.018961723264529e+002

Table B13-Comparison of analytical and numerical force for different geometries and mesh sizes.

δ	Mesh size K×L	ψ_P mV	ψ_W mV	$a\Omega/U$	D_1/D_2	$\tilde{F}_x/\lambda$ Analytic	$\tilde{F}_x/\lambda$ Numeric
3.0	20×50	-300	-500	0.5	2	-67.4523	-66.9059
3.0	14×15	-300	-500	0.5	2	-66.9776	-65.8799
3.0	50×20	-300	-500	0.5	2	-67.1351	-66.9902
0.1	20×50	-100	+200	3	1	-267.3913	-266.8082
0.1	14×15	-100	+200	3	1	-264.9144	-258.9971
0.1	50×20	-100	+200	3	1	-266.1876	-262.8536
0.001	20×50	+150	-50	0.25	0.5	-8.4789e+005	-8.4892e+005
0.001	14×15	+150	-50	0.25	0.5	-8.3343e+005	-8.3715e+005
0.001	50×20	+150	-50	0.25	0.5	-8.3925e+005	-8.4162e+005

Table B14 - Tangential component of electroviscous force, $\tilde{F}_x/\lambda$, obtained with different methods.

δ	Pe	ζ_p mv	ζ_w mv	D_1/D_2	$a\Omega/U$	Inner region Eq. (4.7.5)	Analytical low Pe	Numeric low Pe	Numeric Arbitrary Pe	Formula (4.7.2)
10^2	0.001	-50	0	5	0	-	-0.1518	-0.1503	-0.1480	-
10^1	0.01	-500	0	4	2/3	-	-145.6423	-140.8798	-169.0022	-
1	0.001	-400	-400	3	3/4	-	-27.6555	-27.4469	-33.0319	-
10^{-1}	0.001	+300	-300	2	1/4	-	-207.6034	-208.3347	-224.9133	-
10^{-2}	0.01	-300	+300	1	1/2	-4.8340e+004	-9.0366e+004	-8.9964e+004	-9.1466e+004	-8.6182e+004
10^{-3}	0.1	+100	+100	1/3	3	-1.3833e+007	-2.5741e+007	-2.5649e+007	-2.5621e+007	-2.5696e+007
10^{-4}	1	-300	-100	1/2	2/3	-8.3120e+010	-1.6695e+011	-1.6717e+011	-1.6670e+011	-1.6717e+011
10^{-5}	10	-200	+100	3	2	-3.8164e+013	-7.9100e+013	-7.9434e+013	-7.9098e+013	-7.9144e+013
10^{-6}	100	-200	-150	1/4	1	-6.0809e+016	-1.1620e+017	-1.1717e+017	-1.1652e+017	-1.1626e+017

Table B15 - Normal component of electroviscous force, $\tilde{F}_z/\lambda$, obtained with different methods.

δ	Pe	ζ_p mv	ζ_w mv	D_1/D_2	$a\Omega/U$	Inner region Eq. (4.7.6)	Numeric low Pe	Numeric Arbitrary Pe	Formula (4.7.3)
1	0.001	-400	-400	3	3/4	-	0.0037	0.0037	-
10^{-1}	0.001	+300	-300	2	1/4	-	0.1867	0.1858	-
10^{-2}	0.01	-300	+300	1	1/2	540.6044	1.0855e+003	1.0800e+003	1.0412e+003
10^{-3}	0.1	+100	+100	1/3	3	1.8239e+004	3.5720e+004	3.5536e+004	3.4955e+004
10^{-4}	1	-300	-100	1/2	2/3	2.9320e+010	5.3067e+010	5.2837e+010	5.2847e+010
10^{-5}	10	-200	+100	3	2	6.2731e+014	1.1614e+015	1.1406e+015	1.1576e+015
10^{-6}	100	-200	-150	1/4	1	3.2308e+018	6.1719e+018	6.1183e+018	6.1702e+018

Appendix C

Chapter Four Calculations

Parameters M, N, S, T and O in relationships (4.3.23, 24) are defined by

$$\begin{aligned}M = &-2(1-\mu\cosh\xi)\sum_{1}^{\infty} A_n \sinh\left(n+\frac{1}{2}\right)\xi P_n' \\ &+\mu\sinh\xi\sum_{1}^{\infty}\left[B_n\cosh\left(n+\frac{1}{2}\right)\xi + C_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n' \\ &+\sinh\xi\sum_{0}^{\infty}\left[D_n\cosh\left(n+\frac{1}{2}\right)\xi + E_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n \\ &+(1-\mu^2)\sinh\xi\sum_{2}^{\infty}\left[F_n\cosh\left(n+\frac{1}{2}\right)\xi + G_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n''\end{aligned} \quad \text{(C.1)}$$

$$N = 2(1-\mu^2)\sinh\xi(\cosh\xi-\mu)^{-2} \quad \text{(C.2)}$$

$$\begin{aligned}S = &\,2\mu\cosh\xi\sum_{1}^{\infty} A_n \sinh\left(n+\frac{1}{2}\right)\xi P_n' \\ &+\mu\sinh\xi\sum_{1}^{\infty}\left[B_n\cosh\left(n+\frac{1}{2}\right)\xi + C_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n' \\ &+\sinh\xi\sum_{0}^{\infty}\left[D_n\cosh\left(n+\frac{1}{2}\right)\xi + E_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n \\ &+(1-\mu^2)\sinh\xi\sum_{2}^{\infty}\left[F_n\cosh\left(n+\frac{1}{2}\right)\xi + G_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n''\end{aligned} \quad \text{(C.3)}$$

$$\begin{aligned}T = &\,2\mu\sinh\xi\sum_{1}^{\infty}\left(n+\frac{1}{2}\right) A_n \cosh\left(n+\frac{1}{2}\right)\xi P_n' \\ &+\mu\cosh\xi\sum_{1}^{\infty}\left(n+\frac{1}{2}\right)\left[B_n\sinh\left(n+\frac{1}{2}\right)\xi + C_n\cosh\left(n+\frac{1}{2}\right)\xi\right]P_n' \\ &+\cosh\xi\sum_{0}^{\infty}\left(n+\frac{1}{2}\right)\left[D_n\sinh\left(n+\frac{1}{2}\right)\xi + E_n\cosh\left(n+\frac{1}{2}\right)\xi\right]P_n \\ &+(1-\mu^2)\cosh\xi\sum_{2}^{\infty}\left(n+\frac{1}{2}\right)\left[F_n\sinh\left(n+\frac{1}{2}\right)\xi + G_n\cosh\left(n+\frac{1}{2}\right)\xi\right]P_n''\end{aligned} \quad \text{(C.4)}$$

and

$$O = -2(1-\mu\cosh\xi)\sum_{1}^{\infty}\left(n+\frac{1}{2}\right)^2 A_n \sinh\left(n+\frac{1}{2}\right)\xi P_n'$$
$$+\mu\sinh\xi\sum_{1}^{\infty}\left(n+\frac{1}{2}\right)^2\left[B_n\cosh\left(n+\frac{1}{2}\right)\xi + C_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n'$$
$$+\sinh\xi\sum_{0}^{\infty}\left(n+\frac{1}{2}\right)^2\left[D_n\cosh\left(n+\frac{1}{2}\right)\xi + E_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n \qquad (C.5)$$
$$+(1-\mu^2)\sinh\xi\sum_{2}^{\infty}\left(n+\frac{1}{2}\right)^2\left[F_n\cosh\left(n+\frac{1}{2}\right)\xi + G_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n''$$

In view of the recurrence relationships [Macrobert (1967)]

$$\mu P_n'(\mu) = \frac{n+1}{2n+1}P_{n-1}'(\mu) + \frac{n}{2n+1}P_{n+1}'(\mu) \qquad n \ge 1 \qquad (C.6)$$

$$(1-\mu^2)P_n'(\mu) = \frac{(n+1)(n+2)}{2n+1}P_{n-1}'(\mu) - \frac{(n-1)n}{2n+1}P_{n+1}'(\mu) \qquad n \ge 1 \qquad (C.7)$$

$$P_n(\mu) = \frac{-1}{2n+1}P_{n-1}'(\mu) + \frac{1}{2n+1}P_{n+1}'(\mu) \qquad n \ge 1 \qquad (C.8)$$

the auxiliary functions M, S, T and O can be written in terms of just P_n', with the notation

$$K_{n+i}Sin = K_{n+i}\sinh\left(n+i+\frac{1}{2}\right)\xi, \qquad K_{n+i}Cos = K_{n+i}\sinh\left(n+i+\frac{1}{2}\right)\xi, \quad (C.9)$$

[K = (A, B, C, D, E, F, G)], as

$$M = -2\sum_{1}^{\infty}A_n Sin P_n' + 2\cosh\xi\sum_{1}^{\infty}\left[A_{n+1}Sin\frac{n+2}{2n+3} + A_{n-1}Sin\frac{n-1}{2n-1}\right]P_n' \qquad (C.10)$$
$$+\sinh\xi\sum_{1}^{\infty}\left[(B_{n+1}Cos + C_{n+1}Sin)\frac{n+2}{2n+3} + (B_{n-1}Cos + C_{n-1}Sin)\frac{n-1}{2n-1}\right]P_n'$$
$$+\sinh\xi\sum_{1}^{\infty}\left[(D_{n+1}Cos + E_{n+1}Sin)\frac{-1}{2n+3} + (D_{n-1}Cos + E_{n-1}Sin)\frac{1}{2n-1}\right]P_n'$$
$$+\sinh\xi\sum_{1}^{\infty}\left[(F_{n+1}Cos + G_{n+1}Sin)\frac{(n+2)(n+3)}{2n+3} - (F_{n-1}Cos + G_{n-1}Sin)\frac{(n-2)(n-1)}{2n-1}\right]P_n'$$

$$S = 2\cosh\xi\sum_{1}^{\infty}\left[A_{n+1}\text{Sin}\frac{n+2}{2n+3} + A_{n-1}\text{Sin}\frac{n-1}{2n-1}\right]P_n' \tag{C.11}$$
$$+\sinh\xi\sum_{1}^{\infty}\left[\left(B_{n+1}\text{Cos} + C_{n+1}\text{Sin}\right)\frac{n+2}{2n+3} + \left(B_{n-1}\text{Cos} + C_{n-1}\text{Sin}\right)\frac{n-1}{2n-1}\right]P_n'$$
$$+\sinh\xi\sum_{1}^{\infty}\left[\left(D_{n+1}\text{Cos} + E_{n+1}\text{Sin}\right)\frac{-1}{2n+3} + \left(D_{n-1}\text{Cos} + E_{n-1}\text{Sin}\right)\frac{1}{2n-1}\right]P_n'$$
$$+\sinh\xi\sum_{1}^{\infty}\left[\left(F_{n+1}\text{Cos} + G_{n+1}\text{Sin}\right)\frac{(n+2)(n+3)}{2n+3} - \left(F_{n-1}\text{Cos} + G_{n-1}\text{Sin}\right)\frac{(n-2)(n-1)}{2n-1}\right]P_n'$$

$$T = \sinh\xi\sum_{1}^{\infty}\left[A_{n+1}\text{Cos}(n+2) + A_{n-1}\text{Cos}(n-1)\right]P_n' \tag{C.12}$$
$$+\frac{1}{2}\cosh\xi\sum_{1}^{\infty}\left[\left(B_{n+1}\text{Sin} + C_{n+1}\text{Cos}\right)(n+2) + \left(B_{n-1}\text{Sin} + C_{n-1}\text{Cos}\right)(n-1)\right]P_n'$$
$$+\frac{1}{2}\cosh\xi\sum_{1}^{\infty}\left[-\left(D_{n+1}\text{Sin} + E_{n+1}\text{Cos}\right) + \left(D_{n-1}\text{Sin} + E_{n-1}\text{Cos}\right)\right]P_n'$$
$$+\frac{1}{2}\cosh\xi\sum_{1}^{\infty}\left[\left(F_{n+1}\text{Sin} + G_{n+1}\text{Cos}\right)(n+2)(n+3) - \left(F_{n-1}\text{Sin} + G_{n-1}\text{Cos}\right)(n-2)(n-1)\right]P_n'$$

$$O = -2\sum^{\infty}\left(n+\frac{1}{2}\right)^2 A_n\text{Sin}P_n' + \cosh\xi\sum_{1}^{\infty}\left[A_{n+1}\text{Sin}\left(n+\frac{3}{2}\right)(n+2) + A_{n-1}\text{Sin}\left(n-\frac{1}{2}\right)(n-1)\right]P_n'$$
$$+\frac{1}{2}\sinh\xi\sum_{1}^{\infty}\left[\left(B_{n+1}\text{Cos}+C_{n+1}\text{Sin}\right)\left(n+\frac{3}{2}\right)(n+2) + \left(B_{n-1}\text{Cos}+C_{n-1}\text{Sin}\right)\left(n-\frac{1}{2}\right)(n-1)\right]P_n'$$
$$+\frac{1}{2}\sinh\xi\sum_{1}^{\infty}\left[-\left(D_{n+1}\text{Cos}+E_{n+1}\text{Sin}\right)\left(n+\frac{3}{2}\right) + \left(D_{n-1}\text{Cos}+E_{n-1}\text{Sin}\right)\left(n-\frac{1}{2}\right)\right]P_n'$$
$$+\frac{1}{2}\sinh\xi\sum_{1}^{\infty}\left[\left(F_{n+1}\text{Cos}+G_{n+1}\text{Sin}\right)\left(n+\frac{3}{2}\right)(n+2)(n+3)\right.$$
$$\left. -(n-2)(n-1)\left(F_{n-1}\text{Cos}+G_{n-1}\text{Sin}\right)\left(n-\frac{1}{2}\right)\right]P_n' \tag{C.13}$$

The boundary condition on the sphere is the same as that for the wall, given by (4.3.25), for which F_{cW} is replaced by F_{cP} and ξ is taken to be equal to α, that is

$$\frac{\partial C_{21}}{\partial\xi} = -\frac{F_{cP}\sin\eta}{2c}\left\{N + \left(\cosh\xi - \mu\right)^{-\frac{3}{2}}\left[\frac{1}{4}\sinh^2\xi M\right] \qquad \text{on } \xi = \alpha\right.$$
$$\left. +\left(\cosh\xi - \mu\right)^{-\frac{1}{2}}\left[-\frac{1}{2}\cosh\xi M\right] + \left(\cosh\xi - \mu\right)^{\frac{1}{2}}\left[S + 2T + O\right]\right\} \tag{C.14}$$

In view of (4.3.31) and the identity [Macrobert (1967)]

$$\left(\cosh\xi-\mu\right)^{-\frac{1}{2}}=-2\sum_{1}^{n}\lambda_n P_n' \qquad \text{(C.15)}$$

where λ_n is defined by (4.2.135), the parameter N in (C.14) (the term due to the moving coordinate system), given by (C.2), may be evaluated as

$$\begin{aligned} N &= 2\left(1-\mu^2\right)\sinh\xi\left(\cosh\xi-\mu\right)^{-2} = -4\left(1-\mu^2\right)\sinh\xi\left(\cosh\xi-\mu\right)^{-\frac{3}{2}}\sum_{1}^{n}\lambda_n P_n' \\ &-4\sinh\xi\left(\cosh\xi-\mu\right)^{-\frac{3}{2}}\left\{\sum_{1}^{n}\lambda_n P_n' - \mu\sum_{1}^{n}\left[\lambda_{n+1}\frac{n+2}{2n+3}+\lambda_{n-1}\frac{n-1}{2n-1}\right]P_n'\right\} = \\ &-4\sinh\xi\left(\cosh\xi-\mu\right)^{-\frac{3}{2}}\left\{\sum_{1}^{n}\lambda_n P_n' - \sum_{1}^{\infty}\left[\frac{n+2}{2n+3}\left(\lambda_{n+2}\frac{n+3}{2n+5}+\lambda_n\frac{n}{2n+1}\right)\right.\right. \\ &\left.\left.+\frac{n-1}{2n-1}\left(\lambda_n\frac{n+1}{2n+1}+\lambda_{n-2}\frac{n-2}{2n-3}\right)\right]P_n'\right\} \end{aligned} \qquad \text{(C.16)}$$

Thus, if we write

$$N=\left(\cosh\xi-\mu\right)^{-\frac{3}{2}}\sum_{1}^{n}\beta_n P_n' \qquad \text{(C.17)}$$

β_n is determined by

$$\begin{aligned} \beta_n = 4\sinh\xi&\left[-\lambda_n+\frac{n+2}{2n+3}\left(\lambda_{n+2}\frac{n+3}{2n+5}+\lambda_n\frac{n}{2n+1}\right)\right. \\ &\left.+\frac{n-1}{2n-1}\left(\lambda_n\frac{n+1}{2n+1}+\lambda_{n-2}\frac{n-2}{2n-3}\right)\right] \end{aligned} \qquad \text{(C.18)}$$

from which and from the identities

$$\begin{aligned} &\left(\cosh\xi-\mu\right)^{-\frac{1}{2}}P_n' = \left(\cosh\xi-\mu\right)^{-\frac{3}{2}}\left(\cosh\xi-\mu\right)P_n' = \\ &\left(\cosh\xi-\mu\right)^{-\frac{3}{2}}\left[\cosh\xi P_n' - \left(\frac{n+1}{2n+1}P_{n-1}'+\frac{n}{2n+1}P_{n+1}'\right)\right] \end{aligned} \qquad \text{(C.19)}$$

$$\begin{aligned} &\left(\cosh\xi-\mu\right)^{\frac{1}{2}}P_n' = \left(\cosh\xi-\mu\right)^{-\frac{1}{2}}\left(\cosh\xi-\mu\right)P_n' = \\ &\left(\cosh\xi-\mu\right)^{-\frac{1}{2}}\left[\cosh\xi P_n' - \frac{n+1}{2n+1}P_{n-1}' - \frac{n}{2n+1}P_{n+1}'\right] = \\ &\left(\cosh\xi-\mu\right)^{-\frac{3}{2}}\left\{\cosh^2\xi P_n' - \cosh\xi\left[\frac{n+1}{2n+1}P_{n-1}'+\frac{n}{2n+1}P_{n+1}'\right]\right. \\ &\left.+\frac{(n+1)n}{(2n+1)(2n-1)}P_{n-2}' + \left[\frac{(n+1)(n-1)}{(2n+1)(2n-1)}+\frac{n(n+2)}{(2n+1)(2n+3)}\right]P_n' + \frac{n(n+1)}{(2n+1)(2n+3)}P_{n+2}'\right\} \end{aligned} \qquad \text{(C.20)}$$

B.C. (C.14) may be written as

$$\frac{\partial C_{21}}{\partial \xi} = -\frac{F_{cP}\sin\eta}{2c}\left(\cosh\xi - \mu\right)^{-\frac{3}{2}} \times \qquad \text{on } \xi = \alpha$$

$$\sum_{1}^{\infty}\left[\beta_n + \gamma_n + \tau 1_n + \tau 2_n + \tau 3_n + \omega 1_n + \omega 2_n + \omega 3_n + \omega 4_n + \omega 5_n + \omega 6_n\right]P_n' \qquad \text{(C.21)}$$

in which β_n is given by (C.6), and γ_n, ($\tau 1_n$, $\tau 2_n$, $\tau 3_n$,) and ($\omega 1_n$, $\omega 2_n$, $\omega 3_n$, $\omega 4_n$, $\omega 5_n$, $\omega 6_n$) are obtained from the second, third and the fourth term in (C.14), upon the use of the identities (C.7, 8), as

$$\gamma_n = 4\sinh^2\xi\left\{2A_n\text{Sin} + 2\cosh\xi\left[A_{n+1}\text{Sin}\frac{n+2}{2n+3} + A_{n-1}\text{Sin}\frac{n-1}{2n-1}\right]\right. \qquad \text{(C.22)}$$

$$+\sinh\xi\left[\left(B_{n+1}\text{Cos} + C_{n+1}\text{Sin}\right)\frac{n+2}{2n+3} + \left(B_{n-1}\text{Cos} + C_{n-1}\text{Sin}\right)\frac{n-1}{2n-1}\right]$$

$$+\sinh\xi\left[\left(D_{n+1}\text{Cos} + E_{n+1}\text{Sin}\right)\frac{-1}{2n+3} + \left(D_{n-1}\text{Cos} + E_{n-1}\text{Sin}\right)\frac{1}{2n-1}\right]$$

$$\left.+\sinh\xi\left[\left(F_{n+1}\text{Cos} + G_{n+1}\text{Sin}\right)\frac{(n+2)(n+3)}{2n+3} - \left(F_{n-1}\text{Cos} + G_{n-1}\text{Sin}\right)\frac{(n-2)(n-1)}{2n-1}\right]\right\}$$

$$\tau 1_n = \cosh^2\xi A_n\text{Sin} - \cosh\xi\left(\cosh^2\xi + \sin^2 h\xi\right)\left[A_{n+1}\text{Sin}\frac{n+2}{2n+3} + A_{n-1}\text{Sin}\frac{n-1}{2n-1}\right]$$

$$-\sinh\xi\cosh^2\xi\left[\left(B_{n+1}\text{Cos} + C_{n+1}\text{Sin}\right)\frac{n+2}{2n+3} + \left(B_{n-1}\text{Cos} + C_{n-1}\text{Sin}\right)\frac{n-1}{2n-1}\right]$$

$$-\sinh\xi\cosh^2\xi\left[\left(D_{n+1}\text{Cos} + E_{n+1}\text{Sin}\right)\frac{-1}{2n+3} + \left(D_{n-1}\text{Cos} + E_{n-1}\text{Sin}\right)\frac{1}{2n-1}\right]$$

$$-\sinh\xi\cosh^2\xi\left[\left(F_{n+1}\text{Cos} + G_{n+1}\text{Sin}\right)\frac{(n+2)(n+3)}{2n+3} - \left(F_{n-1}\text{Cos} + G_{n-1}\text{Sin}\right)\frac{(n-2)(n-1)}{2n-1}\right]$$

$$+\frac{1}{2}\sinh\xi\cosh\xi\left(n + \frac{1}{2}\right)A_n\text{Cos} - \frac{1}{2}\sinh\xi\cosh^2\xi\left[A_{n+1}\text{Cos}(n+2) + A_{n-1}\text{Cos}(n-1)\right]$$

$$-\frac{1}{4}\sinh^2\xi\cosh\xi\left[\left(B_{n+1}\text{Sin} + C_{n+1}\text{Cos}\right)(n+2) + \left(B_{n-1}\text{Sin} + C_{n-1}\text{Cos}\right)(n-1)\right]$$

$$-\frac{1}{4}\sinh^2\xi\cosh\xi\left[-\left(D_{n+1}\text{Sin} + E_{n+1}\text{Cos}\right) + \left(D_{n-1}\text{Sin} + E_{n-1}\text{Cos}\right)\right] \qquad \text{(C.23)}$$

$$-\frac{1}{4}\sinh^2\xi\cosh\xi\left[\left(F_{n+1}\text{Sin} + G_{n+1}\text{Cos}\right)(n+2)(n+3) - \left(F_{n-1}\text{Sin} + G_{n-1}\text{Cos}\right)(n-2)(n-1)\right]$$

$$\tau 2_n = -\frac{n+2}{2n+3}\left\{+\cosh\xi A_{n+1}\mathrm{Sin} - \left(\cosh^2\xi + \sinh^2\xi\right)\left[A_{n+2}\mathrm{Sin}\frac{n+3}{2n+5} + A_n\mathrm{Sin}\frac{n}{2n+1}\right]\right.$$
$$-\sinh\xi\cosh\xi\left[\left(B_{n+2}\mathrm{Cos} + C_{n+2}\mathrm{Sin}\right)\frac{n+3}{2n+5} + \left(B_n\mathrm{Cos} + C_n\mathrm{Sin}\right)\frac{n}{2n+1}\right]$$
$$-\sinh\xi\cosh\xi\left[\left(D_{n+2}\mathrm{Cos} + E_{n+2}\mathrm{Sin}\right)\frac{-1}{2n+5} + \left(D_n\mathrm{Cos} + E_n\mathrm{Sin}\right)\frac{1}{2n+1}\right]$$
$$-\sinh\xi\cosh\xi\left[\left(F_{n+2}\mathrm{Cos} + G_{n+2}\mathrm{Sin}\right)\frac{(n+3)(n+4)}{2n+5} - \left(F_n\mathrm{Cos} + G_n\mathrm{Sin}\right)\frac{(n-1)(n)}{2n+1}\right]$$
$$+\frac{1}{2}\sinh\xi\left(n+\frac{3}{2}\right)A_{n+1}\mathrm{Cos} - \frac{1}{2}\sinh\xi\cosh\xi\left[A_{n+2}\mathrm{Cos}(n+3) + A_n\mathrm{Cos}(n)\right]$$
$$-\frac{1}{4}\sinh^2\xi\left[\left(B_{n+2}\mathrm{Sin} + C_{n+2}\mathrm{Cos}\right)(n+3) + \left(B_n\mathrm{Sin} + C_n\mathrm{Cos}\right)(n)\right]$$
$$-\frac{1}{4}\sinh^2\xi\left[-\left(D_{n+2}\mathrm{Sin} + E_{n+2}\mathrm{Cos}\right) + \left(D_n\mathrm{Sin} + E_n\mathrm{Cos}\right)\right]$$
$$\left.-\frac{1}{4}\sinh^2\xi\left[\left(F_{n+2}\mathrm{Sin} + G_{n+2}\mathrm{Cos}\right)(n+3)(n+4) - \left(F_n\mathrm{Sin} + G_n\mathrm{Cos}\right)(n-1)(n)\right]\right\}$$

(C.24)

$$\tau 3_n = -\frac{n-1}{2n-1}\left\{+\cosh\xi A_{n-1}\mathrm{Sin} - \left(\cosh^2\xi + \sin^2 h\xi\right)\left[A_n\mathrm{Sin}\frac{n+1}{2n+1} + A_{n-2}\mathrm{Sin}\frac{n-2}{2n-3}\right]\right.$$
$$-\sinh\xi\cosh\xi\left[\left(B_n\mathrm{Cos} + C_n\mathrm{Sin}\right)\frac{n+1}{2n+1} + \left(B_{n-2}\mathrm{Cos} + C_{n-2}\mathrm{Sin}\right)\frac{n-2}{2n-3}\right]$$
$$-\sinh\xi\cosh\xi\left[\left(D_n\mathrm{Cos} + E_n\mathrm{Sin}\right)\frac{-1}{2n+1} + \left(D_{n-2}\mathrm{Cos} + E_{n-2}\mathrm{Sin}\right)\frac{1}{2n-3}\right]$$
$$-\sinh\xi\cosh\xi\left[\left(F_n\mathrm{Cos} + G_n\mathrm{Sin}\right)\frac{(n+1)(n+2)}{2n+1} - \left(F_{n-2}\mathrm{Cos} + G_{n-2}\mathrm{Sin}\right)\frac{(n-3)(n-2)}{2n-3}\right]$$
$$+\frac{1}{2}\sinh\xi\left(n-\frac{1}{2}\right)A_{n-1}\mathrm{Cos} - \frac{1}{2}\sinh\xi\cosh\xi\left[A_n\mathrm{Cos}(n+1) + A_{n-2}\mathrm{Cos}(n-2)\right]$$
$$-\frac{1}{4}\sinh^2\xi\left[\left(B_n\mathrm{Sin} + C_n\mathrm{Cos}\right)(n+1) + \left(B_{n-2}\mathrm{Sin} + C_{n-2}\mathrm{Cos}\right)(n-2)\right]$$
$$-\frac{1}{4}\sinh^2\xi\left[-\left(D_n\mathrm{Sin} + E_n\mathrm{Cos}\right) + \left(D_{n-2}\mathrm{Sin} + E_{n-2}\mathrm{Cos}\right)\right]$$
$$\left.-\frac{1}{4}\sinh^2\xi\left[\left(F_n\mathrm{Sin} + G_n\mathrm{Cos}\right)(n+1)(n+2) - \left(F_{n-2}\mathrm{Sin} + G_{n-2}\mathrm{Cos}\right)(n-3)(n-2)\right]\right\}$$

(C.25)

$$
\begin{aligned}
\omega 1_n = \cosh^2\xi \Bigg\{ & 2\cosh\xi\left[A_{n+1}\mathrm{Sin}\frac{n+2}{2n+3} + A_{n-1}\mathrm{Sin}\frac{n-1}{2n-1}\right] \\
& + \sinh\xi\left[\left(B_{n+1}\mathrm{Cos} + C_{n+1}\mathrm{Sin}\right)\frac{n+2}{2n+3} + \left(B_{n-1}\mathrm{Cos} + C_{n-1}\mathrm{Sin}\right)\frac{n-1}{2n-1}\right] \\
& + \sinh\xi\left[\left(D_{n+1}\mathrm{Cos} + E_{n+1}\mathrm{Sin}\right)\frac{-1}{2n+3} + \left(D_{n-1}\mathrm{Cos} + E_{n-1}\mathrm{Sin}\right)\frac{1}{2n-1}\right] \\
& + \sinh\xi\left[\left(F_{n+1}\mathrm{Cos} + G_{n+1}\mathrm{Sin}\right)\frac{(n+2)(n+3)}{2n+3} - \left(F_{n-1}\mathrm{Cos} + G_{n-1}\mathrm{Sin}\right)\frac{(n-2)(n-1)}{2n-1}\right] \\
& + 2\sinh\xi\left[A_{n+1}\mathrm{Cos}(n+2) + A_{n-1}\mathrm{Cos}(n-1)\right] \\
& + \cosh\xi\left[\left(B_{n+1}\mathrm{Sin} + C_{n+1}\mathrm{Cos}\right)(n+2) + \left(B_{n-1}\mathrm{Sin} + C_{n-1}\mathrm{Cos}\right)(n-1)\right] \\
& + \cosh\xi\left[-\left(D_{n+1}\mathrm{Sin} + E_{n+1}\mathrm{Cos}\right) + \left(D_{n-1}\mathrm{Sin} + E_{n-1}\mathrm{Cos}\right)\right] \\
& + \cosh\xi\left[\left(F_{n+1}\mathrm{Sin} + G_{n+1}\mathrm{Cos}\right)(n+2)(n+3) - \left(F_{n-1}\mathrm{Sin} + G_{n-1}\mathrm{Cos}\right)(n-2)(n-1)\right] \\
& - 2\left(n+\frac{1}{2}\right)^2 A_n\mathrm{Sin} + \cosh\xi\left[A_{n+1}\mathrm{Sin}\left(n+\frac{3}{2}\right)(n+2) + A_{n-1}\mathrm{Sin}\left(n-\frac{1}{2}\right)(n-1)\right] \\
& + \frac{1}{2}\sinh\xi\left[\left(B_{n+1}\mathrm{Cos} + C_{n+1}\mathrm{Sin}\right)\left(n+\frac{3}{2}\right)(n+2) + \left(B_{n-1}\mathrm{Cos} + C_{n-1}\mathrm{Sin}\right)\left(n-\frac{1}{2}\right)(n-1)\right] \\
& + \frac{1}{2}\sinh\xi\left[-\left(D_{n+1}\mathrm{Cos} + E_{n+1}\mathrm{Sin}\right)\left(n+\frac{3}{2}\right) + \left(D_{n-1}\mathrm{Cos} + E_{n-1}\mathrm{Sin}\right)\left(n-\frac{1}{2}\right)\right] \\
& + \frac{1}{2}\sinh\xi\left[\left(F_{n+1}\mathrm{Cos} + G_{n+1}\mathrm{Sin}\right)\left(n+\frac{3}{2}\right)(n+2)(n+3) - \left(F_{n-1}\mathrm{Cos} + G_{n-1}\mathrm{Sin}\right)\left(n-\frac{1}{2}\right)(n-2)(n-1)\right]\Bigg\}
\end{aligned}
\tag{C.26}
$$

$$
\begin{aligned}
\omega 2_n = -\cosh\xi\frac{n+2}{2n+3}\Bigg\{ & 2\cosh\xi\left[A_{n+2}\mathrm{Sin}\frac{n+3}{2n+5} + A_n\mathrm{Sin}\frac{n}{2n+1}\right] \\
& + \sinh\xi\left[\left(B_{n+2}\mathrm{Cos} + C_{n+2}\mathrm{Sin}\right)\frac{n+3}{2n+5} + \left(B_n\mathrm{Cos} + C_n\mathrm{Sin}\right)\frac{n}{2n+1}\right] \\
& + \sinh\xi\left[\left(D_{n+2}\mathrm{Cos} + E_{n+2}\mathrm{Sin}\right)\frac{-1}{2n+5} + \left(D_n\mathrm{Cos} + E_n\mathrm{Sin}\right)\frac{1}{2n+1}\right] \\
& + \sinh\xi\left[\left(F_{n+2}\mathrm{Cos} + G_{n+2}\mathrm{Sin}\right)\frac{(n+3)(n+4)}{2n+5} - \left(F_n\mathrm{Cos} + G_n\mathrm{Sin}\right)\frac{(n-1)(n)}{2n+1}\right] \\
& + 2\sinh\xi\left[A_{n+2}\mathrm{Cos}(n+3) + A_n\mathrm{Cos}(n)\right] \\
& + \cosh\xi\left[\left(B_{n+2}\mathrm{Sin} + C_{n+2}\mathrm{Cos}\right)(n+3) + \left(B_n\mathrm{Sin} + C_n\mathrm{Cos}\right)(n)\right] \\
& + \cosh\xi\left[-\left(D_{n+2}\mathrm{Sin} + E_{n+2}\mathrm{Cos}\right) + \left(D_n\mathrm{Sin} + E_n\mathrm{Cos}\right)\right] \\
& + \cosh\xi\left[\left(F_{n+2}\mathrm{Sin} + G_{n+2}\mathrm{Cos}\right)(n+3)(n+4) - \left(F_n\mathrm{Sin} + G_n\mathrm{Cos}\right)(n-1)(n)\right] \\
& - 2\left(n+\frac{3}{2}\right)^2 A_{n+1}\mathrm{Sin} + \cosh\xi\left[A_{n+2}\mathrm{Sin}\left(n+\frac{5}{2}\right)(n+3) + A_n\mathrm{Sin}\left(n+\frac{1}{2}\right)(n)\right] \\
& + \frac{1}{2}\sinh\xi\left[\left(B_{n+2}\mathrm{Cos} + C_{n+2}\mathrm{Sin}\right)\left(n+\frac{5}{2}\right)(n+3) + \left(B_n\mathrm{Cos} + C_n\mathrm{Sin}\right)\left(n+\frac{1}{2}\right)(n)\right] \\
& + \frac{1}{2}\sinh\xi\left[-\left(D_{n+2}\mathrm{Cos} + E_{n+2}\mathrm{Sin}\right)\left(n+\frac{5}{2}\right) + \left(D_n\mathrm{Cos} + E_n\mathrm{Sin}\right)\left(n+\frac{1}{2}\right)\right] \\
& + \frac{1}{2}\sinh\xi\left[\left(F_{n+2}\mathrm{Cos} + G_{n+2}\mathrm{Sin}\right)\left(n+\frac{5}{2}\right)(n+3)(n+4) - \left(F_n\mathrm{Cos} + G_n\mathrm{Sin}\right)\left(n+\frac{1}{2}\right)(n-1)(n)\right]\Bigg\}
\end{aligned}
\tag{C.27}
$$

$$
\begin{aligned}
\omega 3_n = & -\cosh\xi \frac{n-1}{2n-1}\Bigg\{ 2\cosh\xi\left[A_n \mathrm{Sin}\frac{n+1}{2n+1} + A_{n-2}\mathrm{Sin}\frac{n-2}{2n-3}\right] \\
& +\sinh\xi\left[\left(B_n\mathrm{Cos} + C_n\mathrm{Sin}\right)\frac{n+1}{2n+1} + \left(B_{n-2}\mathrm{Cos} + C_{n-2}\mathrm{Sin}\right)\frac{n-2}{2n-3}\right] \\
& +\sinh\xi\left[\left(D_n\mathrm{Cos} + E_n\mathrm{Sin}\right)\frac{-1}{2n+1} + \left(D_{n-2}\mathrm{Cos} + E_{n-2}\mathrm{Sin}\right)\frac{1}{2n-3}\right] \\
& +\sinh\xi\left[\left(F_n\mathrm{Cos} + G_n\mathrm{Sin}\right)\frac{(n+1)(n+2)}{2n+1} - \left(F_{n-2}\mathrm{Cos} + G_{n-2}\mathrm{Sin}\right)\frac{(n-3)(n-2)}{2n-3}\right] \\
& +2\sinh\xi\left[A_n\mathrm{Cos}(n+1) + A_{n-2}\mathrm{Cos}(n-2)\right] \\
& +\cosh\xi\left[\left(B_n\mathrm{Sin} + C_n\mathrm{Cos}\right)(n+1) + \left(B_{n-2}\mathrm{Sin} + C_{n-2}\mathrm{Cos}\right)(n-2)\right] \\
& +\cosh\xi\left[-\left(D_n\mathrm{Sin} + E_n\mathrm{Cos}\right) + \left(D_{n-2}\mathrm{Sin} + E_{n-2}\mathrm{Cos}\right)\right] \\
& +\cosh\xi\left[\left(F_n\mathrm{Sin} + G_n\mathrm{Cos}\right)(n+1)(n+2) - \left(F_{n-2}\mathrm{Sin} + G_{n-2}\mathrm{Cos}\right)(n-3)(n-2)\right] \\
& -2\left(n-\frac{1}{2}\right)^2 A_{n-1}\mathrm{Sin} + \cosh\xi\left[A_n\mathrm{Sin}\left(n+\frac{1}{2}\right)(n+1) + A_{n-2}\mathrm{Sin}\left(n-\frac{3}{2}\right)(n-2)\right] \\
& +\frac{1}{2}\sinh\xi\left[\left(B_n\mathrm{Cos} + C_n\mathrm{Sin}\right)\left(n+\frac{1}{2}\right)(n+1) + \left(B_{n-2}\mathrm{Cos} + C_{n-2}\mathrm{Sin}\right)\left(n-\frac{3}{2}\right)(n-2)\right] \\
& +\frac{1}{2}\sinh\xi\left[-\left(D_n\mathrm{Cos} + E_n\mathrm{Sin}\right)\left(n+\frac{1}{2}\right) + \left(D_{n-2}\mathrm{Cos} + E_{n-2}\mathrm{Sin}\right)\left(n-\frac{3}{2}\right)\right] \\
& +\frac{1}{2}\sinh\xi\left[\left(F_n\mathrm{Cos} + G_n\mathrm{Sin}\right)\left(n+\frac{1}{2}\right)(n+1)(n+2) - \left(F_{n-2}\mathrm{Cos} + G_{n-2}\mathrm{Sin}\right)\left(n-\frac{3}{2}\right)(n-3)(n-2)\right]\Bigg\}
\end{aligned}
\tag{C.28}
$$

$$
\begin{aligned}
\omega 4_n = & \frac{(n+3)(n+2)}{(2n+5)(2n+3)}\Bigg\{ 2\cosh\xi\left[A_{n+3}\mathrm{Sin}\frac{n+4}{2n+7} + A_{n+1}\mathrm{Sin}\frac{n+1}{2n+3}\right] \\
& +\sinh\xi\left[\left(B_{n+3}\mathrm{Cos} + C_{n+3}\mathrm{Sin}\right)\frac{n+4}{2n+7} + \left(B_{n+1}\mathrm{Cos} + C_{n+1}\mathrm{Sin}\right)\frac{n+1}{2n+3}\right] \\
& +\sinh\xi\left[\left(D_{n+3}\mathrm{Cos} + E_{n+3}\mathrm{Sin}\right)\frac{-1}{2n+7} + \left(D_{n+1}\mathrm{Cos} + E_{n+1}\mathrm{Sin}\right)\frac{1}{2n+3}\right] \\
& +\sinh\xi\left[\left(F_{n+3}\mathrm{Cos} + G_{n+3}\mathrm{Sin}\right)\frac{(n+4)(n+5)}{2n+7} - \left(F_{n+1}\mathrm{Cos} + G_{n+1}\mathrm{Sin}\right)\frac{(n)(n+1)}{2n+3}\right] \\
& +2\sinh\xi\left[A_{n+3}\mathrm{Cos}(n+4) + A_{n+1}\mathrm{Cos}(n+1)\right] \\
& +\cosh\xi\left[\left(B_{n+3}\mathrm{Sin} + C_{n+3}\mathrm{Cos}\right)(n+4) + \left(B_{n+1}\mathrm{Sin} + C_{n+1}\mathrm{Cos}\right)(n+1)\right] \\
& +\cosh\xi\left[-\left(D_{n+3}\mathrm{Sin} + E_{n+3}\mathrm{Cos}\right) + \left(D_{n+1}\mathrm{Sin} + E_{n+1}\mathrm{Cos}\right)\right] \\
& +\cosh\xi\left[\left(F_{n+3}\mathrm{Sin} + G_{n+3}\mathrm{Cos}\right)(n+4)(n+5) - \left(F_{n+1}\mathrm{Sin} + G_{n+1}\mathrm{Cos}\right)(n)(n+1)\right] \\
& -2\left(n+\frac{5}{2}\right)^2 A_{n+2}\mathrm{Sin} + \cosh\xi\left[A_{n+3}\mathrm{Sin}\left(n+\frac{7}{2}\right)(n+4) + A_{n+1}\mathrm{Sin}\left(n+\frac{3}{2}\right)(n+1)\right] \\
& +\frac{1}{2}\sinh\xi\left[\left(B_{n+3}\mathrm{Cos} + C_{n+3}\mathrm{Sin}\right)\left(n+\frac{7}{2}\right)(n+4) + \left(B_{n+1}\mathrm{Cos} + C_{n+1}\mathrm{Sin}\right)\left(n+\frac{3}{2}\right)(n+1)\right] \\
& +\frac{1}{2}\sinh\xi\left[-\left(D_{n+3}\mathrm{Cos} + E_{n+3}\mathrm{Sin}\right)\left(n+\frac{7}{2}\right) + \left(D_{n+1}\mathrm{Cos} + E_{n+1}\mathrm{Sin}\right)\left(n+\frac{3}{2}\right)\right] \\
& +\frac{1}{2}\sinh\xi\left[\left(F_{n+3}\mathrm{Cos} + G_{n+3}\mathrm{Sin}\right)\left(n+\frac{7}{2}\right)(n+4)(n+5) - \left(F_{n+1}\mathrm{Cos} + G_{n+1}\mathrm{Sin}\right)\left(n+\frac{3}{2}\right)(n)(n+1)\right]\Bigg\}
\end{aligned}
\tag{C.29}
$$

$$
\begin{aligned}
\omega 5_n = &\left[\frac{(n+1)(n-1)}{(2n+1)(2n-1)}+\frac{(n)(n+2)}{(2n+1)(2n+3)}\right]\Bigg\{2\cosh\xi\left[A_{n+1}\mathrm{Sin}\frac{n+2}{2n+3}+A_{n-1}\mathrm{Sin}\frac{n-1}{2n-1}\right]\\
&+\sinh\xi\left[\left(B_{n+1}\mathrm{Cos}+C_{n+1}\mathrm{Sin}\right)\frac{n+2}{2n+3}+\left(B_{n-1}\mathrm{Cos}+C_{n-1}\mathrm{Sin}\right)\frac{n-1}{2n-1}\right]\\
&+\sinh\xi\left[\left(D_{n+1}\mathrm{Cos}+E_{n+1}\mathrm{Sin}\right)\frac{-1}{2n+3}+\left(D_{n-1}\mathrm{Cos}+E_{n-1}\mathrm{Sin}\right)\frac{1}{2n-1}\right]\\
&+\sinh\xi\left[\left(F_{n+1}\mathrm{Cos}+G_{n+1}\mathrm{Sin}\right)\frac{(n+2)(n+3)}{2n+3}-\left(F_{n-1}\mathrm{Cos}+G_{n-1}\mathrm{Sin}\right)\frac{(n-2)(n-1)}{2n-1}\right]\\
&+2\sinh\xi\left[A_{n+1}\mathrm{Cos}(n+2)+A_{n-1}\mathrm{Cos}(n-1)\right]\\
&+\cosh\xi\left[\left(B_{n+1}\mathrm{Sin}+C_{n+1}\mathrm{Cos}\right)(n+2)+\left(B_{n-1}\mathrm{Sin}+C_{n-1}\mathrm{Cos}\right)(n-1)\right]\\
&+\cosh\xi\left[-\left(D_{n+1}\mathrm{Sin}+E_{n+1}\mathrm{Cos}\right)+\left(D_{n-1}\mathrm{Sin}+E_{n-1}\mathrm{Cos}\right)\right]\\
&+\cosh\xi\left[\left(F_{n+1}\mathrm{Sin}+G_{n+1}\mathrm{Cos}\right)(n+2)(n+3)-\left(F_{n-1}\mathrm{Sin}+G_{n-1}\mathrm{Cos}\right)(n-2)(n-1)\right]\\
&-2\left(n+\frac{1}{2}\right)^2 A_n\mathrm{Sin}+\cosh\xi\left[A_{n+1}\mathrm{Sin}\left(n+\frac{3}{2}\right)(n+2)+A_{n-1}\mathrm{Sin}\left(n-\frac{1}{2}\right)(n-1)\right]\\
&+\frac{1}{2}\sinh\xi\left[\left(B_{n+1}\mathrm{Cos}+C_{n+1}\mathrm{Sin}\right)\left(n+\frac{3}{2}\right)(n+2)+\left(B_{n-1}\mathrm{Cos}+C_{n-1}\mathrm{Sin}\right)\left(n-\frac{1}{2}\right)(n-1)\right]\\
&+\frac{1}{2}\sinh\xi\left[-\left(D_{n+1}\mathrm{Cos}+E_{n+1}\mathrm{Sin}\right)\left(n+\frac{3}{2}\right)+\left(D_{n-1}\mathrm{Cos}+E_{n-1}\mathrm{Sin}\right)\left(n-\frac{1}{2}\right)\right]\\
&+\frac{1}{2}\sinh\xi\left[\left(F_{n+1}\mathrm{Cos}+G_{n+1}\mathrm{Sin}\right)\left(n+\frac{3}{2}\right)(n+2)(n+3)-\left(F_{n-1}\mathrm{Cos}+G_{n-1}\mathrm{Sin}\right)\left(n-\frac{1}{2}\right)(n-2)(n-1)\right]\Bigg\}
\end{aligned}
\tag{C.30}
$$

$$
\begin{aligned}
\omega 6_n = &\frac{(n-2)(n-1)}{(2n-3)(2n-1)}\Bigg\{2\cosh\xi\left[A_{n-1}\mathrm{Sin}\frac{n}{2n-1}+A_{n-3}\mathrm{Sin}\frac{n-3}{2n-5}\right]\\
&+\sinh\xi\left[\left(B_{n-1}\mathrm{Cos}+C_{n-1}\mathrm{Sin}\right)\frac{n}{2n-1}+\left(B_{n-3}\mathrm{Cos}+C_{n-3}\mathrm{Sin}\right)\frac{n-3}{2n-5}\right]\\
&+\sinh\xi\left[\left(D_{n-1}\mathrm{Cos}+E_{n-1}\mathrm{Sin}\right)\frac{-1}{2n-1}+\left(D_{n-3}\mathrm{Cos}+E_{n-3}\mathrm{Sin}\right)\frac{1}{2n-5}\right]\\
&+\sinh\xi\left[\left(F_{n-1}\mathrm{Cos}+G_{n-1}\mathrm{Sin}\right)\frac{(n)(n+1)}{2n-1}-\left(F_{n-3}\mathrm{Cos}+G_{n-3}\mathrm{Sin}\right)\frac{(n-4)(n-3)}{2n-5}\right]\\
&+2\sinh\xi\left[A_{n-1}\mathrm{Cos}(n)+A_{n-3}\mathrm{Cos}(n-3)\right]\\
&+\cosh\xi\left[\left(B_{n-1}\mathrm{Sin}+C_{n-1}\mathrm{Cos}\right)(n)+\left(B_{n-3}\mathrm{Sin}+C_{n-3}\mathrm{Cos}\right)(n-3)\right]\\
&+\cosh\xi\left[-\left(D_{n-1}\mathrm{Sin}+E_{n-1}\mathrm{Cos}\right)+\left(D_{n-3}\mathrm{Sin}+E_{n-3}\mathrm{Cos}\right)\right]\\
&+\cosh\xi\left[\left(F_{n-1}\mathrm{Sin}+G_{n-1}\mathrm{Cos}\right)(n)(n+1)-\left(F_{n-3}\mathrm{Sin}+G_{n-3}\mathrm{Cos}\right)(n-4)(n-3)\right]\\
&-2\left(n-\frac{3}{2}\right)^2 A_{n-2}\mathrm{Sin}+\cosh\xi\left[A_{n-1}\mathrm{Sin}\left(n-\frac{1}{2}\right)(n)+A_{n-3}\mathrm{Sin}\left(n-\frac{5}{2}\right)(n-3)\right]\\
&+\frac{1}{2}\sinh\xi\left[\left(B_{n-1}\mathrm{Cos}+C_{n-1}\mathrm{Sin}\right)\left(n-\frac{1}{2}\right)(n)+\left(B_{n-3}\mathrm{Cos}+C_{n-3}\mathrm{Sin}\right)\left(n-\frac{5}{2}\right)(n-3)\right]\\
&+\frac{1}{2}\sinh\xi\left[-\left(D_{n-1}\mathrm{Cos}+E_{n-1}\mathrm{Sin}\right)\left(n-\frac{1}{2}\right)+\left(D_{n-3}\mathrm{Cos}+E_{n-3}\mathrm{Sin}\right)\left(n-\frac{5}{2}\right)\right]\\
&+\frac{1}{2}\sinh\xi\left[\left(F_{n-1}\mathrm{Cos}+G_{n-1}\mathrm{Sin}\right)\left(n-\frac{1}{2}\right)(n)(n+1)-\left(F_{n-3}\mathrm{Cos}+G_{n-3}\mathrm{Sin}\right)\left(n-\frac{5}{2}\right)(n-4)(n-3)\right]\Bigg\}
\end{aligned}
\tag{C.31}
$$

Now in view of (4.3.61) and (4.3.50) the equation for the set of I_n's is determined:

$$
\begin{aligned}
&+\frac{(n-2)(n-1)}{2n-1}\sinh\left(n-\frac{3}{2}\right)\alpha\, I_{n-2} \\
&-(n-1)\left[\frac{\sinh\alpha}{2n-1}\cosh\left(n-\frac{1}{2}\right)\alpha+\cosh\alpha\,\sinh\left(n-\frac{1}{2}\right)\alpha\right]I_{n-1} \\
&+\left\{\frac{1}{2}\sinh 2\alpha\,\cosh\left(n+\frac{1}{2}\right)\alpha\right. \\
&\left.+\left[(2n+1)\cosh^2\alpha+\frac{(n+1)(n-1)}{2n-1}+\frac{n(n+2)}{2n+3}\right]\sinh\left(n+\frac{1}{2}\right)\alpha\right\}I_n \qquad (C.32)\\
&-(n+2)\left[\frac{\sinh\alpha}{2n+3}\cosh\left(n+\frac{3}{2}\right)\alpha+\cosh\alpha\,\sinh\left(n+\frac{3}{2}\right)\alpha\right]I_{n+1} \\
&+\frac{(n+3)(n+2)}{2n+3}\sinh\left(n+\frac{5}{2}\right)\alpha\, I_{n+2} \\
&=-\chi_n-\frac{F_{cP}}{c}\left[\beta_n+\gamma_n+\tau 1_n+\tau 2_n+\tau 3_n+\omega 1_n+\omega 2_n+\omega 3_n+\omega 4_n+\omega 5_n+\omega 6_n\right]_{\xi=\alpha}
\end{aligned}
$$

in which χ_n is defined by

$$
\begin{aligned}
\chi_n &= \frac{(n-2)(n-1)}{2n-1}\cosh\left(n-\frac{3}{2}\right)\alpha J_{n-2}-(n-1)\left[\frac{\sinh\alpha}{2n-1}\sinh\left(n-\frac{1}{2}\right)\alpha+\cosh\alpha\cosh\left(n-\frac{1}{2}\right)\alpha\right]J_{n-1} \\
&+\left\{\frac{1}{2}\sinh 2\alpha\sinh\left(n+\frac{1}{2}\right)\alpha+\left[(2n+1)\cosh^2\alpha+\frac{(n+1)(n-1)}{2n-1}+\frac{n(n+2)}{2n+3}\right]\cosh\left(n+\frac{1}{2}\right)\alpha\right\}J_n \\
&-(n+2)\left[\frac{\sinh\alpha}{2n+3}\sinh\left(n+\frac{3}{2}\right)\alpha+\cosh\alpha\cosh\left(n+\frac{3}{2}\right)\alpha\right]J_{n+1}+\frac{(n+3)(n+2)}{2n+3}\cosh\left(n+\frac{5}{2}\right)\alpha J_{n+2}
\end{aligned}
$$

(C.33)

The parameters $\sigma_{\xi\eta}PA, \sigma_{\xi\eta}PBC, \sigma_{\xi\eta}PDE$ and $\sigma_{\xi\eta}PFG$ in relationship (4.5.7) and $\sigma_{\xi\theta}PA, \sigma_{\xi\theta}PBC, \sigma_{\xi\theta}PDE$ and $\sigma_{\xi\theta}PFG$ in relations (4.5. 8) are defined by

$$
\begin{aligned}
&\sigma_{\xi\eta}PA=\left(\cosh\xi-\mu\right)^{-\frac{1}{2}}\left[-3\mu^3\cosh\xi+\mu^2\cosh^2\xi+4\mu^2-\mu\cosh\xi+\sinh^2\xi-1\right]\times \\
&\sum_1^\infty A_n\sinh\left(n+\frac{1}{2}\right)\xi P_n'+\left(\cosh\xi-\mu\right)^{\frac{1}{2}}\left[2\sin^2\eta\left(1-\mu\cosh\xi\right)\sum_1^\infty A_n\sinh\left(n+\frac{1}{2}\right)\xi P_n''\right. \\
&\left.+\left(1-\mu^2\right)\sinh\xi\sum_1^\infty(2n+1)A_n\cosh\left(n+\frac{1}{2}\right)\xi P_n'\right] \qquad (C.34)
\end{aligned}
$$

$$\sigma_{\xi\eta}PBC = \frac{1}{2}\sinh\xi(\cosh\xi - \mu)^{-\frac{1}{2}} \times$$

$$\left[-5\mu^3 + 2\mu^2\cosh\xi + \mu + \cosh\xi\right]\sum_1^\infty\left[B_n\cosh\left(n+\frac{1}{2}\right)\xi + C_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n'$$

$$+(\cosh\xi-\mu)^{\frac{1}{2}}\left\{-\mu\sin^2\eta\sinh\xi\sum_1^\infty\left[B_n\cosh\left(n+\frac{1}{2}\right)\xi + C_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n''\right.$$

$$\left.+(1-\mu^2)\cosh\xi\sum_1^\infty\left(n+\frac{1}{2}\right)\left[B_n\sinh\left(n+\frac{1}{2}\right)\xi + C_n\cosh\left(n+\frac{1}{2}\right)\xi\right]P_n'\right\} \tag{C.35}$$

$$\sigma_{\xi\eta}PDE = \frac{1}{2}\sinh\xi(\cosh\xi - \mu)^{-\frac{1}{2}} \times$$

$$\left[-\mu^2 - \mu\cosh\xi + 2\right]\sum_0^\infty\left[D_n\cosh\left(n+\frac{1}{2}\right)\xi + E_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n$$

$$+(\cosh\xi-\mu)^{\frac{1}{2}}\left\{-\sin\eta^2\sinh\xi\sum_1^\infty\left[D_n\cosh\left(n+\frac{1}{2}\right)\xi + E_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n'\right.$$

$$\left.+(1-\mu\cosh\xi)\sum_0^\infty\left(n+\frac{1}{2}\right)\left[D_n\sinh\left(n+\frac{1}{2}\right)\xi + E_n\cosh\left(n+\frac{1}{2}\right)\xi\right]P_n\right\} \tag{C.36}$$

$$\sigma_{\xi\eta}PGF = \frac{1}{2}\sinh\xi(\cosh\xi - \mu)^{-\frac{1}{2}} \times$$

$$\left[-5\mu^2 + 3\mu\cosh\xi + 2\right]\sum_2^\infty\left[F_n\cosh\left(n+\frac{1}{2}\right)\xi + G_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n''$$

$$+(\cosh\xi-\mu)^{\frac{1}{2}}\left\{-(1-\mu^2)\sin^2\eta\sinh\xi\sum_2^\infty\left[F_n\cosh\left(n+\frac{1}{2}\right)\xi + G_n\sinh\left(n+\frac{1}{2}\right)\xi\right]P_n'''\right.$$

$$\left.+(1-\mu^2)(1-\mu\cosh\xi)\sum_2^\infty\left(n+\frac{1}{2}\right)\left[F_n\sinh\left(n+\frac{1}{2}\right)\xi + G_n\cosh\left(n+\frac{1}{2}\right)\xi\right]P_n''\right\}$$

(C.37)

$$\sigma_{\xi\theta}PA = -2(\cosh\xi-\mu)^{\frac{1}{2}}(1-\mu\cosh\xi)\sum_1^\infty A_n\sinh\left(n+\frac{1}{2}\right)\xi P_n' \tag{C.38}$$

$$\sigma_{\xi\theta}PBC = \left(\cosh\xi - \mu\right)^{\frac{1}{2}}\mu \sin\eta \sinh\xi \sum_{1}^{\infty}\left[B_n \cosh\left(n+\frac{1}{2}\right)\xi + C_n \sinh\left(n+\frac{1}{2}\right)\xi\right]P_n'$$

(C.39)

$$\sigma_{\xi\theta}PDE = -\frac{1}{2}\sinh\xi\left(\cosh\xi - \mu\right)^{\frac{1}{2}}\sum_{0}^{\infty}\left[D_n \cosh\left(n+\frac{1}{2}\right)\xi + E_n \sinh\left(n+\frac{1}{2}\right)\xi\right]P_n$$
$$-\left(\cosh\xi - \mu\right)^{\frac{3}{2}}\sum_{0}^{\infty}\left(n+\frac{1}{2}\right)\left[D_n \sinh\left(n+\frac{1}{2}\right)\xi + E_n \cosh\left(n+\frac{1}{2}\right)\xi\right]P_n$$

(C.40)

$$\sigma_{\xi\theta}PFG = \frac{5}{2}\left(1-\mu^2\right)\sinh\xi\left(\cosh\xi - \mu\right)^{\frac{1}{2}}\sum_{2}^{\infty}\left[F_n \cosh\left(n+\frac{1}{2}\right)\xi + G_n \sinh\left(n+\frac{1}{2}\right)\xi\right]P_n''$$
$$+\left(1-\mu^2\right)\left(\cosh\xi - \mu\right)^{\frac{3}{2}}\sum_{2}^{\infty}\left(n+\frac{1}{2}\right)\left[F_n \sinh\left(n+\frac{1}{2}\right)\xi + G_n \cosh\left(n+\frac{1}{2}\right)\xi\right]P_n''$$

(C.41)

The parameters $\sigma_{\xi\eta}NA$, $\sigma_{\xi\eta}NBC$ and $\sigma_{\xi\eta}NDE$ in relationship (4.5.53) are defined by

$$\sigma_{\xi\eta}NA = \sin\eta\left\{\left(\cosh\xi - \mu\right)^{-\frac{1}{2}}\left[1-\mu\cosh\xi - \sinh^2\xi\right]\sum_{1}^{\infty} A_n \sinh\left(n+\frac{1}{2}\right)\xi P_n\right.$$
$$+\left(\cosh\xi - \mu\right)^{\frac{1}{2}}\left[2\left(\mu\cosh\xi - 1\right)\sum_{1}^{\infty} A_n \sinh\left(n+\frac{1}{2}\right)\xi P_n' \right. \qquad \text{(C.42)}$$
$$\left.\left. -\sinh\xi\sum_{1}^{\infty}(2n+1)A_n \cosh\left(n+\frac{1}{2}\right)\xi P_n\right]\right\}$$

$$\sigma_{\xi\eta}BC = \sin\eta\left\{-\frac{1}{2}\left(\cosh\xi - \mu\right)^{-\frac{1}{2}}\left(\cosh\xi + \mu\right)\sinh\xi \times\right.$$
$$\sum_{1}^{\infty}\left[B_n \cosh\left(n+\frac{1}{2}\right)\xi + C_n \sinh\left(n+\frac{1}{2}\right)\xi\right]P_n$$
$$+\left(\cosh\xi - \mu\right)^{\frac{1}{2}}\left\{\mu\sinh\xi\sum_{1}^{\infty}\left[B_n \cosh\left(n+\frac{1}{2}\right)\xi + C_n \sinh\left(n+\frac{1}{2}\right)\xi\right]P_n'\right. \qquad \text{(C.43)}$$
$$\left.\left.-\cosh\xi\sum_{1}^{\infty}\left(n+\frac{1}{2}\right)\left[B_n \sinh\left(n+\frac{1}{2}\right)\xi + C_n \cosh\left(n+\frac{1}{2}\right)\xi\right]P_n\right\}\right\}$$

$$\sigma_{\xi\eta} DE = \sin\eta \left\{ \frac{1}{2} \sinh\xi \left(\cosh\xi - \mu\right)^{-\frac{1}{2}} \times \right.$$
$$\left[-\mu^2 + 3\mu\cosh\xi - 2\right] \sum_0^\infty \left[D_n \cosh\left(n + \frac{1}{2}\right)\xi + E_n \sinh\left(n + \frac{1}{2}\right)\xi \right] P_n^{'}$$
$$+\left(\cosh\xi - \mu\right)^{\frac{1}{2}} \left\{ \sin\eta^2 \sinh\xi \sum_1^\infty \left[D_n \cosh\left(n + \frac{1}{2}\right)\xi + E_n \sinh\left(n + \frac{1}{2}\right)\xi \right] P_n^{''} \right. \quad \text{(C.44)}$$
$$\left.\left. -\left(1 - \mu\cosh\xi\right) \sum_0^\infty \left(n + \frac{1}{2}\right) \left[D_n \sinh\left(n + \frac{1}{2}\right)\xi + E_n \cosh\left(n + \frac{1}{2}\right)\xi \right] P_n^{'} \right\} \right\}$$